

# Flash vacuum pyrolysis (fvp) of some hexahydroquinazolin-4(1*H*)-ones

Walter J. Peláez,<sup>a</sup> Zsolt Szakonyi,<sup>b</sup> Ferenc Fülöp<sup>b</sup> and Gloria I. Yranzo<sup>a,\*</sup>

<sup>a</sup>INFIQC—Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5016 Córdoba, Argentina

<sup>b</sup>Institute of Pharmaceutical Chemistry, University of Szeged, PO Box 427, Hungary

Received 6 March 2007; revised 16 June 2007; accepted 5 July 2007

Available online 6 August 2007

Dedicated to Professor C. Szantay on the occasion of his 80th birthday

**Abstract**—Some *cis/trans*-2-thioquinazolin-4-ones and their 2,4-dione analogs were subjected to flash vacuum pyrolysis. The *cis*- and *trans*-thio compounds reacted at lower temperatures than the *cis*- and *trans*-dioxo analogs, showing a lower thermal stability. All of these compounds afforded similar reactions: ring opening to the corresponding iso(thio)cyanate, the loss of H<sup>+</sup> and <sup>−</sup>NCS to form three isomeric cyclohexadienes and then aromatization to form the corresponding benzamide. The *cis*-dioxo compound also underwent a competitive retro Diels–Alder (RDA) reaction to form 3-phenylpyrimidine-2,4(1*H*,3*H*)-dione(3-phenyluracil) and butadiene. Kinetic measurements of the ring opening reaction supported a concerted β-elimination as the most probable mechanism.

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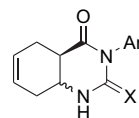
## 1. Introduction

Many retro Diels–Alder (RDA) reactions involve the splitting-off of cyclopentadiene or aromatic moieties, which are stable enough to lower the energy of activation of the reaction. There are many examples of these reactions, which are used for different purposes, for instance in transfer technology,<sup>1</sup> in the synthesis of natural products<sup>2</sup> and in connection with protective groups for unstable reagents such as selenoaldehydes.<sup>3</sup> On the other hand, it is expected that the splitting-off of a butadiene moiety should require higher energy than RDA reactions affording cyclopentadiene or an aromatic fragment, and for this reason the information on this particular type of RDA reaction is scarce. A spontaneous RDA reaction affording 1-(2-furyl)-3-dimethylamino-2-propene-1-thione, a butadiene-like fragment, was reported to occur during the process of purification of 2-aryl-4-(dimethylamino)-3-nitro-6-(2-furyl)-3,4-dihydro-2*H*-thiopyrans.<sup>4</sup> A RDA reaction in the fvp of *cis*-1,2,3,6-tetrahydrophthalic anhydride, affording butadiene and maleic anhydride, has also been described.<sup>5</sup>

The RDA reactions of some norbornene-fused uracils or thiouracils have been extensively studied as routes for the

synthesis of uracils and thiouracils.<sup>6–8</sup> These reactions, in which cyclopentadiene is splitted-off, were carried out without solvent above the melting point, i.e., at temperatures ranging from 150 to 250 °C.

The above-described RDA results encouraged us to carry out flash vacuum pyrolysis (fvp) reactions of *cis/trans*-2-thioquinazolin-4-ones (**1a–d,f**) and their 2,4-dione analogs (**1e,g**) (Fig. 1). These compounds could afford thiouracils or uracils in RDA reactions, but in this case the diene partner is butadiene and not cyclopentadiene, so, these reactions are expected to require higher energy. For this reason, the heterocyclic moiety in these molecules can also lead to different reactions, such as ring opening, isomerization, the loss of small molecules, etc., as competitive or lower energy



- 1a:** *cis*; X = S; Ar = Ph  
**1b:** *cis*; X = S; Ar = *m*-ClC<sub>6</sub>H<sub>4</sub>  
**1c:** *cis*; X = S; Ar = *p*-MeC<sub>6</sub>H<sub>4</sub>  
**1d:** *cis*; X = S; Ar = *m*-MeOC<sub>6</sub>H<sub>4</sub>  
**1e:** *cis*; X = O; Ar = Ph  
**1f:** *trans*; X = S; Ar = Ph  
**1g:** *trans*; X = O; Ar = Ph

Figure 1.

**Keywords:** Flash vacuum pyrolysis; Retro Diels–Alder; Isothiocyanates; Isocyanates.

\* Corresponding author. Tel.: +54 351 433 4170/4173/3030; fax: +54 351 433 4170x151; e-mail: yranzogi@fcq.unc.edu.ar

reactions during fvp experiments. In this article, we describe the results of fvp reactions of **1a–g**, including kinetic measurements of some of these reactions that support the proposed mechanism. The fvp reactions of **1a–g** furnished information on the effects of *cis/trans* isomerism, the heteroatoms and the aryl substituents on the reactivity.

## 2. Results and discussion

### 2.1. Synthesis of **1a–g**

Compounds **1a–g** were prepared as described in Scheme 1 by modification of the previously described methodology.<sup>9–12</sup> The starting material for the *cis* and *trans* isomers was *cis*-1,2,3,6-tetrahydrophthalic anhydride (**2**). For the *cis* isomers, **1** was transformed to amino acid **3** and then to the methyl ester **4**. The reaction of **4** with an aryl isocyanate or isothiocyanate afforded **8a–e**, which gave the cyclic compounds **1a–e** on refluxing in 25% HCl.

Alternatively, **2** was isomerized to the *trans* isomer **5**; on treatment with the same reagents as for **2**, **5** afforded the *trans* isomers **1f,g**. The yields of these reactions were high in the reactions affording the thiureas **8a–d,f** (70–85%) and for the *cis/trans*-2-thioquinazolin-4-ones **1a–d,f** (80–95%). The yields of the 2-oxo compounds were lower

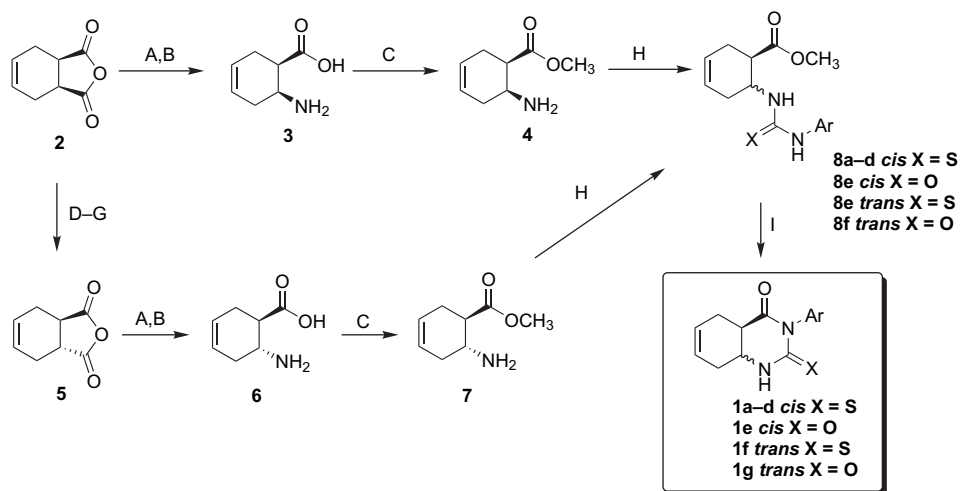
(**8e,g**: 64 and 65%; **1e,g**: 30 and 60%), this fact was attributed to the competition of the hydrolysis reaction.

