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Highly Efficient Dehydrogenation of 5-Benzyl-3-phenyl-2-thioxoimidazolidin-4-one: Microwave versus Flash Vacuum Pyrolysis Conditions

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5-Benzyl-3-phenyl-2-thioxoimidazolidin-4-one underwent thermal dehydrogenation to afford 5-benzylidene-2-thioxoimidaxolidin-4-one under microwave and flash vacuum pyrolysis conditions. A high predominance of the *Z*-isomer over the *E*-isomer of the imidazolidinone product was achieved. By using DFT and NBO calculations, the mechanism of the dehydrogenation and the selectivity were also explored.

Introduction

Pharmaceutically active compounds such as antimycobacterials,[1] immunomodulators,[2] anticonvulsivants,[3] and antifungals[4] that present the 5-arylmethylene-2-thioxoimidazolidin-4-one nucleus have been a motivating factor for developing improved methods for their synthesis and examination of their reactivity. However, these methodologies usually involve several steps that inevitably lead to important decreases in the global yield of the reaction. As an example of a current method applying these multiple-step procedures, we can mention the recent work by Parwal et al., where a multicomponent reaction including benzaldehydes, glycine, and thiocyanate was reported.[5]

In pursuing better reaction conditions and greener approaches to what has previously been reported, hereby we report two efficient ecofriendly methodologies (solventless reaction conditions) to synthesize the 5-phenylmethylene-2-thioxoimidazolidin-4-one core through a selective dehydrogenation reaction on 5-benzyl-3-phenyl-2-thioxoimidazolidin-4-one (**3**) that also provides a remarkable specificity to the synthesis of the *Z*-isomer of the main product. 5-Benzyl-2-thioxoimidazolidin-4-ones structurally differ from the 5-phenylmethylene-2-thioxoimidazolidin-4-ones target in the presence of an exocyclic double bond at C5. Many reactions have been proposed to induce the formation of the exocyclic double bonds through dehydrogenation reactions in heterocyclic systems. In most cases, the use of a coreactant or a catalyst, such as rhodium,[6] iridium,[7] or even the more complex catalyst like Cr-MCM-41,[8] is required to produce this type of dehydrogenation. Furthermore, this process is usually nonselective, involves high temperatures, and long reaction times favoring thermal cracking of the reaction mixture into lighter compounds and coke.

In this work, we report the application of microwave-induced pyrolysis (MIP) and flash vacuum pyrolysis (FVP) procedures to carry out the selective dehydrogenation of 5-benzyl-3-phenyl-2-thioxoimidazolidin-4-one (**3**) to obtain phenylmethylene-3-phenyl-2-thioxoimidazolidin-4-one (**4**) without any additives or catalysts. Dehydrogenations are quite common in high-temperature pyrolysis, especially in the final step in a sequence leading to the formation of an aromatic or stable product.[9] However, information regarding selective dehydrogenations is scarce and few examples have been studied. In our case, an extremely high specificity (98:2) on the *Z*/*E* isomer distribution of **4** was achieved, and a feasible mechanism for the dehydrogenation is hereby proposed based on results fully supported by DFT calculations.

On the other hand, microwave-assisted reactions are invariably faster and often proceed in higher yields than those performed under conventional thermal methods.[10] It has been reported that with high initial powers (150–300 W), solid-phase reactions carried out under microwave irradiation produce results that are similar to FVP due to the high heating rates.[11] To extend the range of FVP and microwave applications we have compared both methodologies in the dehydrogenation process of thioxoimidazolidinone **3**.

Results and Discussion

The selection of starting material **3** was important because it dehydrogenates to give thioxoimidazolidinone **4**. Synthesis of **3** was described previously from phenyl isothiocyanate (**1**) and phenylalanine (**2**) in a 1 N aqueous solution of hydrogen chloride in good yields (80%).[12] Instead of using the traditional protocol, we chose an ecofriendly

