Cyclization of *N*-arylcyclopropanecarboxamides into N-arylpyrrolidinones-2 under electron ionization and in the condensed phase

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RATIONALE: Mass spectrometry is known as an excellent method to predict the behavior of organic compounds in solution. The behavior of organic compounds in the gas-phase inside an ion source of a mass spectrometer allows their intrinsic properties to be defined, avoiding the influence of intermolecular interactions, counter ions and solvent effects.

METHODS: Arylpyrrolidinones-2 were obtained by condensed phase synthesis from the corresponding N-arylcyclopropanecarboxamide**s**. Electron ionization (EI) with accurate mass measurements by high-resolution time-of-flight mass-spectrometry and quantum chemical calculations were used to understand the behavior of the molecular radical cations of N-arylcyclopropanecarboxamide**s** and N-arylpyrrolidinones-2 in the ion source of a mass spectrometer. The geometries of the molecules, transition states, and intermediates were fully optimized using DFT-PBE calculations.

RESULTS: Fragmentation schemes, ion structures, and possible mechanisms of primary isomerisation were proposed for isomeric N-arylcyclopropanecarboxamide**s** and N-arylpyrrolidinones-2. Based on the fragmentation pattern of the N-arylcyclopropanecarboxamides, isomerisation of the original $M^{+\bullet}$ ions into the $M^{+\bullet}$ ions of the N-arylpyrrolidinones-2 was shown to be only a minor process. On the contrary, this cyclization proceeds easily in the condensed phase in the presence of the Brønsted acids.

CONCLUSION: Based on the experimental data and quantum chemical calculations the principal mechanism of decomposition of the molecular ions of *N*-arylcyclopropanecarboxamides involves their direct fragmentation without any rearrangements. An alternative mechanism is responsible for the isomerisation of a small portion of the higher energy molecular ions into the corresponding N-arylpyrrolidinones-2 ions.

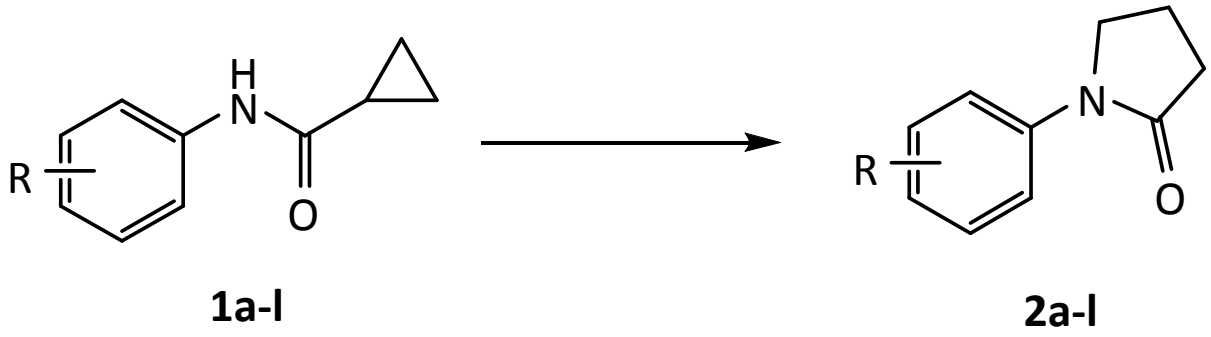
Keywords: *N*-arylcyclopropanecarboxamides, N-arylpyrrolidinones-2, electron ionization, accurate mass measurements, isomerisation, DFT-calculations

Mass spectrometry has proven itself to be a powerful and rapid method for the prediction of the direction and yields of monomolecular reactions of organic compounds in solution. [1-4] The study of the behavior of organic compounds in the gas phase in the ion source of a mass spectrometer allows their intrinsic properties to be defined, thus avoiding the influence of intermolecular interactions, counter ions and solvent effects. [4] Comparison of the results of the reaction taking place in the gas and condensed phases may be very important in revealing the effects of solvent and counter ions. These issues are also relevant for the study of gas-phase ion-molecule reactions. [5] The vast majority of the classic organic chemistry rearrangements have been shown to take place in the ion source of a mass spectrometer in both polarities. [4, 6, 7]

We previously successfully used mass spectrometry to study the transformations of various *ortho*-substituted phenylcyclopropanes as well as diazo compounds in both positive [4] and negative [8] ion modes, mimicking reactions catalyzed by acids and bases in solution. The spectra obtained for several series of *ortho*-substituted cyclopropylbenzenes were used to confirm the presence of the predicted heterocycles in solution. The cyclization products of the molecular ions for these arylcyclopropanes were identical to those synthesized in the condensed phase. [9-12]

In the present study we continue research in this area investigating the possibility of rearrangements of substituted N-arylcyclopropanecarboxamides (**1a-l**) into N-arylpyrrolidones-2 (**2a-l**) (Scheme 1). This reaction is known to

proceed in the condensed phase. [13, 14] Compounds **1** were expected to undergo EI-induced cyclization in a similar manner.



1a-l **2a-l**

Scheme 1.a) R=H, b) R = o-CH_3, c) R = p-CH_3, d) R = o-C_2H_5, e) R = p-C_2H_5, f) R = o-F, g) R = o-Cl, h) R = p-Cl, i) R = p-Br, j) R = p-I, k) R = o-OC_2H_5, l) R = p-NO_2

Experimental

Synthesis of substituted N-arylcyclopropanecarboxamides (1)

These compounds were synthesized using the Schotten-Baumann reaction. [15] A solution of cyclopropanecarbonyl chloride (1.05 g, 10 mM) in dichloromethane (10 mL) was added dropwise to the mixture of the corresponding substituted aniline (10 mM) and triethylamine (1.11 g, 11 mM) in dichloromethane (40 mL) with continuous stirring over a period of 1 hr at room temperature. After 5 hrs the reaction mixture was poured into 100 mL of ice water. The organic phase was washed 3 times with water (100 mL) and dried over anhydrous $MgSO_4$. After solvent evaporation the targeted N-arylcyclopropanecarboxamides **1** were purified by recrystallization from a mixture of MeOH and H_2O (1:1). The purity of the reaction products was checked by NMR and GC/MS. The spectral data are presented in the Supplementary Information.