### 2.2. Flash vacuum pyrolysis of **1a–d**

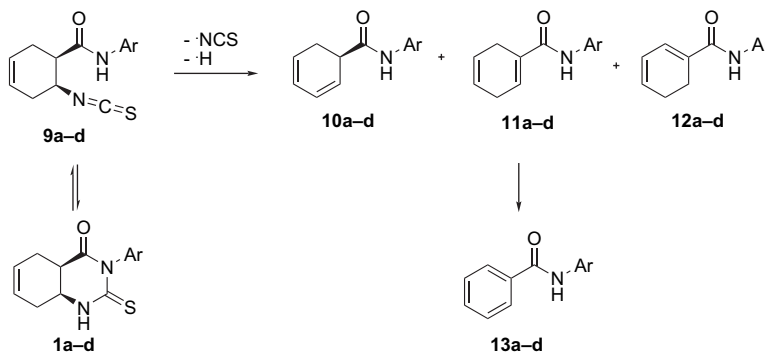
The results of the fvp of **1a–d** are described in Scheme 2 and Tables S1–S4 in Supplementary data. All of them underwent ring opening to an isomeric *cis*-isothiocyanate (**9a–d**), which in turn lost NCS and H or HNCS to give three isomeric dienes **10a–d**, **11a–d** and **12a–d** between 230 and 420 °C. The presence of the three dienes may be taken as an evidence of the first possibility, i.e., the radicals; a concerted elimination of a neutral molecule would lead to one or two dienes. These dienes were aromatized to the corresponding benzamide (**13a–d**) under fvp conditions.

To check whether the first step was an equilibrium, fvp reactions of **9c,d** were carried out at 340 °C, as at this temperature the starting materials, isothiocyanates and dienes, were present in good yields. As expected, **1c,d** and dienes **10–12c,d** were found, confirming the equilibrium proposed in Scheme 2.

The results of fvp reactions of **1a–d** at 300 and 340 °C (Table 1) serve to make an evaluation of substituent effect on reactivity. This analysis reveals that **1a–d** have the same reaction with a slight substituent effect. Compound



**Scheme 1.** (A)  $\text{NH}_4\text{OH}$ ,  $\text{NaOH}$ , 0 °C, then  $\text{HCl}$ ; (B)  $\text{NaOH}$ ,  $\text{NaOCl}$ , 0 °C, then  $\text{HCl}$ ; (C)  $\text{SOCl}_2$ ,  $\text{MeOH}$ , -15 °C, then  $\text{KOH}$ ; (D)  $\text{H}_2\text{SO}_4$ ,  $\text{MeOH}$ , 80 °C; (E)  $\text{NaOMe}$ , reflux; (F)  $\text{NaOH}$ , rt, then  $\text{HCl}$ , 0 °C; (G)  $\text{Ac}_2\text{O}$ , reflux; (H)  $\text{PhNCO}$  or  $\text{ArNCS}$ , toluene, rt; (I) 25%  $\text{HCl}$ , reflux.



**Scheme 2.**

**Table 1.** Fvp reactions of **1a–d** at 300/340 °C

cis, X=S	<b>1<sup>a</sup></b> (%)	<b>9<sup>a</sup></b> %	<b>10+11+12<sup>b</sup></b> (%)	<b>13<sup>a</sup></b> (%)
<b>a</b> , Ar=Ph	72/65	12/15	16/14	0/6
<b>b</b> , Ar= <i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	82/67	11/18	8/7	0/8
<b>c</b> , Ar= <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	77/74	23/9	0/17	0/0
<b>d</b> , Ar= <i>m</i> -OMeC <sub>6</sub> H <sub>4</sub>	91/85	9/15	0/0	0/0

See full tables in [Supplementary data](#).

<sup>a</sup> Relative quantification by <sup>1</sup>H NMR.

<sup>b</sup> See relative ratios in Section 4.

**1a** was the most reactive starting material, whereas the least reactive was **1d**. This fact can easily be seen comparing the recovery of **1a** (72%) and **1d** (91%) in pyrolysis at 300 °C. The most reactive isothiocyanates were **9a** and **9d**, which at all the studied temperatures decomposed to the corresponding dienes, whereas isothiocyanates **9b** and **9c** could be quantified without decomposition at lower reaction temperatures. The dienes were observed to have different stabilities: those arising from **1a–c** could be detected and quantified at temperatures where the corresponding benzamides were not formed.

### 2.3. Flash vacuum pyrolysis of **1e**

Compound **1e** was subjected to fvp at temperatures between 500 and 580 °C. The results are depicted in [Scheme 3](#) and [Table S5](#) in [Supplementary data](#).

There were two main differences in the reactions of **1e** when compared with those of **1a–d**: the reaction temperatures were significantly higher, and uracil **14** and butadiene appeared as new products formed in a competitive RDA

reaction. Isothiocyanate **9e** was detected by IR (2205 cm<sup>-1</sup>) at all temperatures, but could not be quantified because of its decomposition at the given reaction temperatures. Dienes **10a–12a** were detected by GC/MS.

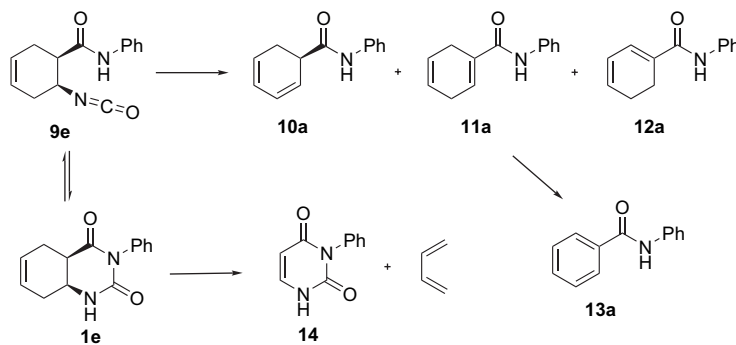
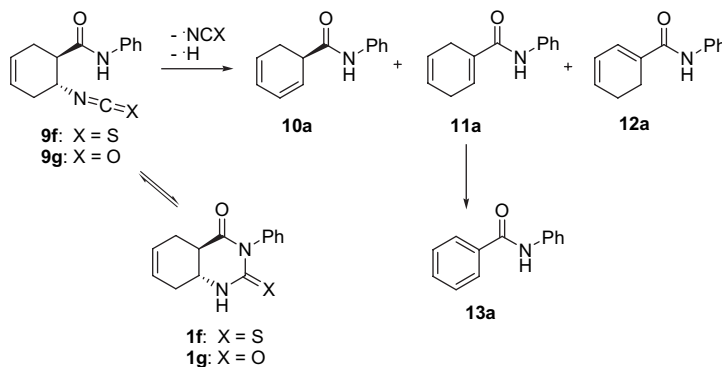
### 2.4. Flash vacuum pyrolysis of **1f**

The fvp reactions of **1f** were carried out between 340 and 440 °C and the results are given in [Scheme 4](#) and [Table S6](#) in [Supplementary data](#). These reactions may be compared with those of **1a–d** because the same products were formed, with the exception that the isothiocyanate was *trans*, as expected (IR: 2090 cm<sup>-1</sup>, *trans*-NCS). It was noteworthy that the *trans* isomers were more stable than the *cis* isomers, which was reflected by the higher reaction temperatures.