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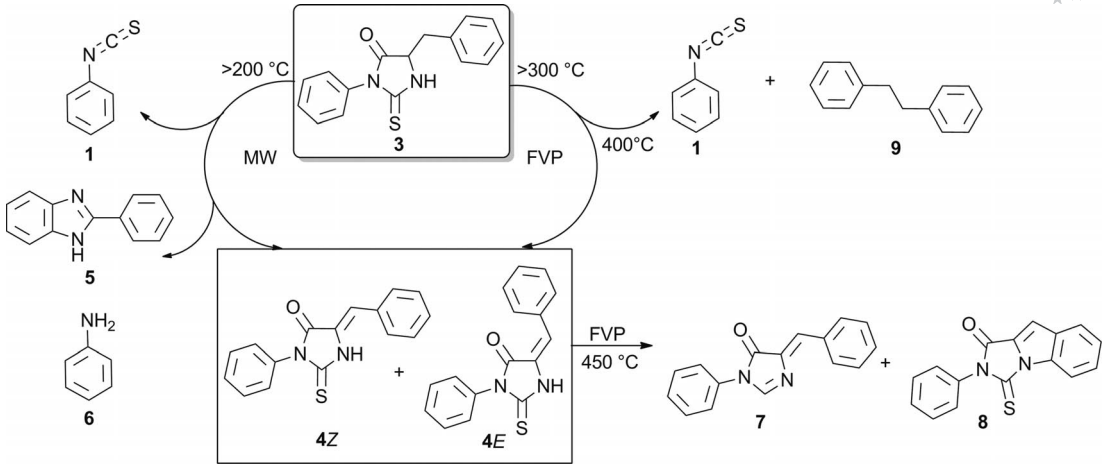


Scheme 1. MIP and FVP reactions of thioxoimidazolinone **3**.

methodology without the use of a solvent and application of microwave irradiation as a heating source to prepare this precursor. Thus, moderate to good yields of **3** (60–80%) were achieved while avoiding a cumbersome synthesis (see the Experimental Section).

In the next step, compound **3** was subjected to MIP at 300 W in a sealed tube in the presence of different solvents as well as under solvent-free conditions at 200 and 250 °C. Reactions below 200 °C were carried out without success, and only the starting material was recovered. From 200 °C, the main product was 5-benzylidene-3-phenyl-2-thioxoimidazolidin-4-one (**4**), which was obtained through dehydrogenation of **3** (Scheme 1). Dimethylformamide (DMF), nitromethane (NM), and *o*-dichlorobenzene (*o*-DCB) were evaluated as solvents. However, better yields (42–47%) were achieved under solvent-free conditions after 25 min of irradiation at 250 °C. The results are summarized in Table 1. It is important to remark that compound **4** was obtained as a mixture of *Z*/*E* isomers under all conditions. ^{1}H NMR spectroscopic analysis of this mixture indicated that the *Z*/*E* ratio was 98:2 and remained unchanged under all reaction conditions.

Table 1. MW reactions of **3**.

T [°C]	Solvent	Time [min]	% Yield[a] **1**	**3**	**4**[b]	**5**	**6**
200	DMF	1	33	18	20	9	20
200	NM	1	3	92	3	1	1
200	*o*-DCB	1	4	91	4	1	0
200	–	5	6	86	2	0	6
		10	9	79	3	0	9
		15	8	78	5	0	9
		20	9	67	13	1	11
		25	15	47	20	1	18
250	–	5	17	46	14	1	23
		10	18	31	29	2	20
		15	21	10	42	3	23
		20	21	8	46	3	22
		25	21	7	47	4	22

[a] Determined by GC–MS. [b] Mixture of *Z*/*E* isomers (98:2).

In addition, fragmentation of the thioxoimidazolidinone ring also occurred, and compounds **1**, **5**, and **6** were obtained in the reaction mixture (Scheme 1). Aniline **6** could be rationalized through the formation of nitrene species capturing hydrogen. The formation of 2-phenylbenzimidazole (**5**) is less clear, as it would involve several steps combining highly reactive intermediates coming from the decomposition of **3**.

Then, FVP of **3** was performed at temperatures between 300 and 450 °C at 10^{-2} Torr, and contact times of 10^{-2} s. Thioxoimidazolidinone **4** was the main product obtained (as a mixture of *Z*/*E*-isomers) at all evaluated temperatures (Table 2), which is similar to the results obtained in the microwave-assisted reactions. It should be noted that over 400 °C, the pyrolyzate showed trace amounts of products **1**, and **7**–**9**. However, acceptable yields of **4** could be obtained without significant formation of secondary or carbonaceous products at 450 °C.

Table 2. FVP reactions of **3**.

