Study of the effect of solvent and different Lewis acids in one pot multicomponent microwave assisted reaction for the chemoselective generation of 1.4-thiazepan-3-ones and 4-thiazolidinones.†

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Abstract: With the aim of exploring the best reaction conditions for the diastereoselective synthesis of the 1,4-thiazepan-3-ones (**4**) and 4-thiazolidinones (**5**), we have studied the effect on solvent variation and the aggregation of $AlCl_3$ and different zeolites as Lewis acid catalysts to the three-component microwave assisted reaction between 2,3:4,5-di-O-isopropylidene-β-D-arabino-hexos-2-ulo-2,6-pyranose (1), benzotiazole (**3**) and thioglycolic acid (**2**). Based on the results of previous studies of our group, we discuss here two microwave assisted methods: multicomponent reaction in the presence of the catalysts (**Method A**) and sequential reaction with generation of the corresponding intermediates and subsequent addition of the catalysts coordinated to thioglycolic acid (**Method B**).

1. Introduction

The synthetic field of Organic Chemistry plays an important role in the study of new substances which present biological and pharmacological activities that can be used for the development of therapeutic agents as the mainstay for the progress of medicinal chemistry. A wide variety of heterocycles are present as the main structural component in different categories of drugs [1]. This facts reflect the contribution of the heterocycle core in a great number of biochemical processes. Between them, functionalized 1,4-thioazepan-3-ones [2] and thiazolidinones [3] represent an important group that has been tested as potential active compounds in pharmaceutical studies

and because of this, they are important "building blocks" in organic synthesis for the design of new versatile molecules with biologic activity.

Thus, the inclusion of a carbohydrate moiety in these heterocyclic molecules is a strategy that can be used for the increasing of the solubility of the drug and/or diminish its toxicity and as a renewable resource with high functionality and a large number of asymmetric sites that allows, through the adequate planification of the synthetic route, the preparation of enantiomeric pure compounds.

Based on the previous studies of our research group, we could established that the tricomponent microwave assisted reaction between 2,3:4,5-di-O-isopropylidene-β-D-arabino-hexos-2-ulo-2,6-pyranose (**1**), mercaptoacetic acid (**2**) and various heteroaromatic amines (**3**), without solvent (**Method A**), proved to be a simple eco-friendly method because of the atoms economy, reaction time, high yields and low cost economic starting products for the synthesis of the corresponding 4-thiazolidinones (**5**) as the only products and as diastereomeric mixtures [4,5]. On the other side, when stoichiometric amounts of the boronic ester **A** (dimethyl-(4S,5S)-2-phenyl-1,3,2-dioxaborolane-4,5-dicarboxylate) was added together with the reactants **1**, **2** and **3,** not only selective formation of diastereomers from 1,4-thiazepan-3-one (**4**) was observed but also an increase in the proportion of one of them (**Figure 1**) [6,7].
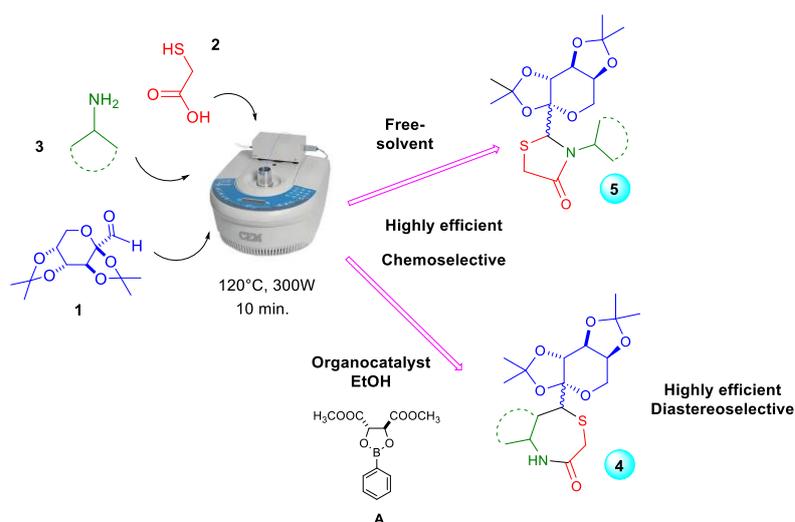

Figure 1. Microwave assisted three component reactions (**Method A**).