### 2.5. Flash vacuum pyrolysis of **1g**

The fvp of **1g** between 540 and 600 °C gave the results reported in [Scheme 4](#) and [Table S7](#) in [Supplementary data](#). As the reaction temperatures were higher than those for **1f**, the corresponding isocyanate and dienes could not be quantified due to their instability under those conditions, but they were detected by IR (2255 cm<sup>-1</sup>, *trans*-NCO) and GC/MS (dienes).

The results of fvp of **1a–g** revealed that the formation of the isomeric isothiocyanates or isocyanates is the lower energy reaction, involving C2–N3 bond breaking and H transfer. At higher temperatures, the RDA reaction is a competitive reaction for **1e**, demonstrating that this is a higher energy reaction. Although the fvp of **1g** was carried out at

**Scheme 3.****Scheme 4.**

temperatures where the RDA reaction might be expected, it was not observed, suggesting a concerted RDA reaction in **1e**. The possible product arising from a concerted RDA in **1g** has high strain energy.

Up to this point, we were interested in the mechanism of formation of compounds **9a–g**, i.e., the first step of the reaction. There was no previous evidence concerning the mechanism of this equilibrium isomerization step that could take place in a stepwise manner via a diradical intermediate or in a concerted way. On the other hand, as these compounds are present in tautomeric equilibrium, it was of interest to examine, which tautomer was reacting. These alternatives are shown in Scheme 5.

Kinetic measurements on the reactions of **1c,d,f** were carried out to get more information on the reaction mechanism. These compounds were the only starting materials that afforded the corresponding isothiocyanates without decomposition to dienes at lower reaction temperatures (see Tables S1–S7 in Supplementary data).

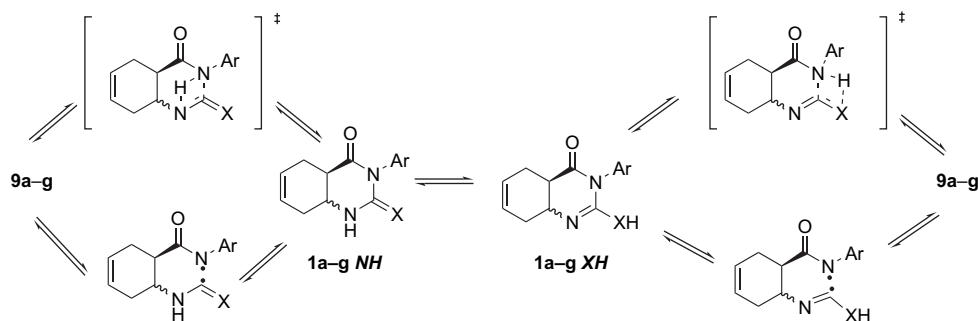
Reaction constants were measured at each temperature with the relative concentrations of the starting materials and products determined by  $^1\text{H}$  NMR and averaged over at least three determinations. Reaction times were calculated as  $V_0/\mu$  (contact time),  $V_0$  being the volume of the reaction tube inside the hot zone and  $\mu$ , the carrier gas flow. Arrhenius parameters were calculated via the classical equation ( $\ln k$  vs  $1/T$ ). To validate the system, the kinetic parameters of ethyl acetate pyrolysis were measured and compared with those reported for a static system; these results, together with a detailed description of the methodology, were described earlier.<sup>13</sup>

The reactions proved to be of first order; the rate constants for the reactions of **1c,d,f** are given in Tables S8–S10 in Supplementary data, and the Arrhenius parameters in Table 2. From the results in Table 2, it can be stated that all these

compounds react by the same mechanism, as shown by the  $\Delta G^\ddagger$  values, which were almost the same. It should be mentioned here that  $\Delta G^\ddagger$  for **1f** was calculated from the results at 340 °C; the calculated value for 300 °C is 33.0 kcal/mol, which is quite similar to the ones of **1c,d**. From the possible reaction mechanisms depicted in Scheme 5, the diradical mechanism should afford positive entropies of activation, while a concerted way should have negative values. The entropies of activation in Table 2 indicate that **1c,d** (*cis*) have strong negative values, while **1f** (*trans*) has a slightly positive value, greatly different from that expected for a diradical mechanism. The  $\log A$  values for a diradical mechanism are between 14.5 and 16,<sup>14,15</sup> while that calculated for the  $\beta$ -elimination through a four-membered transition state in the thermal reaction of pyruvic acid is 13.53.<sup>16</sup> This result is quite similar to that calculated for **1f**, which may be taken as confirmation of a concerted reaction via a cyclic transition state for this compound. The  $\log A$  values for **1c,d** are much lower, indicating more negative entropies of activation; this fact cannot be explained by a substituent effect, so a conformational effect should be explored.

Some  $^1\text{H}$  NMR conformational studies have been carried out on 2,4-dioxodecahydroquinazolines and 2-thioxo-4-oxodecahydroquinazolines,<sup>17</sup> compounds that are similar to those described in this article with the exception that **1a–g** contain a cyclohexene ring. The *trans*-fused 2,4-dioxodecahydroquinazoline was found to have a biased chair–sofa conformation, whereas the *cis* isomer consists of an approximately 61:39 conformational mixture of the *N(1)-out* and *N(1)-in* forms (Fig. 2).<sup>17</sup>

This difference in conformation may be the clue for the difference in  $\Delta S^\ddagger$  as, although the *cis* isomers have two conformations, they are more constrained suggesting a tightened structure in a cyclic transition state. As both isomers react by the same mechanism (as shown by the  $\Delta G^\ddagger$  values),  $\Delta H^\ddagger$  should be much lower for the *cis* isomers to maintain  $\Delta G^\ddagger$ .



Scheme 5.

Table 2. Arrhenius parameters for **1c,d,f**

Compd	Ar	Isomerism	$E_a$ (kcal/mol)	$\log A$	$\Delta S^\ddagger$ (e.u.)	$\Delta H^\ddagger$ (kcal/mol)	$\Delta G^\ddagger$ (kcal/mol)
<b>1c</b>	<i>p</i> -MePh	<i>cis</i>	12.0±0.3	6.2±0.2	−32.3±0.2	−10.9±0.3 <sup>a</sup>	29.4±0.5 <sup>a</sup>
<b>1d</b>	<i>m</i> -OMePh	<i>cis</i>	10.8±0.3	4.9±0.1	−38.1±0.1	9.7±0.3 <sup>a</sup>	31.5±0.4 <sup>a</sup>
<b>1f</b>	Ph	<i>trans</i>	35.3±0.9	13.6±0.5	+1.9±0.5	34.0±0.9 <sup>b</sup>	35.0±1.0 <sup>b</sup>

<sup>a</sup> Obtained at 300 °C.