T [°C]	% Yield[a] **3**	**4**	**7**	**8**	**9**
300	78	22	–	–	–
325	70	30	–	–	–
350	64	36	–	–	–
375	51	49	–	–	–
400[b]	40	55	–	–	traces
450[c]	16	71(60)[d]	3	2	5

[a] Percentage determined by ^{1}H NMR spectroscopy. [b] Trace amounts of product **1** were detected. [c] The presence of coke was detected. [d] Isolated yield.

The formation of imidazolone **7** can be rationalized by the loss of sulfur from **4**; this type of elimination is a predominant process in the thermolysis of thioxoderivatives.[13] Imidazoindolone **8** can be formed by intramolecular cyclization of thioxoimidazolidinone **4** involving an additional dehydrogenation reaction. A similar cyclization was observed in the transformation of anilinopyridines in a con-

tinuous-flow reactor containing K-16 as a dehydrogenating catalyst at 560–580 °C,[14] and other similar processes can be achieved in the presence of lead(IV) oxide.[15]

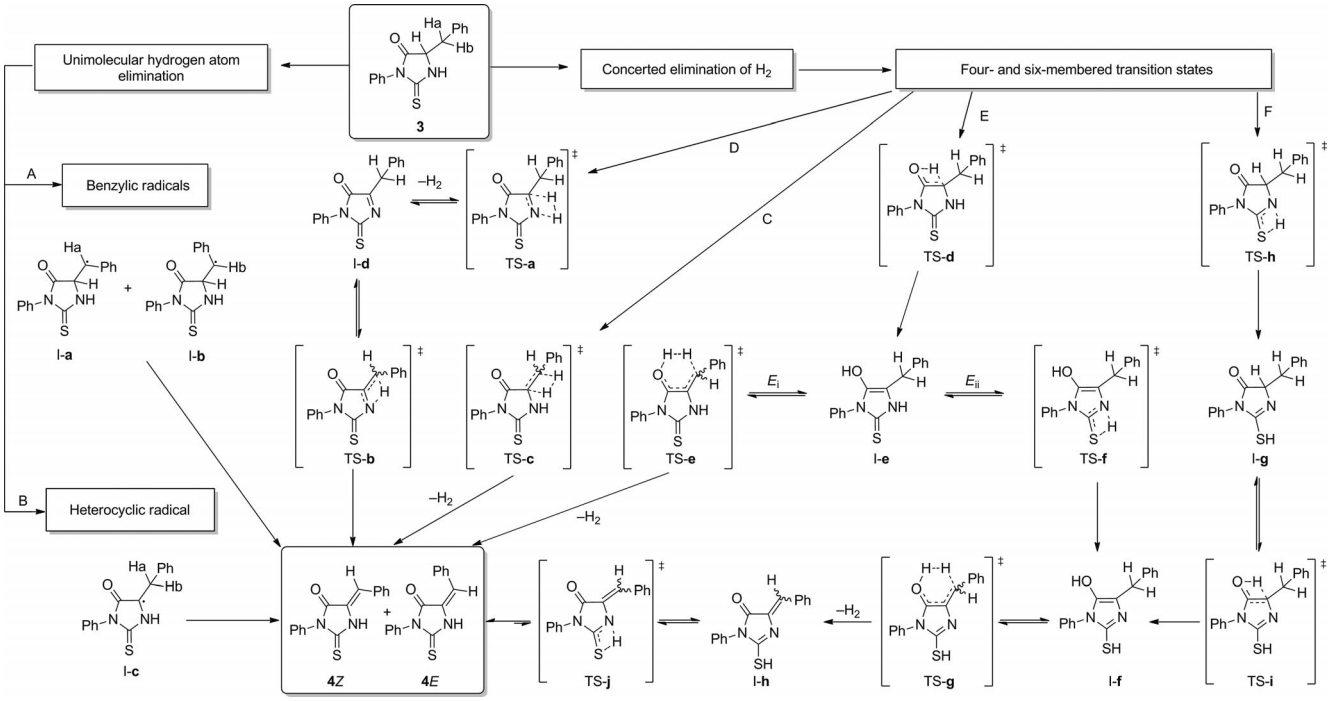
To address the origin of compounds **7** and **8**, FVP reactions of **4** at 450 °C were performed. Thus, products **1**, **7**, and **8** were obtained in low yields (2–4%), confirming our previous assumption and also showing the high thermal stability of **4** (85% was recovered). Further, no change in the isomer ratio of **4** was observed after the gas thermolysis. Although in FVP systems many products were formed, the yield of desired imidazolidinone **4** was slightly better than that achieved in MW-assisted reactions.