Synthesis of substituted N-phenylpyrrolidones-2 (2)

The synthesis of N-arylpyrrolidones-2 from N-arylcyclopropane-carboxamides was successfully achieved earlier. [13] The reaction proceeds in the presence of tetrabromomethane and triphenylphosphine. The same reaction was carried out at the Chemistry Department of Moscow State University (Moscow, Russia) in considerably milder conditions without using any halogenated or phosphorus-containing reagents. Thus, the suggested method could actually satisfy the concept of "green" chemistry. The rearrangement of compounds **1** into **2** was carried out at an elevated temperature (about 190–230 ºC). Since the use of any solvent at these temperatures becomes problematic, we employed condensed phase synthesis with NH_4I, as a protonating agent. At this elevated temperature ammonium iodide undergoes partial sublimation, existing in equilibrium with ammonia and hydrogen iodide. The latter species may protonate reagent **1** molecules.

A powder of 0.244 g (2.4mM) aluminum oxide (II grade activity) was thoroughly mixed and ground with a spatula in a silica vial with 0.128 g (0.88mM) of powdered NH_4I and 0.8 mM of amides **1**. The mixture was heated in a Monowave 300 microwave oven (Anton Paar, Ostfildern-Scharnhausen, Germany) for 30 min at 200 ºC. The reaction products (Scheme 1) were extracted with chloroform (5 mL x 3), concentrated at reduced pressure and purified by column chromatography. The yields of the pyrrolidines **2** are in the wide range between 20% and 80%, depending on the substituents in the aromatic ring. The EI mass spectra of N-arylcyclopropanecarboxamides **1** and N-arylpyrrolidones-2 (**2**) are summarized in the Supplementary Information.

Mass Spectrometry

All experiments were performed with a Pegasus GC-HRT time-of-flight (TOF) high-resolution mass-spectrometer (LECO Corporation, Saint Joseph, MI, USA) with Folded Flight Path multiple reflecting geometry coupled with an Agilent 7890A Gas Chromatograph (Agilent, Palo Alto, CA, USA). The system

was controlled by ChromaTOF-HRT software, version 1.80 (LECO Corporation), which was also used for data collection and data processing. The data were collected using 10 full (*m/z* 10-500 range) spectra per second in high-resolution mode (25,000 at FWHH), reliably determining the elemental composition of all the ions. Multi-point mass calibration on FC-43 (PFTBA) mass spectra was performed before running the samples as a part of the automated tuning routine. The mass spectrometer hardware and acquisition software allow mass drift during data collection to be minimized. The electron ionization source was kept at 250°C, while the electron energy was 70 eV. Chromatographic separation was performed using a Rxi - 5Sil M 30m length column, of internal diameter 250 mm and phase thickness 0.25μm. The carrier gas was helium at a flow rate of 1 mL min-1; the column temperature was programmed as follows: 50°C (2 min) then ramped at 10°C/ min to 280°C; and the transfer line temperature was 320°C. 1 mL of dichloromethane solution was introduced into the injector heated at 280°C at a split ratio of 50:1.

NMR spectra

^{1}H NMR spectra of compounds **1** and **2** were recorded with Avance-400 spectrometer (Bruker BioSpin, Rheinstetten, Germany) in $CDCl_3$ and $(CD_3)_2CO$ solution (400 MHz) using tetramethylsilane (TMS) as an internal standard. The spectra were used exclusively to confirm the structures of compounds **1** and **2**.

Computational Details

The geometries of molecules, transition states, and intermediates were fully optimized using DFT-PBE calculations. The full electron TZ basis set L2 was used. The numbers of contracted and primitive functions used in L2 were, respectively, {3,2,1}/{8,4,2} for H, {4,3,2,1}/{12,8,4,2} for C, N, and O. [16] Stationary points on the potential energy surface were identified by analyzing Hessians. The thermodynamic functions (Gibbs energies, G) at 298.15 K were

calculated using an approximation of rigid rotator and harmonic oscillator. Atomic charges were calculated according to Hirschfeld. [17] Reaction paths were found by the intrinsic reaction coordinate method. [18] All calculations were performed using the MBC100k cluster at the Joint Supercomputer Center (Moscow, Russia) with the use of the PRIRODA04 program written by Laikov. [19]

Results and discussion

Acid-catalyzed rearrangement of *N*-arylcyclopropanecarboxamides (**1**) theoretically could result in the formation of several products including alkenes due to cleavage of the cyclopropyl moiety or heterocyclic compounds formed as a result of *ortho*-substitution in the aromatic ring. [9-12] However, in all the cases condensed phase transformation of **1** yielded a single product **2**, while some portion of the original reagent remained unreacted. Figure 1 presents a TIC chromatogram of the reaction mixture of *ortho*-chlorinated cyclopropane **1c** after 6 hrs of heating at 200 ºC with NH_4I. There are only 2 peaks: the first belongs to the initial compound **1c** and the second to the targeted pyrrolidone **2c**.

