



EFFICIENT SYNTHESIS OF CYCLIC ENAMINES FROM MORPHOLINE AND CYCLOALKANONES CATALYZED BY ZEOLITE H-Y

Yasmine Rahma Hachemi^{1*}, Nabila Bouchiba², Mohammed Hamadouche^{1*}

¹ *Laboratoire de Chimie Fine*

² *Laboratoire de Chimie des Matériaux*

^{1,2} *Département de Chimie, Faculté des Sciences Exactes et Appliquées, Université Oran1,
BP 1524 El M'naouer, Oran 31000, Algérie*

**E-mail: hamadouchemed@yahoo.fr
yasmine.h31@gmail.com*

ABSTRACT: In recent years, there has been a lot of interest in the application of green heterogeneous materials as catalysts in organic chemistry. We report in this paper the preparation of cyclic enamines using zeolite H-Y as catalyst. In the first step, zeolite Y was prepared using hydrothermal method and characterized by various techniques such as X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), nitrogen sorption at 77 K, scanning electronic microscopy (SEM). The second pathway involved the preparation of H-Y as catalyst for the reaction between cyclic ketones and secondary amines to generate cyclic enamines. The results of our experiments have shown that the use of H-Y in this reaction compared to the use of other catalysts heterogeneous or homogeneous accelerates time and increases the yield of the reaction. In order to confirm the catalytic activity of zeolite H-Y, it was used in five consecutive experiments without significant loss of activity.

KEYWORDS: Catalyst materials, Catalyst characterization, Zeolite Y, Heterogeneous catalysis, Enamines

INTRODUCTION:

Enamines play an important role in chemistry and biology, frequently used as versatile intermediates in organic chemistryⁱ and the synthesis of biologically active compoundsⁱⁱ. They are recognized as key intermediates in organocatalysis^{iii-vi}, and have been also used as dipolarophiles in 1,3-Dipolar cycloaddition^{vii-ix}. Enamine derivatives present a wide spectrum of physiological, biological, and energetic activities. Some cyclic α -keto enamines were identified as intense cooling compounds^x. More enamine derivatives have shown a great antiproliferative, cytotoxicity against cancer cells^{xi-xiii}, and antibacterial activity^{xiv}. Recently, new enamine-based and carbazole-based enamine have been developed as low-cost and efficient hole transporting material for perovskite solar cells^{xv-xvi}.

Before 1950, the chemistry of enamines has been explored^{xvii} and following Gilbert Stork's studies^{xviii-xix}, several methods have been reported in the literature for their synthesis^{i,xx-xxv}. The

usual conditions to prepare enamines involve either strong Lewis acids (TiCl₄, ZnCl₂, AlCl₃, SnCl₄, etc.)^{xxvi-xxiii} or Bronsted acids (AcOH, PTSA)^{xxix} in refluxing solvents (benzene, toluene, or xylene). However, most of the previous studies do not take into account environmental catalysis. The use of homogenous catalysts like Lewis acids poses several problems, such as difficulty in separation, recovery, high toxicity, corrosion and they cannot be reused.

Therefore, in the area of interest regarding environment, more catalysts that are recyclable have been developed. Due to their easily reproducible structure from aluminosilicate, zeolites have been used extensively as ion exchangers, adsorbents and separation materials^{xxx-xxxiv}. Zeolites still represent the most studied system in acid heterogeneous catalysis and are applied to a wide variety of reactions^{xxxv-xxxvii}. Within this context, our attention has been focused on the preparation of zeolite H-Y which exhibits both Bronsted and Lewis acidity characteristics^{xxxviii-xxxx}. Therefore, this research intends to report a simple synthetic procedure of cyclic enamines by the addition of cyclic ketones to secondary amines using zeolite H-Y as a green catalyst and demonstrates its performance compared to other catalysts.

EXPERIMENTAL:

REAGENTS:

Sodium aluminate (50.38% Al₂O₃; 36.70% Na₂O₃; 13.63% H₂O; Aldrich) was used as the aluminium source, Zeosil 175MP (84.96% SiO₂; 0.31% Al₂O₃; 0.93% Na₂O₃; 13.78% H₂O; Rhône Poulenc) as a silica source, Sodium hydroxide (99%; Prolabo) as a base and demineralized water as solvent.

PREPARATION OF THE CATALYST:

ZEOLITE Y SYNTHESIS:

Sample of zeolite Y was prepared by using the direct synthesis hydrothermal method^{xxxxi}, with a molar composition of [5 Na₂O ; Al₂O₃ ; 10 SiO₂ ; 160 H₂O]. The synthesis consisted in first time to prepare an alkaline solution containing sodium hydroxide and sodium aluminate. After 1 hour of agitation, the silica was slowly added. The reaction mixture was homogenized 2 hours at room temperature. Afterwards, the hydrogel obtained was transferred into autoclave for the crystallization at 100 °C during 48 h. Finally, the product was washed many times with demineralized water, filtered and dried at 60 °C overnight.