The main goal of this contribution was the study of the dehydrogenation mechanism to give imidazolidinone **4**. Therefore, it became very important to acknowledge that precursor **3** can be present in tautomeric equilibrium and, therefore, the mechanism would strongly depend on which tautomer is reacting. In addition, this kind of mechanistic information can be better retrieved through the use of FVP techniques to obtain kinetic and thermodynamic parameters.[16]

There are no previous mechanistic studies on the gas-phase dehydrogenation of benzylimidazolidinones. We suggest two main ways of analyzing the mechanism: a stepwise manner via a radical intermediate (Scheme 2, paths A and B) and a concerted route (Scheme 2, paths C–F). Regarding all the possible reaction mechanisms, radical mechanisms were expected to give positive entropies of activation, as previously reported;[17,18] on the other hand, concerted ways were expected to give negative values. Several reactions, such as ring opening of hexahydroquinazolinones,[19] isomerization of angular to linear fused triazolobenzotriazines,[20] and β-elimination of CO_2 from pyruvic acid,[21] are nice examples of thermal processes with a concerted character.

Thus, kinetic measurements on the FVP of **3** were carried out to get more information on the reaction mechanism (see Table 3). Thioxoimidazolidinone **3** was the only starting material that afforded **4** without decomposition to other by-products at lower reaction temperatures (300–400 °C). Reaction constants were measured at each temperature by at least three determinations. Not only the relative concentrations of the starting material but also the concentrations of product were determined by ^{1}H NMR spectroscopy. Reaction times were calculated as V_0/m (contact time), where V_0 is the volume of the reaction tube inside the hot zone and m is the carrier gas flow. Arrhenius parameters were calculated by using the classical equation ($\ln k$ vs. $1/T$). To validate the system, the kinetic parameters for the pyrolysis of ethyl acetate were measured and compared with those reported for a static system; these results, together with a detailed description of the methodology, were exhaustively described earlier.[22] From the results in Table 3, the calculated negative value of $\Delta S^{\#}$ (–34.8 eu) indicated that the mechanism greatly differed from the expected radical process, where this value should have been positive. Thus, the dehydrogenation reaction could be taking place through one of the concerted mechanisms described in Scheme 2.

Despite this experimental result, all paths proposed in Scheme 2 were studied by quantum chemistry calculations to obtain further information about the reaction mechanism. The optimized geometries of reactant **3** and products **4***Z* and **4***E* are shown in Figure 1. The calculated energy difference values were 24.0 and 26.4 kcal mol^{-1} for **4***Z* and



Scheme 2. Proposed mechanisms for the dehydrogenation of thioxoimidazolinone **3**.

Table 3. Arrhenius parameters for the dehydrogenation reaction of **3**.

T [°C]	C/C_0	Contact time [10^{-2} s]	k [10^{-2} s][a]	E_a [kcal mol^{-1}]	$\Delta S^{\#}$ [eu]
300	0.78 ± 0.02	1.08 ± 0.07	0.23 ± 0.01	11.2 ± 0.6	–34.8 ± 0.4
325	0.70 ± 0.02	1.03 ± 0.06	0.35 ± 0.02		
350	0.64 ± 0.02	0.99 ± 0.06	0.45 ± 0.02		
375	0.51 ± 0.02	0.95 ± 0.05	0.71 ± 0.03		
400	0.40 ± 0.01	0.92 ± 0.05	1.00 ± 0.05		

[a] Values averaged over at least three determinations.

4*E*, respectively. Thus, **4***E* was less stable by 2.4 kcal mol^{-1} than **4***Z*. Radical pathways (Scheme 2, paths A and B) should involve a double elimination of hydrogen atoms in stages through intermediacy of species I-**a**, I-**b**, and I-**c**. DFT calculations revealed that the first step was a unimolecular dissociation reaction, where the potential energy raised monotonically.