<sup>b</sup> Obtained at 340 °C (calculated 33.0 kcal/mol at 300 °C).

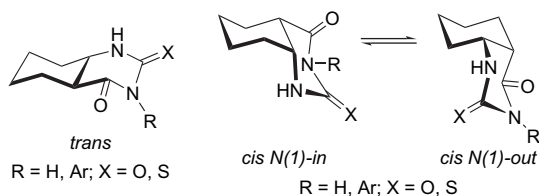
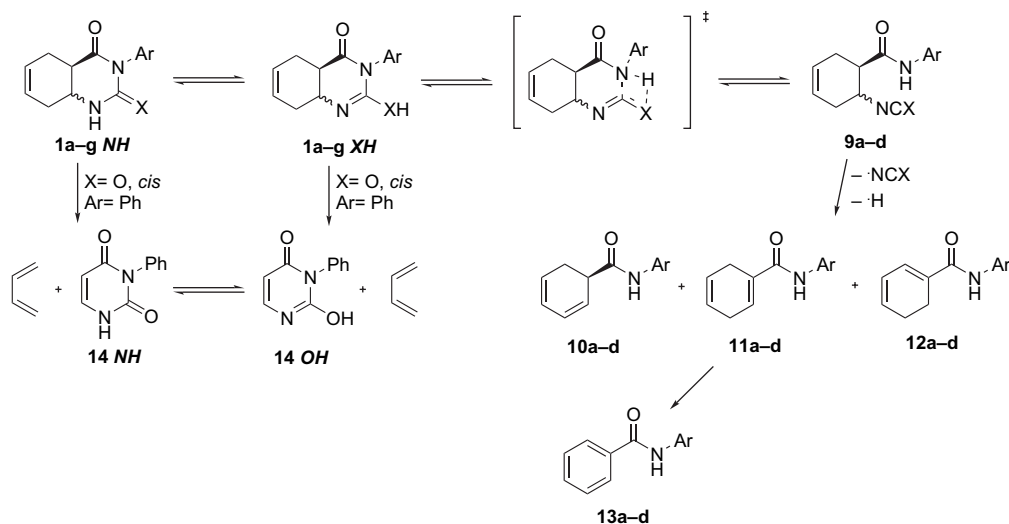


Figure 2.

As depicted in Scheme 5, **1a–g** have a tautomeric equilibrium, thiocarbonyl/thioenol and keto/enol, so it is important to determine, which tautomer is reacting. There are many references concerning the predominant species in the gas phase, some of which will be discussed here. Theoretical calculations on the tautomerism of neutral and protonated 6-thioguanine predict that the N9(H) thiol is the most stable tautomer. Results at the highest computational level indicated the surprisingly high stability of the thiol tautomer.<sup>18</sup> Theoretical calculations on 6-thiopurine,<sup>19</sup> 6-thioguanine<sup>20</sup> and 2-thiocytosine<sup>21</sup> also showed that these compounds exist as thiol-amino forms in the gas phase, whereas thione-amino forms predominate in aqueous solution. In the cases of 2,4-dithiouracil and 2,4-dithiothymine, the dithione tautomers are the most stable in both phases.<sup>21</sup> As concerns keto/enol tautomerism, gas-phase <sup>1</sup>H NMR studies of acetylacetone, methyl acetoacetate and ethyl acetoacetate revealed the predominance of the enol tautomers in the gas phase.<sup>22</sup> Theoretical calculations and mass spectrometric studies confirmed a noteworthy tendency to enolic structure formation when the sulfur is replaced by oxygen in different ketones.<sup>23</sup> The fvp reactions and theoretical calculations on pyrazolinones pointed out the enol as the reacting tautomer in the gas phase.<sup>24</sup>

We do not have direct evidences on which is the most stable tautomer of our compounds in the gas phase, but taking into account the above-described results, we propose that the reacting tautomer is **1a–g XH** (thioenol or enol). Besides, on the basis of kinetic measurements, mainly the entropies of activation, we propose a concerted reaction as the mechanism for the fvp of **1a–g** as depicted in Scheme 6.



Scheme 6.

### 3. Conclusions

The reactions described in this article confirmed that the RDA reaction affording butadiene involves higher energy than that affording cyclopentadiene, but it is possible to produce it in fvp experiments.

Ring opening and formation of isothiocyanates or isocyanates is the lower energy reaction in **1a–g**. This reaction is proposed to take place via a cyclic transition state from the thiol or enol tautomer. The only competing reaction is RDA in the cis-oxygenated compound **1e**, as oxygenated compounds are more stable than the sulfur ones and thus the reaction temperatures are higher. The trans oxygenated compound does not afford uracil and butadiene by RDA as the expected compound formed by a concerted RDA reaction has a high strain energy; this fact confirms the concerted reaction for the cis isomer.

The trans isomers are more stable than the cis ones and have slight positive entropies of activation, while the cis isomers have strong negative values, which were attributed to a conformational effect.

### 4. Experimental

#### 4.1. General

<sup>1</sup>H NMR (400 MHz or 200 MHz) and <sup>13</sup>C NMR (50 MHz) spectra were recorded at 300 K with TMS as an internal reference (0 ppm for all). IR spectra were measured with an FTIR spectrophotometer. Melting points are uncorrected. GC/MS were performed with an SE-30 column, using helium as eluent at a flow rate of 1 mL/min, with a heating ramp of 7 °C/min from 240 to 270 °C and of 10 °C/min up to 280 °C. Mass spectra were obtained in the electron impact mode (EI), with 70 eV ionization energy. Column and thin-layer chromatographies were performed on silica gel. Solvents were of analytical grade.



Fvp reactions were carried out in a Vycor glass reactor, using a tube furnace with a temperature-controller device. Oxygen-free dry nitrogen was used as carrier gas. Approximately 40 mg samples were pyrolyzed. Contact times were around  $10^{-2}$  s and a pressure of  $\sim 0.02$  Torr was used. Products were trapped at liquid air temperature, extracted with solvent ( $\text{CDCl}_3$ ) and subjected to different analyses or separation techniques. In all fvp experiments, the recovery of material was  $>90\%$ .

Compounds **3–7** and **8a** were prepared according to the previously described methodology.<sup>9–12</sup>

#### 4.2. General procedure for the preparation of thiourea (**8b–d,f**) and urea (**8e,g**) derivatives

The appropriate aryl isothiocyanate or phenyl isocyanate (10 mmol) was added to **4** (1.47 g, 9.5 mmol) dissolved in 30 mL of dry toluene, and the mixture was stirred at room temperature for 1 h. The solution was then evaporated and the product obtained was recrystallized from ethyl acetate/*n*-hexane.