H-Y ZEOLITE PREPARATION:

As shown in **Fig. 1** the zeolite Y synthesized was saturated with an aqueous solution of sodium chloride (NaCl) 1 M during 24 h then filtered and dried at 60 °C overnight. Afterward Na-Y was exchanged with an ammonium chloride solution (NH₄Cl) 1 M. The product was washed several times with demineralized water, filtered, dried at 60 °C and finally calcined under air at 550 °C for 6 h^{xxxii}.

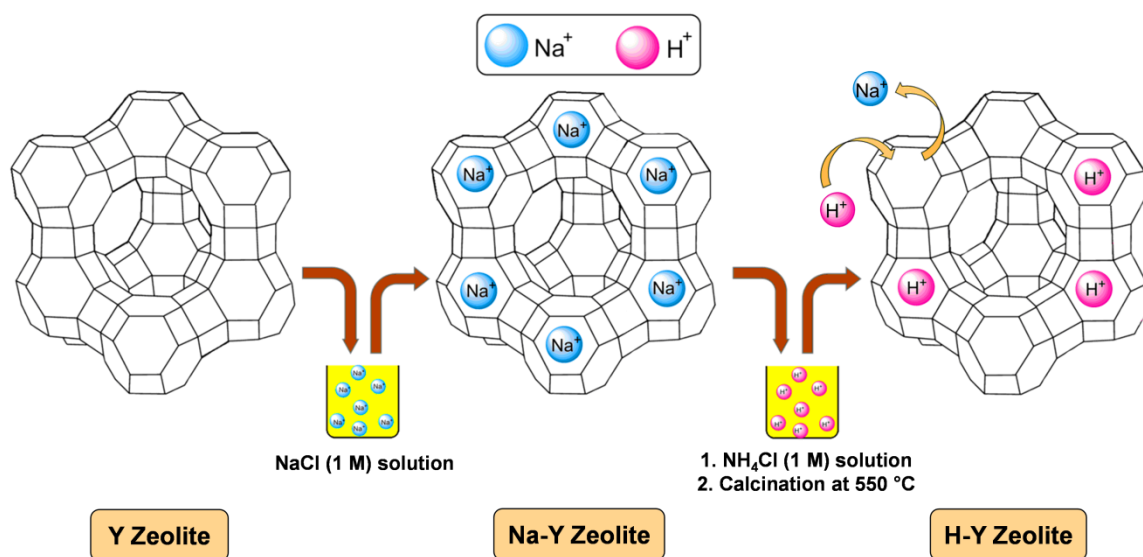
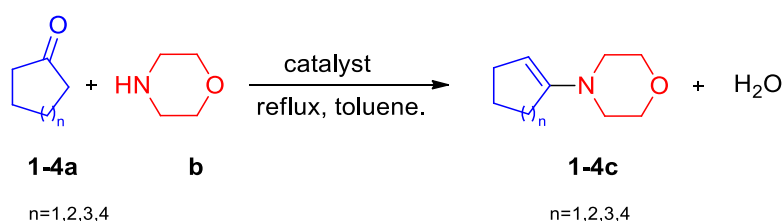


Figure1. Schematic illustration for the preparation of H-Y zeolite.

CATALYST CHARACTERIZATION:

The structural features of zeolite Y were determined by X-ray diffraction (XRD) patterns using Bruker AXS D8 diffractometer (Cu-K α radiation). The textural properties of zeolite were measured by nitrogen adsorption/desorption in a Micromeritics ASAP 2010 volumetric instrument. The surface area was calculated by the Brunauer–Emmet–Teller (BET) method. The functional groups of the catalyst were analyzed by IR spectroscopy using Bruker Platinum-ATR. The surface morphology of the zeolite was observed by Hitachi S-4800 microscope

GENERAL PROCEDURE FOR THE SYNTHESIS OF CYCLIC ENAMINES:



Scheme1. Synthetic procedure of cyclic enamines.

To synthesize cyclic enamines(**1-4c**), the simplest method consists in heating cyclic ketones and secondary amines, using Dean-Stark apparatus^{xxxxiii}. In a two-necked round-bottomed flask equipped with a refrigerant under an argon atmosphere, a Dean-stark and magnetic stirring bar, was charged with morpholine(**b**) (11.32 mL, 0.13 mol), 0.5 g of dried catalyst at 60 °C and cyclic ketone(**1-4a**)(0.12 mol) in 30 mL of anhydrous toluene refluxing. The reaction complete until no further water formation is observed, the catalyst was removed by simple filtration, the solvent was then evaporated and the crude was purified by distillation under reduced pressure.