We have also observed that the use of the same organoboron catalyst in the sequential reaction (**Method B**) generates the corresponding 4-thiazolidinones (**5**) as the only reaction products. In addition, catalysis produces diastereoselectivity between type **5** products, contrary to what is observed in the absence of catalyst. The possible reaction mechanism in shown in **Figure 2**. The addition of thioglycolic acid coordinated to bulky organoboron catalyst **A** on the intermediate imine preformed (**II**) prevents the attack on one of the faces of the intermediate and high diastereoselectivity was imparted to the reaction.
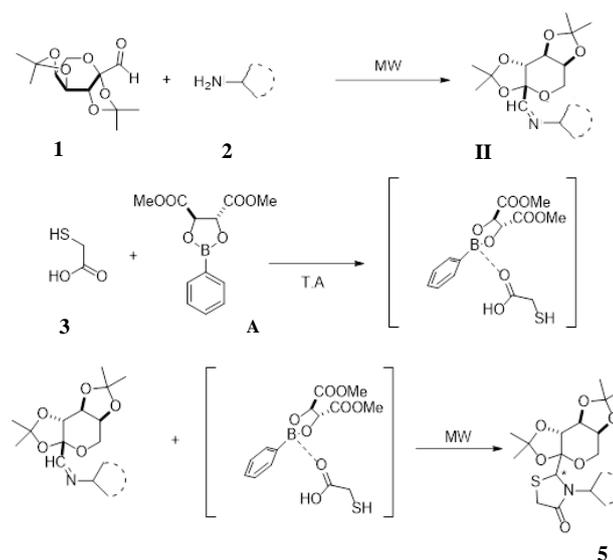
Figure 2. Sequential microwave assisted reaction (**Method B**). *First step*: generation of the intermediate (**II**). *Second step*: addition of the thioglicolic acid coordinated to the organoboroncatalyst.

2. Results and Discussion

According to previous reported studies, [8] we know that the proposed intermediates **I** and **II** generated in the reaction are fundamental for the synthesis of each one of the products (**Figure 4**). In order to synthetize, in a quimioselective way, the generation of 1,4-thioacepan-3-ones (**4**) or 4-thiazolidinones (**5**) we studied the possible factors that could affect the tricomponent reaction using **Method A** and the diastereoselectivity in the sequential reaction through **Method B** conditions. We will evaluate which products are obtained monitoring the reactions by CG-MS, taking samples every five minutes.
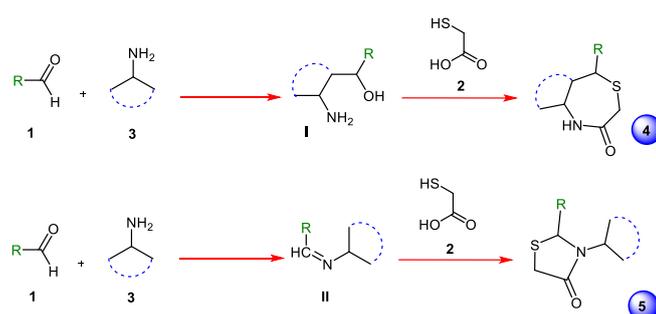

Figure 4. Proposed intermediates **I** and **II** and products of the tricomponent assisted microwave reaction.

Then, we will extend the study using AlCl$_3$ and commercial zeolites (Mordenite, Zeolite 13X and Zeolite ZSM-5) as Lewis acid catalysts supported on a mesoporous material. Previously, we performed the corresponding determination of the surface area of the zeolites by the BET method [9] (**Table 1**) and the Diffuse Reflectance FTIR Sample Techniques (DRIFTS) for the analysis of acid sites through pyridine adsorption (**Figure 6**) [10].

Table 1: Determined BET area for the zeolites used as Lewis acid catalysts.