Compound **8b**: yield 77%. Mp: 102–105 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 2.14–2.20 (1H, m), 2.45–2.58 (3H, m), 3.03 (1H, s), 3.66 (3H, s), 4.96 (1H, s), 5.60–5.68 (2H, m), 7.14 (2H, br d,  $J=6.0$  Hz), 7.25 (2H, br d,  $J=6.0$  Hz), 7.36 (1H, br m), 7.76 (1H, br s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 27.0, 28.4, 42.2, 51.9, 52.8, 123.2, 125.2, 125.5, 125.6, 127.6, 131.7, 134.7, 137.9, 174.2, 182.8. IR (KBr)  $\text{cm}^{-1}$ : 3331, 3162, 1702, 1597, 1531. Anal. Calcd for  $\text{C}_{15}\text{H}_{17}\text{ClN}_2\text{O}_2\text{S}$  (324.83): C, 55.46; H, 5.28; N, 8.62. Found: C, 55.09; H, 4.89; N, 8.24.

Compound **8c**: yield 70%. Mp: 121–124 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 2.12–2.21 (1H, m), 2.37–2.54 (3H, m), 2.42 (3H, s), 3.02 (1H, s), 3.61 (3H, s), 4.96 (1H, s), 5.61 (2H, m), 6.93 (1H, br s), 7.09 (2H, d,  $J=8.1$  Hz), 7.23 (2H, d,  $J=8.1$  Hz), 7.55 (1H, br s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 21.5, 27.0, 29.6, 41.9, 51.6, 52.3, 125.3, 125.4, 131.0, 132.2, 137.4, 173.8, 180.4. IR (KBr)  $\text{cm}^{-1}$ : 3332, 3153, 1707, 1526, 1242. Anal. Calcd for  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$  (304.41): C, 63.13; H, 6.62; N, 9.20. Found: C, 62.79; H, 6.22; N, 8.84.

Compound **8d**: yield 84%. Mp: 137–139 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 2.12–2.19 (1H, m), 2.36–2.57 (3H, m), 3.04 (1H, s), 3.63 (3H, s), 3.82 (3H, s), 4.98 (1H, s), 5.62 (2H, m), 6.76 (1H, s), 6.81 (1H, dd,  $J=8.3, 16.4$  Hz), 7.15 (1H, br s), 7.33 (1H, t,  $J=8.1$  Hz), 7.70 (1H, br s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 27.3, 29.8, 42.2, 52.0, 52.6, 56.1, 110.7, 113.6, 117.2, 125.6, 131.5, 132.0, 137.5, 160.6, 174.1. IR (KBr)  $\text{cm}^{-1}$ : 3374, 3172, 1736, 1530. Anal. Calcd for  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$  (320.41): C, 59.98; H, 6.29; N, 8.74. Found: C, 60.36; H, 6.65; N, 9.18.

Compound **8e**: yield 65%. Mp: 109–111 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 2.16–2.27 (1H, m), 2.31–2.44 (2H, m), 2.46–2.56 (1H, m), 2.84–2.91 (1H, m), 3.67 (3H, s), 4.39–4.48 (1H, m), 5.63 (2H, dd,  $J=10.3, 19.1$  Hz), 5.74–5.76 (1H, m), 7.04 (1H, t,  $J=6.6$  Hz), 7.12 (1H, br s), 7.22–7.32 (4H, m).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 26.4, 31.5, 42.9, 46.5, 52.6, 121.3, 124.1, 125.6, 125.7, 129.8, 139.5, 156.2,

175.2. IR (KBr)  $\text{cm}^{-1}$ : 3318, 1743, 1656, 1556. Anal. Calcd for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_3$  (274.32): C, 65.68; H, 6.61; N, 10.21. Found: C, 65.30; H, 6.42; N, 9.83.

Compound **8f**: yield 92%. Mp: 167–169 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.83–1.96 (1H, m), 2.15–2.26 (1H, m), 2.51–2.73 (2H, m), 2.91 (1H, dd,  $J=14.2, 7.5$  Hz), 3.69 (3H, s), 4.80–4.94 (1H, m), 5.58 (1H, d,  $J=10.6$  Hz), 5.66 (1H, d,  $J=10.6$  Hz), 6.11–6.19 (1H, m), 7.20 (2H, d,  $J=7.0$  Hz), 7.29 (1H, t,  $J=7.4$  Hz), 7.45 (2H, t,  $J=7.8$  Hz), 7.92 (1H, br s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 26.6, 30.9, 44.0, 52.2, 52.8, 124.6, 125.6, 125.9, 127.9, 130.8, 136.7, 156.3, 173.1. IR (KBr)  $\text{cm}^{-1}$ : 3327, 1741, 1653, 1551. Anal. Calcd for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$  (290.38): C, 62.04; H, 6.25; N, 9.65. Found: C, 62.43; H, 6.62; N, 9.28.

Compound **8g**: yield: 81%. Mp: 151–153 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.99 (1H, m), 2.33 (1H, d,  $J=18.1$  Hz), 2.48–2.58 (2H, m), 2.72 (1H, m), 3.70 (3H, s), 4.18 (1H, m), 5.45 (1H, br), 5.64 (2H, coalesced signals), 7.09 (1H, m), 7.2–7.33 (4H, m), 7.46 (1H, br).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 28.0, 32.4, 45.9, 48.1, 52.7, 121.1, 124.0, 125.2, 125.5, 129.7, 139.5, 156.4, 175.5. IR (KBr)  $\text{cm}^{-1}$ : 3279, 3036, 1730, 1640. Anal. Calcd for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_3$  (274.32): C, 65.68; H, 6.61; N, 10.21. Found: C, 65.28; H, 6.20; N, 9.82.

#### 4.3. Cyclic compounds **1a–e**

The appropriate thioureas (**8a–d**) or urea (**8e**) (5 mmol) were refluxed in 30 mL of 25% HCl solution for 30 min. After cooling, the crystalline products (**1a–d**) were separated by vacuum filtration, washed with water and dried. Compound **1e** was obtained after extraction with  $\text{CHCl}_3$  ( $3 \times 50$  mL), drying ( $\text{Na}_2\text{SO}_4$ ) and evaporation. The solid obtained was purified by column chromatography on silica gel with a mixture of toluene/EtOH (9:1) as eluent.

Compound **1a**: this compound was obtained as a white crystalline product, yield: 85%. Mp: 241–244 °C (lit.<sup>10</sup> 243–245 °C). The spectral data and physical properties matched those reported previously.

Compound **1b**: yield 81%. Mp: 208–212 °C.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  (ppm): 2.32 (3H, br s), 2.54 (1H, br s), 3.25 (1H, m), 3.93 (1H, m), 5.60 (1H, d,  $J=10.1$  Hz), 5.70 (1H, d,  $J=10.6$  Hz), 7.13 (1H, br s), 7.30 (1H, br s), 7.42 (2H, m), 10.22 (1H, br s).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  (ppm): 22.5, 26.6, 37.6, 46.3, 123.2, 124.7, 127.8, 129.8, 132.4, 140.7, 169.3, 180.0. IR (KBr)  $\text{cm}^{-1}$ : 3164, 1733, 1541, 1181. Anal. Calcd for  $\text{C}_{14}\text{H}_{13}\text{ClN}_2\text{OS}$  (292.78): C, 57.43; H, 4.48; N, 9.57. Found: C, 57.80; H, 4.85; N, 9.95.