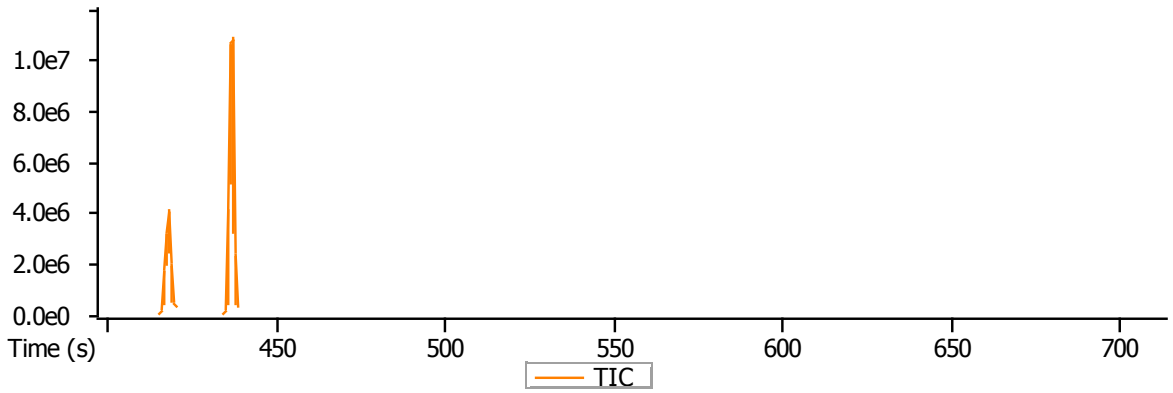


Fig.1. Total ion chromatogram of the reaction mixture of *ortho*-chlorinated cyclopropane **1c**

The electron ionization spectra of isomers **1** and **2** appeared to be very different from one another. Figures 2a and 2b present these spectra for the unsubstituted compounds **1a** and **2a,** respectively.

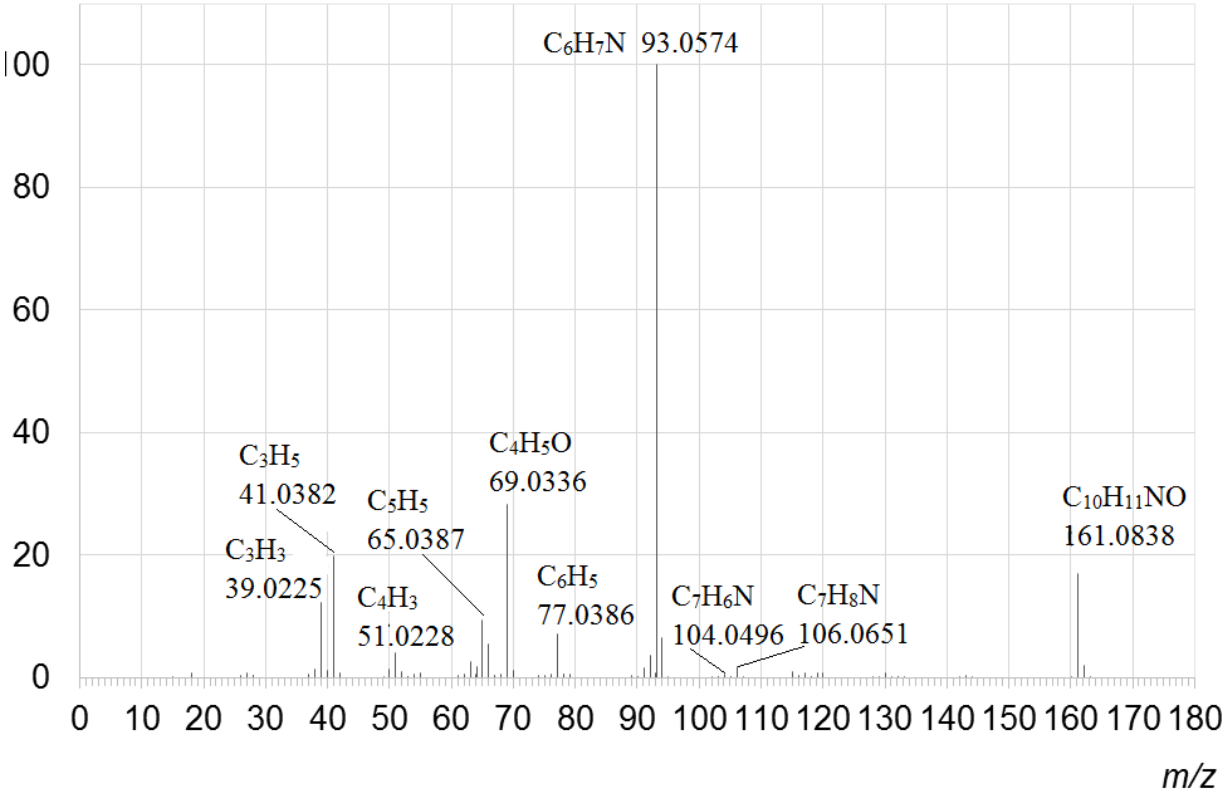


Fig. 2a. EI spectrum of *N*-arylcyclopropanecarboxamide (**1a**)