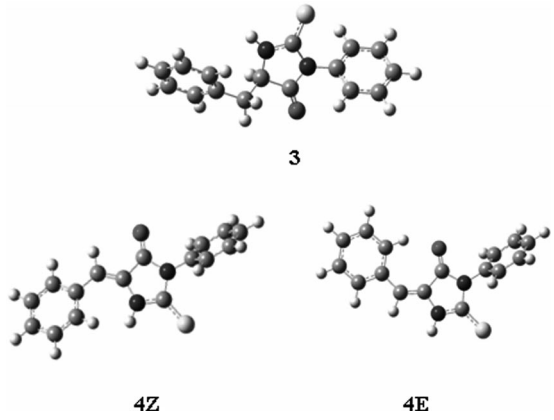


Figure 1. Optimized geometries of **3** and **4**.

In the proposed path A, the elimination of either one of both hydrogen atoms affords benzyl radicals I-**a** and I-**b**. The energies required were 96.5 and 94.8 kcal mol^{-1}, respectively (see Table 4), whereas in the case of path B, dissociation could lead to the formation of heterocyclic radical I-**c** and the energy considered necessary was 91.6 kcal mol^{-1}. It is important to note that any of the radicals formed should allow free rotation of either the phenyl or benzyl group, and therefore, the next hydrogen elimination would initially lead to the formation of **4***Z* and **4***E* isomers in equal proportions. The measured values of $\Delta G^{\#}$ and $\Delta S^{\#}$ could not be supported by these radical processes and they were accordingly discarded as outlined mechanisms of the dehydrogenation reaction.

Regarding the proposed concerted hydrogen eliminations, paths C and D involve direct loss of H_2 through four-centered transition states TS-**c** and TS-**a**, respectively. Path C affords **4** in one step, whereas path D leads first to the formation of intermediate I-**d**, which later can tautomerize into **4** through TS-**b**. The energy barrier for path C is 110 kcal mol^{-1}, whereas path D requires 105 kcal mol^{-1} for hydrogen elimination and 57 kcal mol^{-1} for tautomerization. Both paths C and D need almost 20 kcal mol^{-1} more than the radical processes.

It is known that imidazolidinones like **3** can exist in different tautomeric forms depending on the medium.[23] For that reason, dehydrogenation from intermediates enol I-**e** and thioenol I-**g** was calculated (paths E and F, which involve tautomerization followed by H_2 elimination through a six-membered transition state). Thus, in path E, tautomerization to enolic form I-**e** (TS-**d**: 80.4 kcal mol^{-1}) was proposed. This intermediate can either directly eliminate H_2 to afford **4** ($E \rightarrow E_i$, TS-**e**: 50.0 kcal mol^{-1}) or tautomerize to thiol form I-**f** ($E \rightarrow E_{ii}$, TS-**f**: 72.0 kcal mol^{-1}). In both cases, the higher energy step was the enolization to I-**e**.

Path F involves the conversion of **3** into thioenol form I-**g** (TS-**h**: 41.2 kcal mol^{-1}) followed by a new tautomerization ($E \rightarrow E_{ii}$), which ends up with the same intermediate I-**f** (TS-**i**: 72.3 kcal mol^{-1}). Nevertheless, the energy required for this path was almost 10 kcal mol^{-1} lower than that involved in path E. From intermediate I-**f**, dehydrogenation was possible (TS-**g**: 45.0 kcal mol^{-1}) and required 5 kcal mol^{-1} less energy than that estimated for path $E \rightarrow E_i$.

In summary, from all the calculations, we propose that the lowest channel for the dehydrogenation reaction of compound **3** is path F, which is the enolization rate-determining step that gives I-**f**. Nevertheless, the absolute values found in this study were considerably different to those found experimentally.

On the basis of steric and electrostatic factors, calculations showed that the bulky phenyl ring would not have an influence on the experimentally observed *Z*/*E* ratio. Thus, it was not possible to explain why high selectivity was observed (98:2) on these terms. There are no records in the literature for that particular selectivity, though there is a significant number of articles reporting the existence of both types of isomers.[24,25] Our experimental results showed that the ratio of isomers of **4** remained the same, irrespective of the methodology employed, namely, MIP or FVP. Therefore, we believe that the explanation, supported by calculations on specific NBO donor–acceptor interactions, lies before the final product was formed but after the rate-determining step, that is, during the formation of the

Table 4. B3LYP energy of transient species in the gas phase.