Compound **1c**: yield 93%. Mp: 243–243 °C.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  (ppm): 2.27–2.32 (3H, m), 2.32 (3H, s), 3.17–3.39 (2H, m), 3.90 (1H, m), 5.60 (1H, d,  $J=10.1$  Hz), 5.67 (1H, d,  $J=10.1$  Hz), 6.97 (2H, d,  $J=7.0$  Hz), 7.17 (2H, d,  $J=8.1$  Hz), 10.1 (1H, br s).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  (ppm): 20.7, 22.7, 26.7, 37.7, 46.2, 123.2, 124.9, 128.9, 129.3, 136.8, 136.9, 169.4, 180.6. IR (KBr)  $\text{cm}^{-1}$ : 3163, 3023, 1730, 1541, 1234. Anal. Calcd for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{OS}$  (272.37): C, 66.15; H, 5.92; N, 10.29. Found: C, 66.52; H, 6.29; N, 10.65.

Compound **1d**: yield 94%. Mp: 242–245 °C.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  (ppm): 2.31 (3H, br s), 3.20–3.40 (2H, m), 3.74 (3H, s), 3.90 (1H, m), 5.60 (1H, d,  $J=9.6$  Hz), 5.67 (1H, d,  $J=9.1$  Hz), 6.70 (2H, br s), 6.90 (1H, d,  $J=8.1$  Hz), 7.28 (1H, t,  $J=8.1$  Hz), 10.12 (1H, br s).  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  (ppm): 22.6, 26.6, 37.6, 46.2, 55.2, 113.1, 115.6, 121.9, 123.2, 124.8, 128.9, 140.4, 159.3, 169.2, 180.3. IR (KBr)  $\text{cm}^{-1}$ : 3166, 1718, 1545, 1184. Anal. Calcd for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$  (288.36): C, 62.48; H, 5.59; N, 9.71. Found: C, 62.10; H, 5.19; N, 9.32.

Compound **1e**: yield 34%. Mp: 155–158 °C (lit.:<sup>9</sup> 167–170 °C).  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  (ppm): 2.25 (1H, d,  $J=15.1$  Hz), 2.45 (2H, m), 2.76 (1H, d,  $J=18.1$  Hz), 3.08 (1H, m), 3.93 (1H, m), 5.63 (2H, br d,  $J=12.1$  Hz), 5.76 (1H, d,  $J=9.1$  Hz), 7.16 (2H, d,  $J=7.6$  Hz), 7.41 (3H, m). IR (KBr)  $\text{cm}^{-1}$ : 3236, 3103, 1732, 1690. Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$  (242.27): C, 69.41; H, 5.82; N, 11.56. Found: C, 69.17; H, 5.53; N, 11.21.

Compound **1f**: this compound was obtained as a white crystalline product, yield: 95%. Mp: 263–266 °C (lit.:<sup>10</sup> 265–266 °C). The spectral data and physical properties matched those reported previously.

Compound **1g**: yield 67%. Mp: 227–230 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 2.15–2.31 (2H, m), 2.47 (1H, m), 2.65–2.78 (2H, m), 3.7 (1H, m), 5.61 (1H, s, br), 5.67 (1H, m), 5.80 (1H, m), 7.19 (2H, d,  $J=7.0$  Hz), 7.39 (1H, t,  $J=7.3$  Hz), 7.45 (2H, t,  $J=7.3$  Hz). IR (KBr)  $\text{cm}^{-1}$ : 3303, 3032, 1741, 1688. Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$  (242.27): C, 69.41; H, 5.82; N, 11.56. Found: C, 69.10; H, 5.44; N, 11.18.

#### 4.4. Flash vacuum pyrolysis of **1a**

The fvp of **1a** was performed between 240 and 420 °C, at a pressure of  $\sim 10^{-2}$  Torr and contact time of  $\sim 10^{-2}$  s. Between 240 and 320 °C, the only products were isothiocyanate **9a** and dienes **10a–12a**, while at higher temperatures (over 340 °C), amide **13a** was formed. Reactions were studied up to recovery of 46% of **1a**; at higher temperatures competitive decomposition reactions with formation of tarry products were present.

Compound **9a**: it was obtained by column chromatography on silica gel 60 with  $\text{CHCl}_3/n$ -hexane (1:1, 6:4, 7:3 and 8:2) as eluent. Mp: 149–150 °C.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 2.38–2.81 (m, 5H), 4.51 (m, 1H), 5.77 (m, 2H), 7.15 (t,  $J=7.3$  Hz, 1H), 7.34 (t,  $J=7.7$  Hz, 2H), 7.40 (br, 1H, NH), 7.53 (d,  $J=7.7$  Hz, 2H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 24.4, 32.5, 45.4, 53.4, 120.6, 123.0, 125.1, 129.2, 137.4, 144.5, 169.5. MS: 258 (6%), 200 (33%), 139 (7%), 120 (11%), 107 (6%), 93 (100%), 79 (90%). IR (KBr)  $\text{cm}^{-1}$ : 3434, 3250, 3185, 3138, 2933, 2105 (NCS), 1657, 1592, 1545, 1454, 749, 676.

Compounds **10a–12a**: these dienes were separated as a mixture with amide **13a** and were identified by GC/MS and  $^1\text{H}$  NMR (one characteristic signal for each).

Compound **10a**: GC/MS (ret. time/min): 6.32. MS: 199 ( $\text{M}^+$ , 22%), 198 (61%), 107 (48%), 105 (33%), 79 (55%), 77

(100%), 51 (27%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): individual signal: 4.16 (m, 1H). Relative % (**10a–12a**) at 340 °C: 42%.

Compound **11a**: GC/MS (ret. time/min): 5.96. MS: 199 ( $\text{M}^+$ , 20%), 198 (33%), 107 (100%), 105 (39%), 79 (45%), 77 (97%), 51 (27%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): individual signal: 6.20 (dd,  $J_1=9.50$  Hz,  $J_2=4.7$  Hz, 1H). Relative % (**10a–12a**) at 340 °C: 14%.

Compound **12a**: GC/MS (ret. time/min): 4.93. MS: 199 ( $\text{M}^+$ , 22%), 198 (15%), 121 (17%), 105 (11%), 93 (66%), 80 (80%), 79 (100%), 77 (94%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): individual signal: 6.68 (br s, 1H). Relative % (**10a–12a**) at 340 °C: 44%.

Compound **13a**: GC (ret. time/min): 5.86 min. MS: 197 ( $\text{M}^+$ , 28%), 106 (6%), 105 (100%), 77 (45%), 65 (4%), 51 (18%); 95% match with NIST database, spectrum no. 33395, CAS no. 93-98-1.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): individual signal: 7.86 (d,  $J=7.9$  Hz).