Zeolite (comercial)	Calculated BET area [m²/g]	Cristalinity X-Ray difraction	Si/Al	% Na	BET área [m²/g] (literature)
H-mordenite (Zeolist) CBV 21A	291	100%[c]	10[b c]	----	500 [c] 346 [d]
13X, tamix molecular	376	----	1,5	----	515 [e]
ZSM-5 (Zeocat Pentasil) PZ-2/54	333	99,4 % [a]	20[a]	0,43[a]	350 [a]

[a]See reference [11]. [b] See reference [12]. [c] See reference [13]. [d] See reference [14]. [e] See reference [15].

The FT-IR spectra registered at room temperature, after pyridine adsorption and purge under 100°C for the different zeolites, show important absorption bands around 1450, 1500 and 1600 cm^{-1}, typical for the C-C bonds of the pyridine structure. The coordination between pyridine and the Lewis acid center can be identified by the 1450 cm^{-1} absorption band while the coordination with the Brönsted acid center is around 1540 cm^{-1}. The absorption band at 1600 cm^{-1} is generally associated to the pyridine-hydrogen bond. Rosenthal et al. [16] found that the extinction coefficients for Lewis acid-pyridine and Brönsted acid-pyridine were the same, so the relation Brönsted acid / Lewis acid for our zeolites could be calculated. In **Figure 5**, it can be seen that all the samples showed only Lewis acid activity because the absorption band corresponding to 1540 cm^{-1} is not observed in the analyzed spectra.
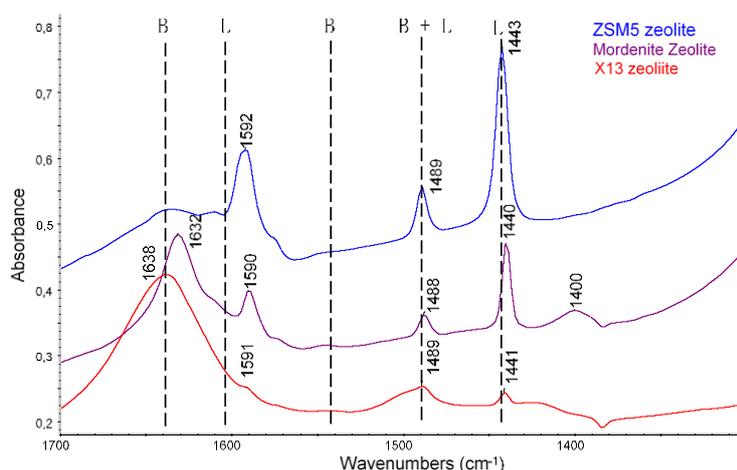
Figure 5. IR spectra of pyridine adsorbed at 20 °C on the different zeolites pre-treated in N$_2$ flow at 400 °C.

Considering that the pore size of these catalysts increases in the presence of solvents, we started the evaluation of several solvents in the tricomponent reactions assisted by microwave (300 W, 120°C, **Method A**) with the aim of evaluate which solvent gives better yields and no effect in the diastereoselectivity of the reaction. The model starting heterocyclic amine employed was aminobenzothiazole. The results for the generation of products **4** and/or **5** and their corresponding

proposed intermediates **I** and **II** together with the CG-MS spectra are shown in **Table 2** and **Figure 6** respectively.

Table 2. Solvent effect on the synthesis of compounds **4** and **5** and their corresponding proposed intermediates **I** and **II**

Entry	Solvent	Intermediates, Products and Distributions [%(diasteroisomers relations)[a]]			
		I	II	4	5
1	-----	---	traces	---	95 (47:53)
2	methanol	---	18	---	82 (53:47)
3	Toluene	---	27	16(51:59)	47 (60:40)
4	Ethanol	---	22	---	78 (49:51)
5	Diclorometane	---	16	45 (52:58)	39 (63:37)