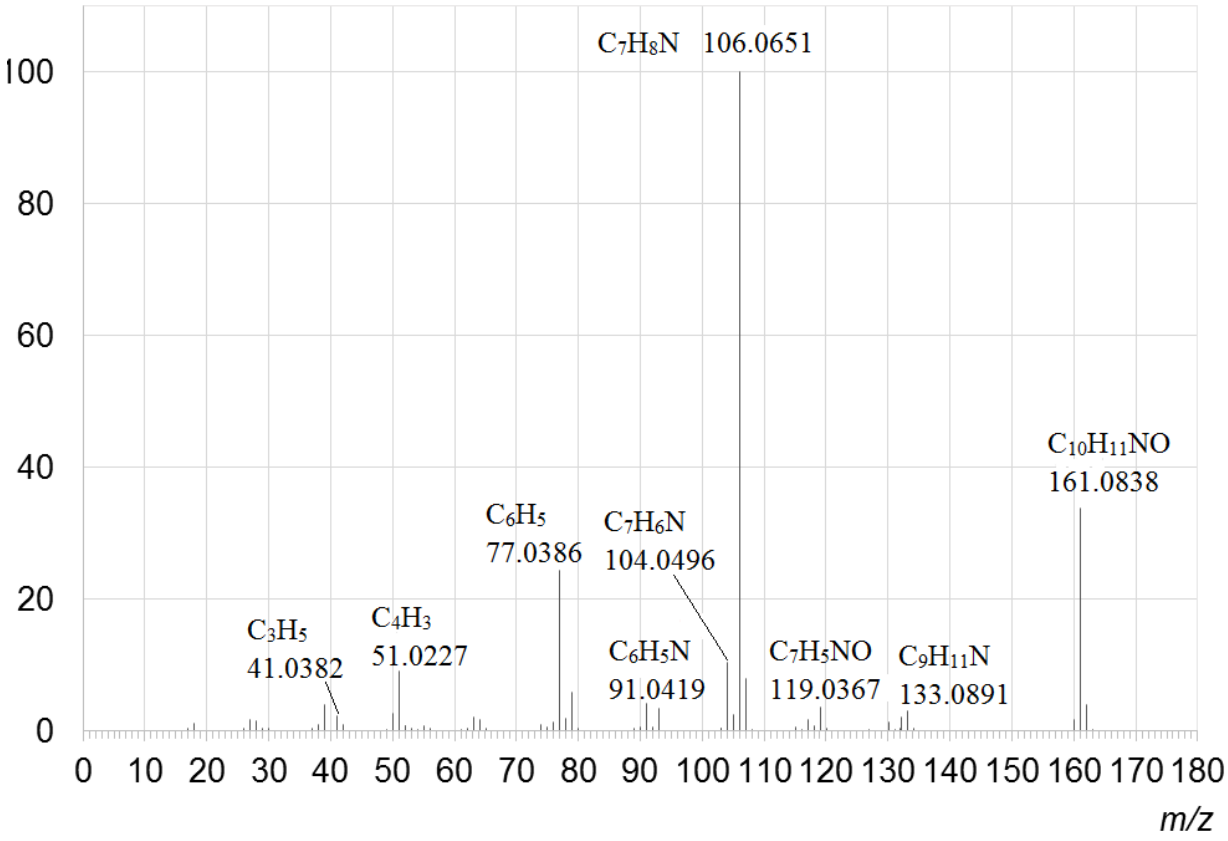


Fig. 2b. EI spectrum of N-phenylpyrrolidone-2 (**2a**)

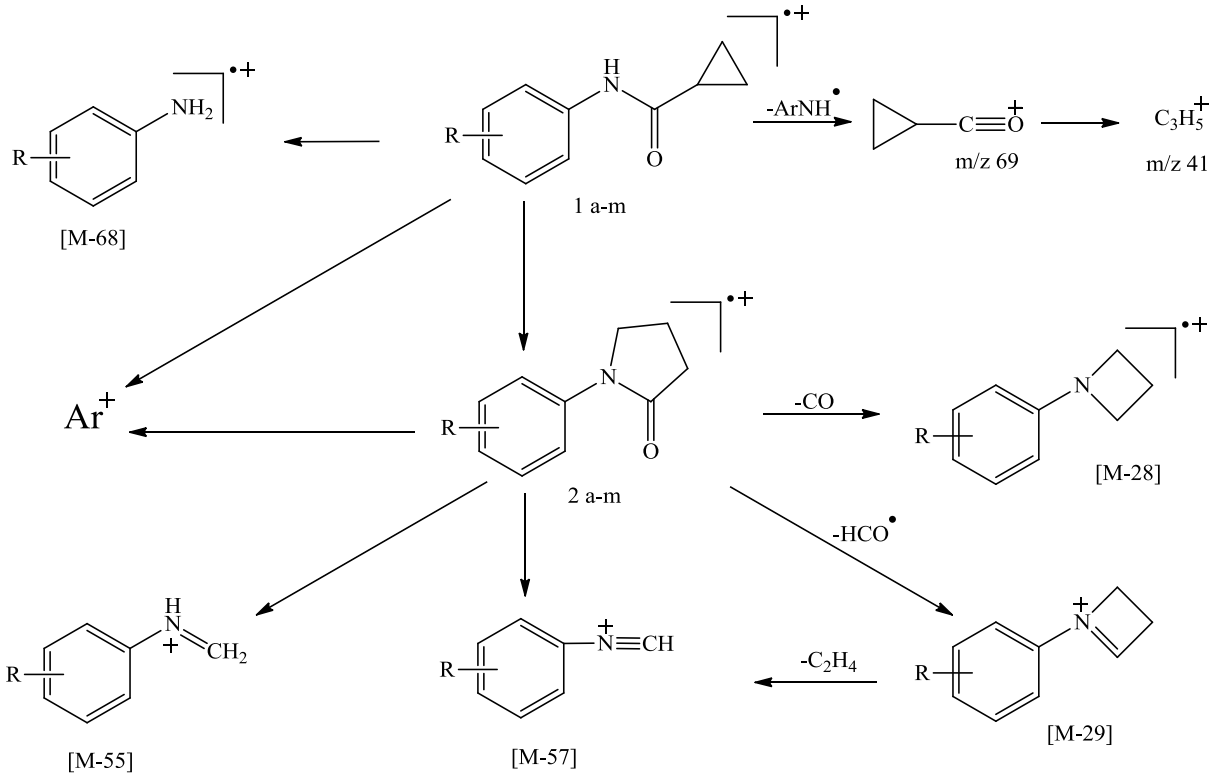
The molecular ion peaks are quite pronounced in all the spectra which is a typical feature of aromatic compounds.[20] The base peak in the spectra of *N*-arylcyclopropanecarboxamides **1** is always due to the ion with the structure of the molecular ion of the substituted aniline (*m/z* 93 in Fig. 2a) formed as a result of N-C(O) bond cleavage accompanied by a hydrogen shift. This process is typical for N-phenylalkylamides and involves the charged site triggering a four-membered transition state.[20] The hydride-anion migrates from the CH-group of the cyclopropyl moiety. The process is accompanied by the loss of the cyclopropylketene molecule. Alternatively, the charge may be retained on the complementary ion of *m/z* 69 (Scheme 2), where it is formed by cleavage of the same N-C(O) bond, but without hydrogen migration. The intensity of that peak is quite pronounced in the spectra of all the *N*-arylcyclopropanecarboxamides **1** (Table 1). Another ion worth mentioning is $C_3H_5^+$ (*m/z* 41), which is formed by