#### 4.5. Flash vacuum pyrolysis of **1b**

The fvp of **1b** was carried out between 260 and 380 °C, at a pressure of  $\sim 10^{-2}$  Torr and contact time of  $\sim 10^{-2}$  s. Between 240 and 320 °C, the only products were isothiocyanate **9b** and dienes **10b–12b**, while at higher temperatures (over 320 °C), amide **13b** was formed. Reactions were studied up to 33.2% of **1b** because the mass balance decreased by more than 90% at higher yields due to decomposition reactions.

Compound **9b**: this was obtained by column chromatography on silica gel 60 with  $\text{CHCl}_3/n$ -hexane (1:1, 6:4, 7:3 and 8:2) as eluent. Mp: 124–125 °C.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 2.38–2.82 (m, 5H), 4.48 (m, 1H), 5.76 (m, 2H), 7.11 (d,  $J=8.0$  Hz, 1H), 7.26 (t,  $J=8.0$  Hz, 1H), 7.37 (d,  $J=8.4$  Hz, 1H), 7.39 (br s, 1H, NH), 7.67 (m, 1H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 24.5, 32.4, 45.4, 53.3, 118.5, 120.7, 123.0, 124.9, 125.1, 130.2, 131.8, 134.9, 138.5, 169.6. MS: 292 ( $\text{M}^+$ , 5%), 234 (20%), 129 (14%), 127 (45%), 107 (10%), 81 (17%), 80 (30%), 79 (100%), 77 (35%), 72 (18%). IR (KBr)  $\text{cm}^{-1}$ : 3553, 3297, 3258, 3037, 2911, 2850, 2100 (NCS), 1675, 1597, 1536, 1428, 785, 678.

Compounds **10b–12b**: these dienes were separated as a mixture with amide **13b** and were identified by GC/MS and  $^1\text{H}$  NMR (one characteristic signal for each).

Compound **10b**: GC/MS (ret. time/min): 6.74. MS: 235 (5%), 234 (5%), 233 ( $\text{M}^+$ , 16%), 157 (3%), 156 (3%), 155 (11%), 154 (7%), 129 (6%), 127 (22%), 79 (100%), 77 (44%), 51 (19%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): individual signal: 6.68 (br s, 1H). Relative % (**10b–12b**) at 340 °C: 50%.

Compound **11b**: GC/MS (ret. time/min): 6.43. MS: 235 (7%), 234 (8%), 233 ( $\text{M}^+$ , 19%), 232 (15%), 108 (7%), 107 (100%), 106 (8%), 105 (60%), 80 (6%), 79 (38%), 78 (16%), 77 (83%), 51 (32%).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): individual signal: 6.25 (dd,

$J_1=9.13$  Hz,  $J_2=5.47$  Hz, 1H). Relative % (**10b–12b**) at 340 °C: 15%.

Compound **12b**: GC/MS (ret. time/min): 5.31. MS: 235 (5%), 234 (5%), 233 ( $M^+$ , 16%), 155 (11%), 154 (7%), 129 (6%), 127 (21%), 80 (67%), 79 (100%), 78 (13%), 77 (44%), 51 (19%).  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  (ppm): individual signal: 6.70 (br s, 1H). Relative % (**10b–12b**) at 340 °C: 35%.

Compound **13b**: GC/MS (ret. time/min): 6.20. MS: 233 (6%), 232 (3%), 231 ( $M^+$ , 19%), 105 (100%), 77 (53%), 76 (5%), 51 (23%).  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  (ppm): individual signal: 7.69 (d,  $J=8.03$  Hz, 2H).

#### 4.6. Flash vacuum pyrolysis of **1c**

The fvp of **1c** was carried out between 230 and 400 °C, at a pressure of  $\sim 10^{-2}$  Torr and contact time of  $\sim 10^{-2}$  s. Between 230 and 300 °C, the only product was isothiocyanate **9c**, dienes **10c–12c** were formed over 320 °C, while over 360 °C, amide **13c** was formed. Reactions were studied up to 73.7% of **1c** because the mass balance decreased by more than 90% due to decomposition reactions at higher yields.

Compound **9c**: this was obtained by column chromatography on silica gel 60 with  $CHCl_3/n$ -hexane (1:1, 6:4, 7:3 and 8:2) as eluent. Mp: 138–140 °C.  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  (ppm): 2.32 (s, 3H), 2.38–2.79 (m, 5H), 4.49 (br s, 1H), 5.65–5.84 (m, 2H), 7.13 (d,  $J=8.4$  Hz, 2H), 7.34 (br s, 1H), 7.39 (d,  $J=8.4$  Hz, 2H).  $^{13}C$  NMR (50 MHz,  $CDCl_3$ )  $\delta$  (ppm): 21.0, 24.3, 32.5, 45.2, 53.4, 120.8, 122.9, 125.9, 129.7, 134.7, 134.8, 169.4. MS: 272 ( $M^+$ , 10%), 214 (26%), 167 (7%), 149 (19%), 134 (10%), 108 (11%), 107 (100%), 106 (38%), 91 (10%), 80 (34%), 79 (74%), 77 (44%), 57 (14%). IR (KBr)  $cm^{-1}$ : 3290, 3188, 3126, 2922, 2849, 2102 (NCS), 1660, 1598, 1513, 1315, 811, 743, 675.

Compounds **10c–12c**: these dienes were separated as a mixture with amide **13c** and were identified by GC/MS and  $^1H$  NMR (one characteristic signal for each).

Compound **10c**: GC (ret. time/min): 4.99. MS: 213 ( $M^+$ , 29%), 135 (22%), 107 (52%), 106 (74%), 91 (21%), 78 (100%), 79 (77%).  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  (ppm): individual signal: 4.18 (m, 1H). Relative % (**10c–12c**) at 340 °C: 57%.

Compound **11c**: GC (ret. time/min): 5.94. MS: 213 ( $M^+$ , 26%), 212 (23%), 107 (100%), 105 (64%), 79 (32%), 77 (96%).  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  (ppm): individual signal: 6.23 (dd,  $J_1=9.50$  Hz,  $J_2=5.7$  Hz, 1H). Relative % (**10c–12c**) at 340 °C: 10%.

Compound **12c**: GC (ret. time/min): 6.23. MS: 213 ( $M^+$ , 28%), 212 (50%), 107 (69%), 105 (64%), 77 (100%), 79 (46%).  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  (ppm): individual signal: 6.66 (br s, 1H). Relative % (**10c–12c**) at 340 °C: 33%.

Compound **13c**: GC (ret. time/min): 5.77. MS: 211 ( $M^+$ , 33%), 106 (9%), 105 (100%), 77 (55%), 51 (14%).  $^1H$

NMR (200 MHz,  $CDCl_3$ )  $\delta$  (ppm): individual signal: 7.87 (d,  $J=7.9$  Hz, 2H).