Path	Radical pathways A	B	Concerted pathways C	D			E				F							
Species	I-**a**	I-**b**	I-**c**	TS-**c**[b]	TS-**a**[b]	I-**d**	TS-**b**[c]	TS-**d**[c]	I-**e**	TS-**e**[b]	TS-**f**[c]	TS-**h**[c]	I-**g**	TS-**i**[c]	I-**f**	TS-**g**[b]	I-**h**	TS-**j**[c]
ΔE[a]	94.8	96.5	91.6	110.0	105.0	42.8	57.4	80.4	17.8	50.0	72.0	41.2	16.1	72.3	28.4	45.0	41.2	15.3

[a] Values in kcal mol^{-1}. [b] Hydrogen elimination. [c] Tautomerization.

transition state that led to the very dehydrogenation step. The NBO data showed that there were effective energy interactions between the O17 oxygen lone pair of electrons as well as the C12 antibonding lone pair of electrons, both with the σ antibonding orbital (σ*) of H13–H18 favoring the formation of the TS-g*Z* isomer by about 10 kcal mol^{-1} (see Figure 2).

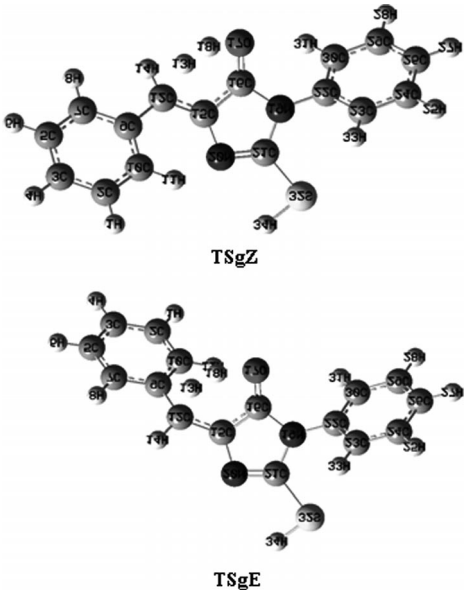


Figure 2. Atom numbering for TS-g*Z* and TS-g*E*.

Despite the fact that the experimental energy barrier obtained was much lower than the calculated numbers, we believe that the overall trend of the calculations was quite significant, because we can not only explain the products but also justify the high selectivity.

Conclusions

A high selective synthesis of *Z*-5-phenylmethylene-2-thioxoimidazolidin-4-one (**4**) was nicely carried out by dehydrogenation of imidazolidinone **3**. We have developed two efficient routes toward the target compound: microwave-induce pyrolysis (MIP) and flash vacuum pyrolysis (FVP). In the case of the FVP reactions, yields were better than those obtained in the MW experiments.

According to theoretical calculations, we fully rationalize and suggest that dehydrogenation can be achieved in a concerted way involving a thio-enol intermediate (i.e., I-**f**). In addition, the experimentally observed selectivity can arise from orbital interactions between the O17–C12 atoms before the formal dehydrogenation takes place.

This work strongly increases the interest of dehydrogenation studies of other heterocyclic compounds using MIP and FVP as alternative synthetic tools.