the loss of a CO molecule from *m/z* 69. Its intensity is quite high in the spectra of all the *N*-arylcyclopropanecarboxamides **1** (Table 1).

The intensity of the three mentioned peaks ($ArNH_2^{+\cdot}$, *m/z* 69, and *m/z* 41) is quite low in the EI spectra of N-arylpyrrolidones-2 (Table 1). The base peak in these spectra arises due to a loss from the molecular ion of 55 Da (CH_2CHCO radical according to the accurate mass measurements). This fragmentation process involves the stepwise cleavage of the C-C and N-C(O) bonds of the pyrrolidine ring. Hydrogen migration to the positively charged nitrogen atom in the intermediate results in the formation of a stable ammonium type fragment ion (*m/z* 106 in Fig. 2b). An alternative hydrogen migration from the arylamino moiety rationalizes the loss of the CH_3CH_2CO radical (57 Da) with the formation of an isonitrile-type ion (*m/z* 104 in Fig. 2b). The minor process involves the losses of CO and HCO species from the molecular ions of pyrrolidines **2**. Their composition is confirmed by the accurate mass measurements, while their structure may be cyclic (azetidines in Scheme 2) or linear. It is worth mentioning that the $[M - 57]^+$ ion may form stepwise through the consecutive losses of a HCO radical and an ethylene molecule.

It is important to emphasize that two characteristic pyrrolidines **2** ions, ($[M - 55]^+$ and $[M - 57]^+$), are also present in the spectrum of *N*-arylcyclopropane-carboxamide (Fig. 2a; *m/z* 104 and 106). They are also present in the spectra of all other *N*-arylcyclopropanecarboxamides **1**, although their intensities are quite low. As these species definitely cannot be formed directly from the molecular ions of *N*-arylcyclopropanecarboxamides, transformation of a small portion of the latter into N-arylpyrrolidones-2 may be proposed.

Because there are few ions in these mass spectra and the elemental compositions of all the ions is known due to accurate mass measurements, it is possible to propose the following general fragmentation scheme, covering both isomeric classes of compounds (**1** and **2**).



Scheme 2. The most efficient general fragmentation pathways of isomeric compounds **1** and **2**

Table 1. The relative intensities of the characteristic ions in the EI mass spectra of compounds **1** and **2** (% in total ion current)

Comp	***m/z 41***	***m/z 69***	**M-HCO**	**M-CO**	**[M–55]**	**[M–57]**	**[M–68]**	**[M–84]**
1a	7.74	11.0	0.09	-	0.71	0.24	38.9	2.73
2a	0.89	-	0.77	1.12	38.1	3.94	1.30	9.30
1b	6.04	10.1	-	-	0.71	0.24	38.8	1.51
2b	1.02	0.07	2.48	2.22	19.5	5.92	0.26	5.27
1c	5.68	7.49	0.10	0.04	0.83	0.16	40.2	1.19
2c	0.73	0.1	0.50	0.28	42.4	1.99	0.25	4.94
1d	6.70	8.47	-	-	0.68	0.12	22.9	0.19
2d	1.08	1.24	0.06	0.06	22.2	1.58	-	0.73
1e	6.78	10.0	-	-	0.21	0.16	17.2	0.19
2e	5.4	8.49	0.11	-	1.21	2.00	11.7	0.52
1f	8.55	12.4	-	-	0.83	0.28	37.8	0.53
2f	0.62	0.44	0.39	0.39	44.0	4.02	0.22	3.83
1g	8.04	12.6	-	-	0.45	0.09	21.4	0.39
2g	0.85	0.04	0.05	-	15.6	2.23	0.06	3.3
1h	9.49	15.7	-	-	0.32	0.08	28.7	0.75
2h	0.76	0.09	0.41	0.22	32.95	2.57	0.11	4.98
1i	8.14	13.9	-	-	0.19	0.04	17.9	0.37
2i	0.62	-	0.1	0.52	16.79	1.71	0.09	2.6
1j	6.93	11.2	-	0.01	0.34	0.06	35.3	0.28
2j	1.04	0.54	0.16	0.35	27.9	1.44	1.17	1.59
1k	6.59	9.91	-	-	0.15	0.07	22.9	0.12
2k	1.22	0.53	0.2	-	2.58	3.29	-	1.02
1l	12.9	38.0	0.06	0.01	0.09	0.03	5.68	3.23
2l	1.48	0.98	0.16	0.97	33.7	0.33	0.08	0.21

The intensities of the $[M - 55]^+$ and $[M - 57]^+$ ions are much higher in spectra of compounds **2**. It is hardly possible to propose a mechanism of formation of these ions directly from the molecular ions of **1**. Therefore, the intensities of these ions theoretically could be considered as a measure of the yield of the transformation of molecular ions of **1** into **2**. The following formula may then be treated as a measure of transformation in the gas phase.

where the numerator contains the sum of the intensities of the $[M - 55]^+$ and $[M - 57]^+$ ions for compound **1** and the denominator the sum of the intensities of the $[M - 55]^+$ and $[M - 57]^+$ ions for compound **2.** Table 2 presents the yields of the transformation of **1** into **2** calculated by this proposed formula.