Reaction Conditions: *One pot* microwave-assisted multicomponent reaction of 2,3:4,5-di-O-isopropylidene-β-D-arabino-hexos-2-ulo-2,6-pyranose (**1 mmol**) using benzotiazole (**1 mmol**), thioglycolic acid (**1 mmol**) and solvent (**1 mL**) at 300 W and 120°C during 30 min.[a] Determined by CG-MS analysis of crude reaction through a standard curve generated from isolated pure product.
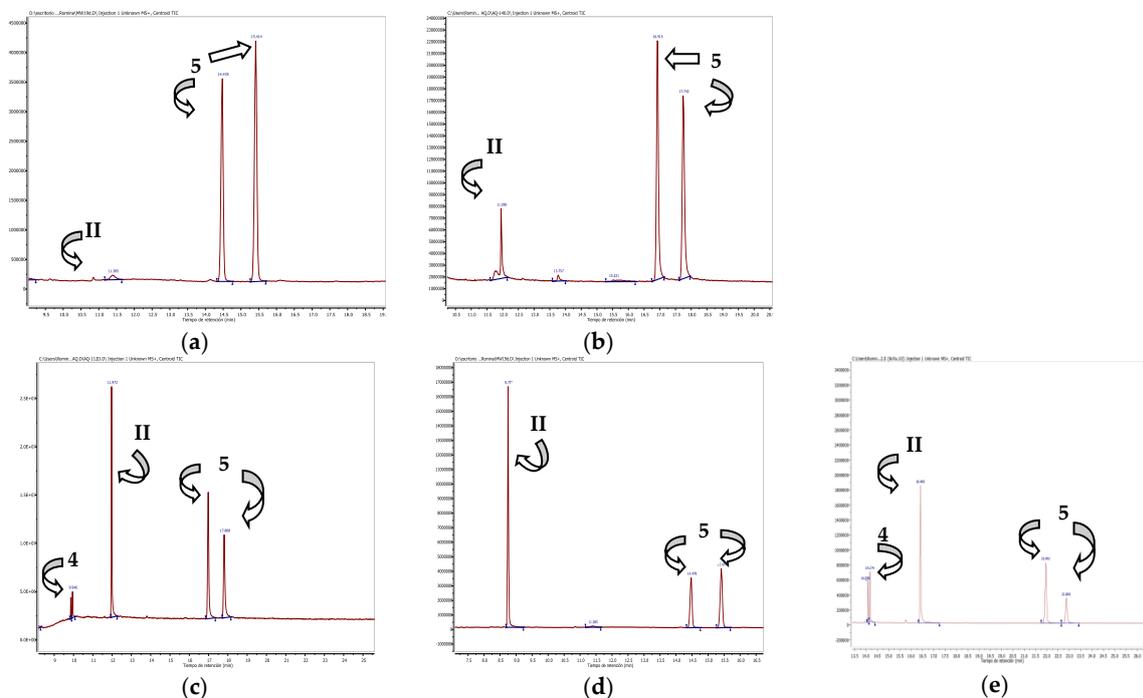

Figure 6. CG-MS of the crude products of the multicomponent reaction: without solvent (**a**), in methanol (**b**); in toluene (**c**); in ethanol (**d**); in dichloromethane (**e**).

When toluene and dicholoromethane are used as the only solvent reaction (**entry 3 and 5** respectively), both type **4** and **5** compounds are obtained in similar diastereomeric mixtures. Intermediate **II** was detected and remained unreacted after 30 minutes. However, intermediate **I** was not observed and, because of this, we can assume that its high reactivity promotes that the type **4** corresponding products are rapidly formed, although with low diastereoselectivity.

Taking into account that the results obtained with methanol and ethanol (**entry 2 and 4** respectively) as solvent are very similar, this is, only the products with five members cycle (**5**) were observed as a diastereoisomeric mixture with similar proportions of both stereoisomers, we decided to choose ethanol because it is an eco-friendly-economic solvent which would not exert influence on the diastereoselectivity of the reaction and will allow us to evaluate just the effect of the catalysts.

The monitoring of the progress of the reaction was made by CG-MS. The results obtained using **Method A** and **B** with AlCl₃ and Zeolites as Lewis acids in the reaction of 2,3:4,5-di-O-isopropylidene-β-D-arabino-hexos-2-ulo-2,6-pyranose, benzotiazole, thioglycolic acid and the catalysts in ethanol at 300 W and 120°C are shown in **Table 3**.