Experimental Section

General Methods: FVP reactions were carried out in a Vycor glass reactor by using a tube furnace with a temperature-controller device. Oxygen-free dry nitrogen was used as the carrier gas. Contact times were around 10^{-2} s and a pressure of 0.02 Torr was used. Products were trapped at liquid air temperature, extracted with a solvent, and subjected to different analyses or separation techniques. In all FVP experiments, the recovery of material was >90%. Reactions under microwave irradiation were performed in cylindrical quartz tubes (Φ = 1.5 cm) located in a CEM microwave reactor (2.455 GHz), with adjustable power within the range 0–300 W and a wave guide (monomode) fitted with a stirring device and an IR temperature detector. Melting points were determined with an Electrothermal 9100 melting point apparatus. All compounds were characterized by standard spectroscopic techniques (^{1}H NMR, ^{13}C NMR, HMBC, HSQC, UV, IR) and mass spectrometry, and all data are in agreement with the proposed structures. ^{1}H, ^{13}C, HSQC and HMBC spectra were recorded in [D_6]-DMSO and [D_6]acetone with a Bruker Avance II 400 MHz spectrometer (BBI probe, z gradient) (^{1}H at 400.16 MHz and ^{13}C at 100.56 MHz). Chemical shifts are reported in parts per million (ppm) downfield from TMS. The spectra were measured at 22 °C. Absorption spectra of the solution was recorded with a UV-1601 Shimadzu spectrophotometer using a quartz cell with an optical path length of 1 cm and acetonitrile as solvent. Infrared solid spectra were recorded with an FTIR Bruker IFS 28v spectrometer, with a resolution of 2 cm^{-1} in the range from 4000 to 400 cm^{-1} by using KBr disks. All calculations were performed with the Gaussian03 program system[26] by using a DFT-B3LYP/6-31+G(d,p) approach. Transition-state theory was used to evaluate the energy of the different channels. The transition states were characterized by the presence of one negative frequency and the internal reaction′s coordinate (IRC) method was applied to verify that the correct states were connected. Though we knew that more precise methods were available, we had a compromise between the size of the molecules under study and the computational cost. Gas chromatography/mass spectrometry (GC/MS) analyses were performed with a Shimadzu GC–MS-QP 5050 spectrometer equipped with a VF column (30 m × 0.25 mm × 5 μ) by using helium as eluent at a flow rate of 1.1 mL min^{-1}. The injector and ion source temperature was 280 °C, the oven heating ramp was 15 °C min^{-1} from 150 up to 280 °C, and the interface temperature was 280 °C. The pressure in the MS instrument was 10^{-5} Torr, precluding ion-molecule reactions from taking place, and MS recordings were made in the electron impact mode (EI) at ionization energy of 70 eV. In particular, the structure of compound **4*Z*** was unambiguously determined through single-crystal X-ray diffraction analysis by using a Bruker SMART APEX CCD diffractometer (see the Supporting Information).

General Procedures for the Synthesis of Thioxoimidazolidinone 3: This compound was prepared by modification of a previously reported methodology[12] using two procedures:

Method A: Phenyl isothiocyanate (**1**; 0.446 g, 3.3 mmol) was added to L-phenylalanine (**2**; 0.496 g, 3.0 mmol) suspended in a mixture of water/acetone (1:1, 30 mL). Then, freshly powdered NaOH (0.120 g) was added. The mixture was heated at reflux 2 h and left to stand overnight. Crystalline product **3** was isolated by vacuum filtration, washed with water, and dried (60% yield).

Method B: In a cylindrical quartz tube, L-phenylalanine (**2**; 0.496 g, 3.0 mmol) and phenyl isothiocyanate (**1**; 0.446 g, 3.3 mmol) were placed in that order. Nitromethane (0.3 mL) was added only to homogenize the mixture to perform the reaction. Then, the tube was introduced into the CEM microwave reactor. The mixture was stirred at room temperature and then irradiated at 150 °C for 10 min. The reaction crude was extracted with ethyl acetate (3 × 15 mL), the organic layer was dried with anhydrous Mg_2SO_4,

and after removal of the solvent under reduced pressure the solid was recrystallized (acetone/water) to give pure thioxoimidazolinone **3** (78.5% yield).

5-Benzyl-3-phenyl-2-thioxoimidazolidin-4-one (3): M.p. 187–188 °C (ref.[12] 187 °C). ^{1}H NMR (400.16 MHz, [D$_6$]DMSO): δ = 3.12 (d, J = 4.4 Hz, 2 H); 4.78 (m, 1 H), 6.78 (dd, J = 7.9, 2.0 Hz, 2 H), 7.21 (dd, J = 7.9, 2.0 Hz, 2 H), 7.30 (m, 3 H), 7.38 (m, 3 H), 10.61 (br. s, 1 H) ppm. ^{13}C NMR (100.56 MHz, [D$_6$]DMSO): δ = 36.6, 60.6, 127.5, 128.6 (2 C), 128.9 (2 C), 129.0, 129.1 (2 C), 130.2 (2 C), 133.6, 134.9, 173.9, 182.7 ppm. GC–MS: t = 16.61 min. MS (EI): m/z (%) = 282 (34) [M]$^+$. IR (KBr): $\tilde{\nu}$ = 3157 (NH st), 2903 (C–H sp^3 st), 1750 (C=O st), 1252 (C=S st) cm^{-1}. UV/Vis (CH$_3$CN): λ ($\varepsilon \times 10^4$, M^{-1} cm^{-1}) = 269 (1.654 ± 0.006) nm.