Table 2. Calculated yields of the cyclization of molecular ions of cyclopropanes **1** into pyrrolidines **2**

Compound	**R_i, %**
1a	2.3
1b	3.7
1c	2.1
1d	21.3
1e	11.5
1f	2.3
1g	2.9
1h	1.1
1i	1.2
1j	1.4
1k	3.7
1l	0.4

The results shown Table 2 are difficult to rationalize on the basis of inductive, mesomeric or steric effects. Therefore, for some reason the EI mass spectra of the *N*-arylcyclopropanecarboxamides **1** cannot be used to mimic their transformation into N-arylpyrrolidones-2 in the condensed phase. This conclusion gives rise to the following question. Why does it not work with this particular group of cyclopropanes, if it worked nicely with other types of cyclopropanes? [9-12]

To answer this question we used DFT calculations. Three versions of the transformation of **1** into **2** (Scheme 1) were calculated: i) thermal isomerisation of the neutral molecule; 2) isomerisation catalyzed by the Brønsted acids

(protonated molecule) mimicking the experimental condensed phase reaction; and 3) isomerisation of the ionized molecule (radical-cation) formed in the ion source of a mass spectrometer.

According to the calculations, isomerisation of the neutral molecule **1a** should proceed stepwise. The first stage involves the opening of the 3-membered ring accompanied by tcleavage of the existing N-C(O) bond and formation of a new N-C bond, leading to ketene **3** via transition state TS1 (Fig. 3).

The second step involves transformation of ketene 3 into phenylpyrrolidone 2 through the formation of the 5-membered ring followed by hydrogen migration from the N atom to the C4 atom (TS2, Fig. 3).

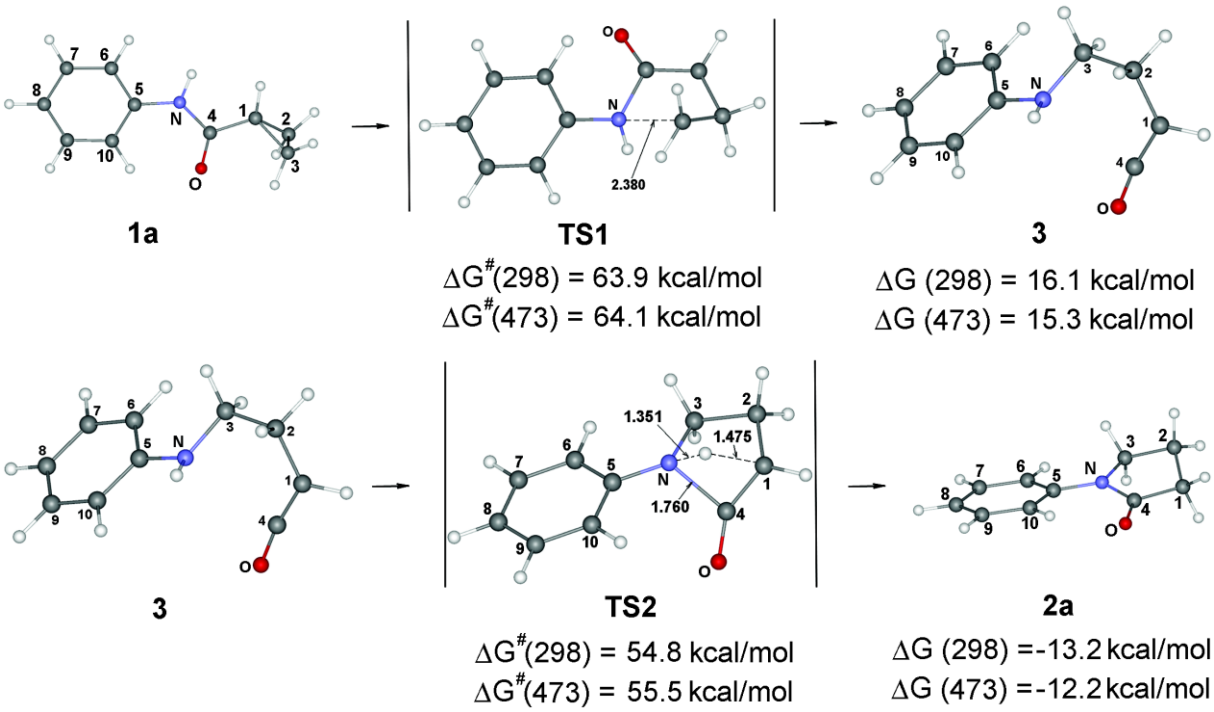


Fig. 3. The mechanism of thermal isomerisation **1** → **2**.

The Cartesian coordinates and energy parameters of all the discussed structures are presented in the Supplementary Information. Due to the high activation barrier (64.1 kcal/mol of the first stage) and (55.4 kcal/mol of the second stage), one can conclude, that the reaction **1** → **2** is hardly possible even at the elevated temperature (200º C).