#### 4.7. Flash vacuum pyrolysis of **1d**

The fvp of **1d** was carried out between 280 and 400 °C, at a pressure of  $\sim 10^{-2}$  Torr and contact time of  $\sim 10^{-2}$  s. Between 280 and 340 °C, the only product was isothiocyanate **9d**, while over 360 °C, dienes **10d–12d** and amide **13d** were formed. The reactions were studied up to 75.3% of **1d** because the mass balance decreased by more than 90% due to decomposition reactions at higher yields.

Compound **9d**: this was obtained by column chromatography on silica gel 60 with  $CHCl_3/n$ -hexane (1:1, 6:4, 7:3 and 8:2) as eluent. Mp: 128–130 °C.  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  (ppm): 2.37–2.80 (m, 5H), 3.80 (s, 3H), 4.48 (m, 1H), 5.75 (m, 2H), 6.69 (d,  $J=8.2$  Hz, 1H), 6.99 (d,  $J=8.5$  Hz, 1H), 7.22 (t,  $J=8.0$  Hz, 1H), 7.29 (s, 1H), 7.40 (br s, 1H, NH).  $^{13}C$  NMR (50 MHz,  $CDCl_3$ )  $\delta$  (ppm): 24.4, 32.5, 45.3, 53.3, 55.5, 106.3, 110.9, 112.7, 122.9, 125.1, 129.9, 134.5, 138.6, 160.4, 169.5. MS: 289 (4%), 288 ( $M^+$ , 22%), 230 (34%), 176 (9%), 150 (17%), 149 (15%), 124 (16%), 123 (100%), 107 (17%), 94 (19%), 93 (10%), 81 (26%), 80 (31%), 79 (79%), 77 (46%), 72 (15%), 51 (14%). IR (KBr)  $cm^{-1}$ : 3297, 3010, 2930, 2849, 2096 (NCS), 1668, 1607, 1550, 1494, 1433, 1296, 1220, 1057, 914, 746, 677.

Compounds **10d–12d**: these dienes were separated as a mixture with amide **13d** and were identified by GC/MS and  $^1H$  NMR (one characteristic signal for each).

Compound **10d**: GC (ret. time/min): 7.66. MS: 229 ( $M^+$ , 22%), 228 (46%), 107 (36%), 105 (98%), 79 (38%), 77 (100%).  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  (ppm): individual signal: 4.13 (m, 1H). Relative % (**10d–12d**) at 360 °C: 50%.

Compound **11d**: GC (ret. time/min): 7.24. MS: 229 ( $M^+$ , 7%), 228 (11%), 227 (35%), 105 (100%), 79 (12%), 77 (68%).  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  (ppm): individual signal: 6.24 (dd,  $J_1=9.50$  Hz,  $J_2=5.1$  Hz, 1H). Relative % (**10d–12d**) at 360 °C: 19%.

Compound **12d**: GC (ret. time/min): 6.06. MS: 229 ( $M^+$ , 54%), 149 (29%), 123 (83%), 107 (26%), 92 (17%), 79 (100%), 77 (86%).  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  (ppm): individual signal: 3.80 (s, 3H). Relative % (**10d–12d**) at 360 °C: 31%.

Compound **13d**: GC (ret. time/min): 7.03 min. MS: 227 ( $M^+$ , 36%), 106 (7%), 105 (100%), 77 (53%), 51 (18%).  $^1H$  NMR (200 MHz,  $CDCl_3$ )  $\delta$  (ppm): individual signal: 7.87 (d,  $J=7.9$  Hz, 2H).

#### 4.8. Flash vacuum pyrolysis of **1e**

The fvp of **1e** was carried out between 500 and 580 °C, at a pressure of  $\sim 10^{-2}$  Torr and contact time of  $\sim 10^{-2}$  s. At all the studied temperatures, the reaction products were amide **13a**, uracil **14** and butadiene. Reactions were studied up to 4.8% of **1e** because the mass balance decreased by



more than 90% due to decomposition reactions at higher yields. Butadiene was identified by GC/MS with a 95% match with the NIST library, spectrum no. 80, CAS no. 106-99-0.

Compound **14**: this was separated from the reaction crude products by column chromatography on silica gel 60 with  $\text{CHCl}_3/n$ -hexane (1:1, 6:4, 7:3 and 8:2) as eluent. Mp: 242–245 °C (lit.:<sup>6</sup> 246–247 °C).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 5.84 (d,  $J=7.7$  Hz, 1H), 7.14 (d,  $J=7.7$  Hz, 1H), 7.23 (d,  $J=8.4$  Hz, 2H), 7.30 (br s, 1H, NH), 7.43–7.54 (m, 3H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  (ppm): 101.8, 129.3, 129.8, 136.9, 141.0, 152.5, 164.7.

#### 4.9. Flash vacuum pyrolysis of **1f**

The fvp of **1f** was carried out between 340 and 440 °C, at a pressure of  $\sim 10^{-2}$  Torr and contact time of  $\sim 10^{-2}$  s. Compound **9f** was the only product up to 360 °C; at 380 °C, **9f** and dienes **10a–12a** were found; from 400 °C, amide **13a** was also formed.

Compound **9f**: this was obtained by column chromatography on silica gel 60 with  $\text{CHCl}_3/n$ -hexane (1:1, 6:4, 7:3 and 8:2) as eluent. Mp: 138–139 °C.  $^1\text{H}$  NMR (200 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm): 2.24–2.71 (m, 5H), 4.14 (m, 1H), 5.66 (m, coalesced signals, 2H), 7.14 (t,  $J=7.1$  Hz, 1H), 7.29 (t,  $J=7.5$  Hz, 2H), 7.52 (d,  $J=7.6$  Hz, 2H), 7.66 (br s, 1H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 28.4, 32.4, 48.9, 54.9, 120.8, 123.2, 125.8, 125.3, 129.2, 133.9, 137.4, 170.7. IR (KBr)  $\text{cm}^{-1}$ : 3244, 3190, 3139, 3073, 3037, 2915, 2844, 2090 (NCS), 1652, 1555, 1448, 765, 686. MS: 259 (2%), 258 ( $\text{M}^+$ , 13%), 200 (52%), 138 (6%), 120 (18%), 107 (11%), 93 (100%), 79 (91%), 66 (13%), 65 (19%), 53 (14%).

#### 4.10. Flash vacuum pyrolysis of **1g**

The fvp of **1g** was carried out between 540 and 600 °C, at a pressure of  $\sim 10^{-2}$  Torr and contact time of  $\sim 10^{-2}$  s. At all the studied reaction temperatures, the only isolated product was **13a**; isocyanate **9g** was detected by IR on the reaction crude ( $2255\text{ cm}^{-1}$ , *trans*-NCO) and dienes by GC/MS; all of them were present in traces. Reactions were studied up to 74.1% of **1g** because the mass balance decreased by more than 90% due to decomposition reactions at higher yields.

#### Acknowledgements

Thanks are due for the financial support provided by CONICET, FONCyT, SECyT-UNC and SECyT for the joint Argentina–Hungary project. W.J.P. thanks CONICET for a doctoral fellowship.

#### Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.07.010.

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