General Procedures for the Synthesis of Thioxoimidazolidinone Isomers 4*Z* and 4*E*

Microwave Irradiation: A cylindrical quartz tube (Φ = 1.5 cm) was charged with 2-thioxoimidazolidin-4-one (**3**; 25 mg, 88.5 μmol). After introduction into the CEM microwave reactor, it was irradiated at 200 and 250 °C between 5 and 25 min (Table 3). The mixture was extracted with acetone and subjected to GC–MS analysis. Then, the crude was purified by preparative thin-layer chromatography (dichloromethane/hexane, 6:4) as solvent mixture to afford title compound **4** in moderate yield (35–40%).

Flash Vacuum Pyrolysis Reaction: In a typical experiment, the sample (30 mg) was pyrolyzed. After the reaction, the crude was extracted with [D$_6$]acetone and subjected to GC–MS and NMR analysis. In this case the mixture was also purified by preparative thin-layer chromatography (dichloromethane/hexane, 6:4) to afford product **4** in good yields (60%).

Compounds **1**, **6**, and **9** were characterized by comparison with authentic samples.

***Z*-5-Benzylidene-3-phenyl-2-thioxoimidazolidin-4-one (4*Z*):** M.p. 208–209 °C (1-hexanol). ^{1}H NMR (400.16 MHz, [D$_6$]DMSO): δ = 6.70 (s, 1 H), 7.38–7.56 (m, 8 H), 7.33 (d, J = 6.9 Hz, 2 H), 12.60 (br. s, 1 H) ppm. ^{13}C NMR (100.56 MHz, [D$_6$]DMSO): δ = 113.3, 126.9, 128.8, 129.2, 129.3 (4 C, br. s.), 129.9 (2 C), 130.8 (2 C), 132.8, 133.8, 164.4, 179.2 ppm. GC–MS: t = 19.98 min. MS (EI): m/z (%) = 280 (100) [M]$^+$. IR (KBr): $\tilde{\nu}$ = 3213 (N–H st), 1743 (C=O st), 1252 (C=S st) cm^{-1}. UV/Vis (CH$_3$CN): λ ($\varepsilon \times 10^4$, M^{-1} cm^{-1}) = 356 (3.30 ± 0.01), 371 (3.21 ± 0.01).

***E*-5-Benzylidene-3-phenyl-2-thioxoimidazolidin-4-one (4*E*):** This compound was identified from a mixture with 4*Z*. ^{1}H NMR (400.16 MHz, [D$_6$]DMSO): δ = 6.75 (s, 1 H), 7.38–7.56 (m, 8 H), 8.04 (dd, J = 7.8, 3.9 Hz, 2 H); 12.55 (br. s, 1 H) ppm. ^{13}C NMR (100.56 MHz, [D$_6$]DMSO): δ = 120.1, 126.9, 128.9, 129.2, 129.3 (4 C, br. s.), 130.1 (2 C), 131.0 (2 C), 132.9, 133.7, 161.8, 175.9 ppm. GC–MS: t = 20.73 min. MS (EI): m/z (%) = 280 (100) [M]$^+$.

2-Phenyl-1*H*-benzo[*d*]imidazole (5): This compound was identified by GC–MS analysis with >90% match with the NIST library[27] GC–MS: t = 8.39 min. MS (EI): m/z (%) = 194 (100) [M]$^+$.

***Z*-4-Benzylidene-1-phenyl-1*H*-imidazol-5-one (7):** This compound was identified by GC–MS analysis, t = 14.83 min. MS (EI): m/z (%) = 248 (57) [M]$^+$.

2-Phenyl-3-thioxo-2,3-dihydro-1*H*-imidazo[1,5-*a*]indol-1-one (8): This compound was identified by GC–MS: t = 17.81 min. MS (EI): m/z (%) = 278 (47) [M]$^+$.

1,2-Diphenylethane (9): This compound was characterized by comparison with authentic sample. GC–MS: t = 5.94 min. MS (EI): m/z (%) = 182 (27) [M]$^+$.

Supporting Information (see footnote on the first page of this article): Characterization of compounds **1** and **3**–**9** and computational calculations.

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