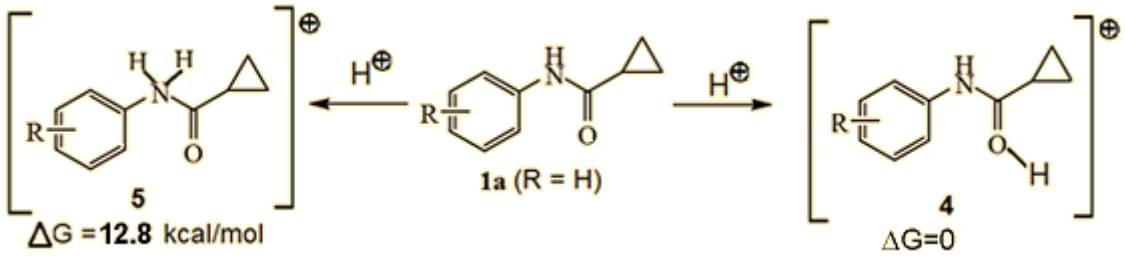


Fig. 4. Two directions of protonation of *N*-arylcyclopropanecarboxamides **1**

Protonation of cyclopropanes 1 may involve either the carbonyl oxygen atom (cation 4) or the amide nitrogen atom (cation 5). Both ions are presented in Fig. 4. In the gas phase the protonation of oxygen is more efficient (12.8 kcal/mol). However, in the applied experimental conditions in the condensed phase compounds **1** are adsorbed at the acidic Lewis centers of the aluminum oxide due to the bonding C=O:→Al(O-)$_3$. Thus, oxygen protonation to form cation **4** is hampered. Isomerisation of the protonated cyclopropanes **1** was, however, calculated for both structures **4** and **5**.

According to the calculations, cleavage of the cyclopropyl moiety in cation **4** and formation of a C_3-N bond, leading to the protonated pyrrolidine ring, require a transition state TS3 (Fig. 5) with a partially double C_4-C_1 bond and a high energy barrier. The formation of oxygen-protonated pyrrolidine **6** is energetically unfavorable, while the following proton shift from O or N atoms to C_1 cannot proceed as an intramolecular process (barriers 71 kcal/mol and 65 kcal/mol, respectively) as it is banned by symmetry. In the condensed phase

these processes are possible as intermolecular reactions with participation of the proton carrier-molecules. Nevertheless the above-mentioned facts clearly show that isomerisation **1** → **2** with participation of cation **4** is hardly possible.

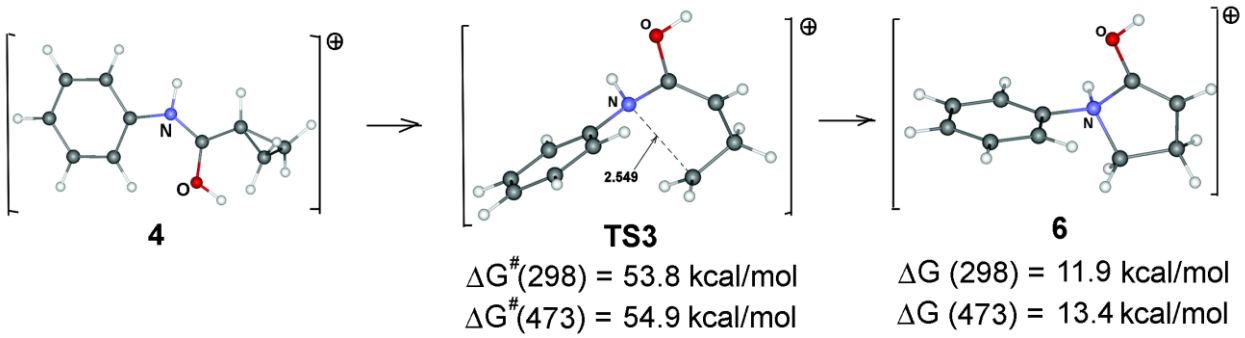


Fig. 5. Isomerisation of cation **4** with the opening of the small ring

Figure 6 illustrates the isomerisation of cation **5**. Similarly to the isomerisation of the neutral molecule the process in cation **5** involves the opening of the 3-membered ring accompanied by the cleavage of the N-C(O) bond. It is worth mentioning that the N-C(O) bond in cation **5** elongates from 1.383 Å in the neutral molecule to 1.693 Å, demonstrating its notable weakening, and this results in the considerable (~30 kcal/mol) decrease of the energy barrier in TS4. The first stage of the whole process is thermodynamically neutral, resulting in the formation of N-protonated ketene **7**. Its cyclization via TS5 being exothermic takes place quite easily. Therefore, the results obtained allow us to concluse that isomerisation **1** → **2** catalyzed by Brønsted acids at elevated temperatures passes via the N-protonated cation **5**. The energy barrier of the rate-limiting stage calculated for the gas phase (35.7 kcal/mol at 200^0C) makes this reaction quite possible at elevated temperatures. Since the transition state TS4 is highly polar (calculated dipole momentum is 4.3D), a polar solvent or adsorption of the reagent may reduce the barrier even more significantly.