Table 3. Catalyst effect of different Lewis Acids on the synthesis of compounds **4** and **5** and the intermediate **II.**

Method A   Method B

Entry	Catalyst	Intermediates, Products and Its Distributions [%(diasteroisomers relations)[a]]			
		Method	II	4	5
1	AlCl₃	A	9	30 (35:65)	61 (53:47)
		B	49	---	51 (52:48)
2	Mordenite	A	7	33 (40:60)	60 (55:45)
		B	38	---	62 (74:26)
3	Zeolite 13X	A	traces	43 (21:79)	57 (77:23)
		B	10	---	90 (12:88)
4	Zeolite ZSM-5	A	---	100 (40:60)	---
		B	30	---	70 (79:21)

[a] Determined by CG-MS analysis of crude reaction during 30 min of irradiation through a standard curve generated from isolated pure product.

As can be seen from **Table 3,** the reaction with AlCl₃ as Lewis acid (**entry 1**) showed no significant results because both type **4** and **5** products are formed under the **Method A** conditions. Although **Method B** gave only type **5** products, the diastereomeric relation observed was poor together with a low yield. This is probably because ALCl₃ is not capable of inducing in a suitable way the diastereoselectivity of the reaction. In both cases, 9 and 49% respectively of intermediate **II** remained unreacted.

When Mordenite is used (**entry 2**), it can be observed that the results obtained under **Method A** conditions are very similar to those found when AlCl₃ was employed, although only traces of intermediate II was detected at the end of the reaction. However, with **Method B**, only type **5**

products were generated with good diastereoselectivity (74:26) and 62% yield. Again, in both cases, 7 and 38% respectively of intermediate **II** remained unreacted.

In the case of the utilization of zeolites 13X (**entry 3**) the best results were obtained regarding to the synthesis of type **5** products with **Method B**, not only because of the high diastereomeric relation (12:88) but in the excellent yield observed (90%), although 10% of intermediate **II** was detected at the end of the reaction. **Method A** gave a mixture of type **4** and **5** products with good dr and only traces of the intermediate **II** was detected.

Finally, **entry 4** shows that ZSM-5 gave only type products **4** in quantitative yield in a diastereomeric relation 40:60 under **Method A** conditions. In the case of the sequential method (**Method B**), the formation of the type **5** product was observed in a very good diastereoselectivity (79:21) and 70% of reaction yield. Intermediate II was detected only in the last case (30%).

From all these results, the zeolite nature proved to be critical. It can be seen that zeolite 13X is the best catalyst regarding to the diastereoselectivity found in the generation of type **4** and **5** products under **Methods A** and **B** respectively and this is probably because this catalyst has the biggest pore size (see **Table 1**). It is well known that the internal shapes of the zeolites have a great influence in reaction efficiency and that this is directly correlated with pore size.[17] So, the reacting molecules should be in a favorable location to provide a good accessibility to the catalyst acid center in order to favor the attack on one of the faces of the intermediate.

Similar analysis can be done for ZSM-5 and Mordenite. The diastereoselectivity diminishes respectively in the same way that the pore size of these catalysts decrease.

2. Materials and Methods

2.1. General Information:

Mass spectra were obtained with a GC/MS instrument (HP5-MS capillary column, 30 m / 0.25 mm / 0.25 mm) equipped with 5972 mass selective detector operating at 70 eV (EI). Infrared spectra were recorded with a Nicolet Nexus 470 FT spectrometer. Microwave reactions were performed with a microwave oven (CEM Discover®) with a continuous focused microwave power delivery system in a pressure glass vessel (10 mL) sealed with a septum under magnetic stirring. The reaction mixture temperature was monitored using a calibrated infrared temperature control under the reaction vessel, and control of the pressure was performed with a pressure sensor connected to the septum of the vessel.

2.2. General reaction conditions:

Method A: *One pot* microwave-assisted multicomponent reaction: A mixture of 2,3:4,5-di-O-isopropylidene-β-D-arabino-hexos-2-ulo-2,6-pyranose (0.242 g, 1 mmol), benzothiazole (0.15 g, mmol), thioglycolic acid (0.07 mL, 1 mmol) and the corresponding solvent used in each case (1 mL) were heated in the microwave apparatus at 300 W and 120 ° C for 30 minutes. In cases where zeolites were used, they were filtered from the respective crude reaction using 2 mL of ethanol as washing solvent. The analysis of the ratio of intermediate and products generated during the course of the reaction were monitored taking aliquots for consecutive periods of 5 minutes for GC-MS analysis.