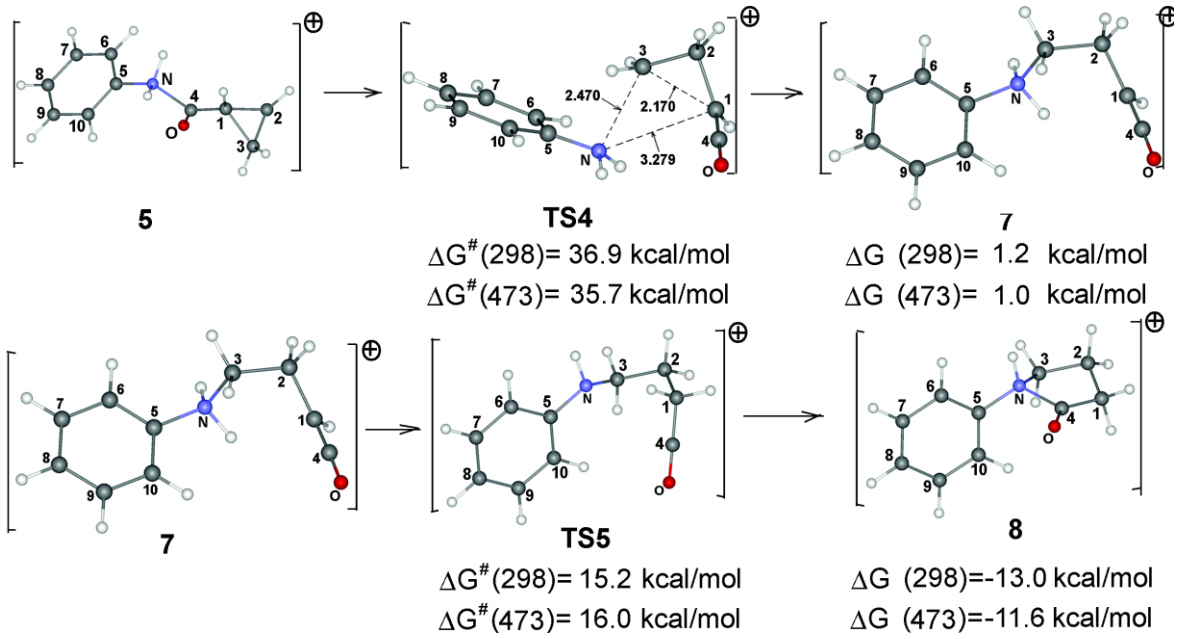


Fig.6. Isomerisation of cation **5** with the opening of the small ring.

Electron ionization of compound **1a** results in formation of the odd-electron $M^{+\cdot}$ (**9**) due to the loss of an electron from the HOMO orbital. Ionization therefore leads to certain changes in the geometry of the particle before it starts to fragment. For example, the length of the N-C(O) bond increases from 1.386 to 1.462 Å. The applied calculations demonstrate that the above described mechanism of isomerisation of the closed shell species (Figs. 3-6) in the case of the radical-cation results in the decomposition of the original molecular ion into two species via TS7 (Fig. 7). These species are ions of *m/z* 93 and 69 and they are the most abundant peaks in the mass spectrum of compound **1a** (Fig. 2a).

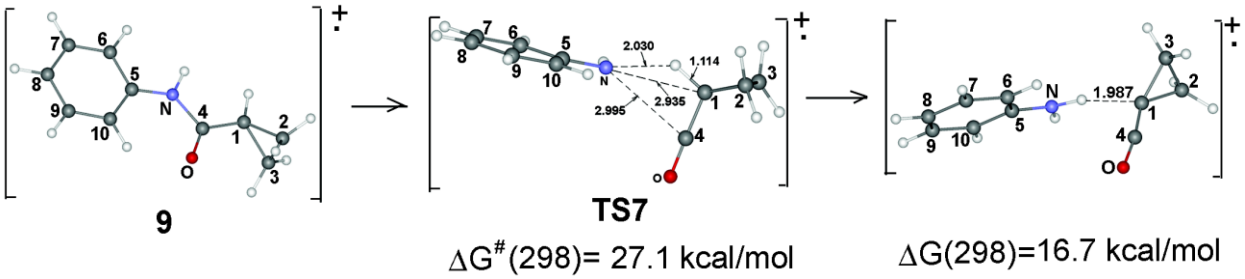


Fig. 7. Energy parameters of the isomerisation of radical-cation **1a** resulting in fragmentation with the formation of ions of *m/z* 93 and 69

An alternative process involves the opening of the 3-membered ring accompanied by simultaneous cyclization into the 5-membered pyrrolidine (Fig. 8). The energy barrier for this transformation at 200^{0}C is 45.3 kcal/mol. Although this value is ~20 kcal/mol higher than that leading to the decomposition (Fig. 7), it is achievable for the species under electron ionization due to the wide range of the internal energies of the molecular ions. [20] The number of cyclizing molecules is low anyway. Therefore, the quantum chemical calculations nicely correlate with the mass spectrometry results.

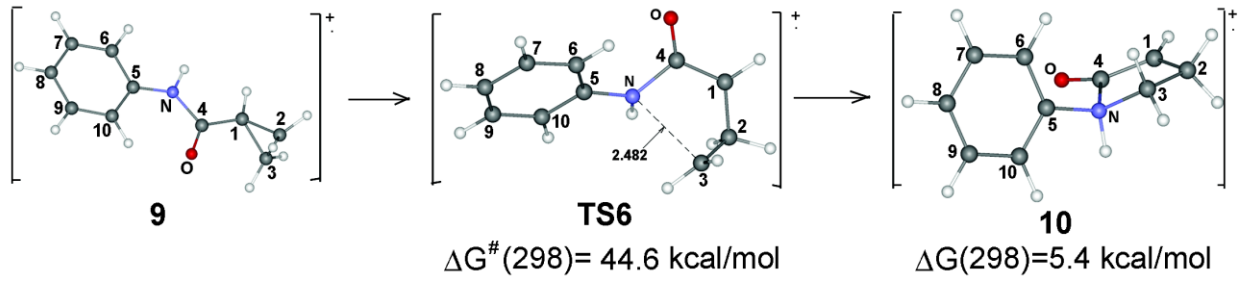


Fig.8. Energy parameters of the isomerisation of radical-cation **9** resulting in the formation of pyrrolidone cycle

Conclusion

The combined application of the chemical experiment in the condensed phase, electron ionization in the gas phase, and DFT calculations allowed reaction mechanisms to be proposed for the isomerisation of *N*-arylcyclopropanecarboxamides into N-arylpyrrolidinones-2. The difference in the behavior of the initial *N*-arylcyclopropanecarboxamides in conditions of protonation and electron ionization is energy dependent. The principal mechanism of isomerisation of the protonated species leads in the case of the radical-cation species to fragmentation. An alternative transformation mechanism is, however, responsible for the isomerisation of a small portion of the higher energy molecular ions of *N*-arylcyclopropanecarboxamides into the corresponding N-arylpyrrolidinones-2 structures**.**

Acknowledgments

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