Method B: Sequential reaction: 2,3:4,5-di-O-isopropylidene-β-D-arabino-hexos-2-ulo-2,6-pyranose (0.242 g, 1 mmol), benzothiazole (0.15 g, mmol) and ethanol (1 mL) were irradiated at 300 W and 120°C during 30 min. On the other hand, thioglycolic acid (0.07 mL, 1 mmol) is kept under stirring at room temperature in the presence of the corresponding catalyst (20 mg) for 10 minutes.

Then, thioglycolic acid coordinated to the catalyst is added to the preformed imine and irradiated under the same conditions 30 minutes, monitoring aliquots taken every 5 min by GC-MS. In cases where zeolites were used, they were filtered from the respective crude reaction using 2 mL of ethanol as washing solvent.

2.3. BET Area Analysis:

The surface area of the commercial zeolites (mordenite, 13X zeolite and ZSM-5 zeolite) was determined by the technique developed by Brunauer, Emmet, and Teller (BET) [9]. The measured was performed by nitrogen adsorption isotherms at 77 K in a Quantachrome Nova 1200e. Samples before each analysis were degassed at 200 °C under vacuum. To obtain the adsorption isotherm, the sample was encapsulated and increasing pressure of N_2 was applied. The results obtained by linear regression equation of BET determined the specific surface area in m^2/g.

2.4. Isotherms of Pyridine Adsorption:

Diffuse spectral reflectance infrared (DRIFTS) spectra were recorded on a Nicolet 6700 FT-IR spectrometer in the region of 4000-400 cm^{-1}. The spectra were recorded with a resolution of 4 cm^{-1} and 100 scans with a DTGS detector in KBr. The samples (approximately 10 mg) were finely ground and 5% diluted in KBr, placed in a ceramic crucible in a DRIFTS (Nexus Smart Collector, Nicolet) chamber.

Before collecting the spectra, the samples were pre-treated ex situ as shown in **Figure 3**. First, they were heated in N_2 flow at 400 °C for 45 minutes to remove surface contaminants. The adsorption of pyridine was carried out at 100 °C with a stream of N_2 saturated at room temperature (RT). Then, pure N_2 was again passed over the samples at 100 °C to be able to sweep the weakly adsorbed pyridine residues on samples and then cooled to RT to perform further analysis by IR.
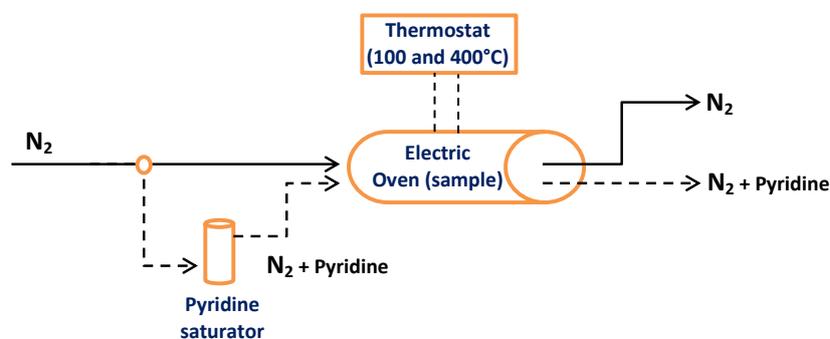

Figura 3: Schematic diagram of the system employed for the previous and post treatment on the pyridine adsorption of zeolites samples for the determination of acid sites by IR.

4. Conclusions

From all these studies, we can conclude that Mordenite, 13X and ZSM-5 zeolites are highly efficient and eco-friendly Lewis acid catalyst in the tricomponent and sequential reaction presented here for the diastereoselective synthesis of 1,4-thiazepan- 3-ones (**4**) and 4-thiazolidinones (**5**). Besides, these reactions were fast and with a very easy workup (just filtering the zeolite) that allows getting the synthetized products without further treatment for the CG-MS determination. In future works we will extend these studies to more substrates and zeolites, with the aim of separate the diastereomeric products and evaluate their biological activity.

5. References

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