RESULTS AND DISCUSSION:

CHARACTERIZATION OF THE CATALYST:

The XRD patterns of zeolite Y are given in **Fig. 2**, as seen in this figure, all the characteristic peaks of zeolite Y are presently confirming the stability of this zeolite during the different treatment procedures. No other phase was observed, which confirms that the success of the preparation of this zeolite.

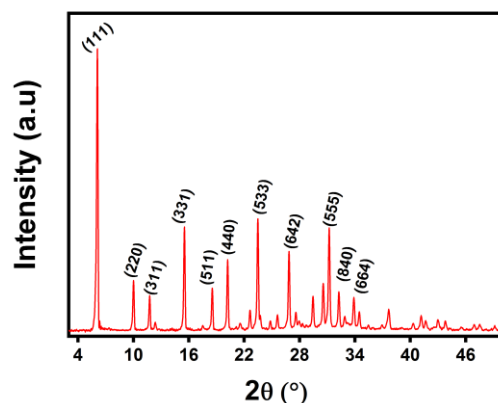


Figure2.XRD patterns of Y zeolite.

The FTIR spectra of zeolite Y is shown in **Fig. 3**, as seen in this figure, all the characteristic bands of the Y zeolite are present in the spectra. The bands in the range of 950-1200 cm^{-1} indicate the presence of Si-O, assigned to external asymmetrical stretching while the bands between 500-650 cm^{-1} are assigned to the internal tetrahedral symmetrical stretching. Absorption at approximately 450 cm^{-1} was assigned to Si-O-Al stretching where Al is in the octahedral coordination. The presence of a weak band at 1630 cm^{-1} and a broadband around 3400 cm^{-1} of OH group coming from physisorbed water.

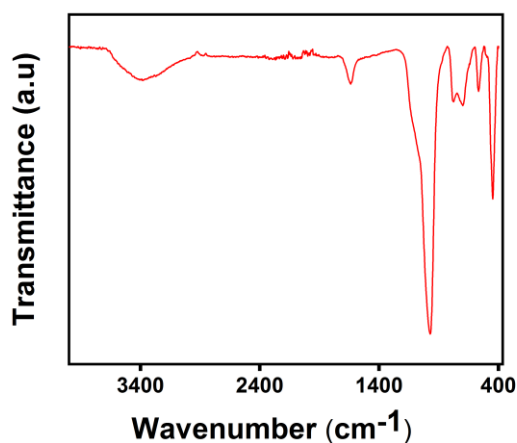


Figure3.FTIR of Y zeolite.

Fig. 4 shows the nitrogen sorption isotherm at 77 K for zeolite Y. According to the IUPAC classification nitrogen adsorption/desorption isotherms of the zeolite Y is the type I which is characteristic of microporous materials. It is characterized by an almost horizontal range from a very low P/P_0 value to a P/P_0 value near 1. The surface area and micropore volume are given

in Table 1. The synthesized zeolite Y has a surface area around $608 \text{ m}^2 \cdot \text{g}^{-1}$. The surface is similar compared to that pure commercial zeolite. This result indicates that zeolite Y is an excellent microporous material.

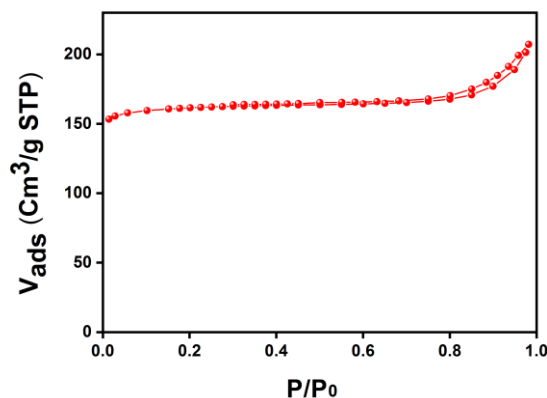


Figure4. Nitrogen adsorption-desorption isotherm of Zeolite Y.

Table1. Surface area, micropore volume and pore diameter of zeolite Y.

	$S_{\text{BET}} (\text{m}^2/\text{g})$	$S_{\text{ext}} (\text{m}^2/\text{g})$	$S_{\text{micro}} (\text{m}^2/\text{g})$	$V_{\text{ads}} (\text{cm}^3/\text{g})$
Zeolite Y	620.48	12.16	608.32	0.246
Pure commercial Y	648	44	604	0,28

The SEM image of Zeolite Y shown in Fig. 5 reveals the presence of uniformly sizes with crystalline features, fused together forming agglomerate and indicate clearly the absence of amorphous phase, which was already confirmed by XRD. This morphology is very similar compared to other works published previously^{xxxxiv-xxxxv}.

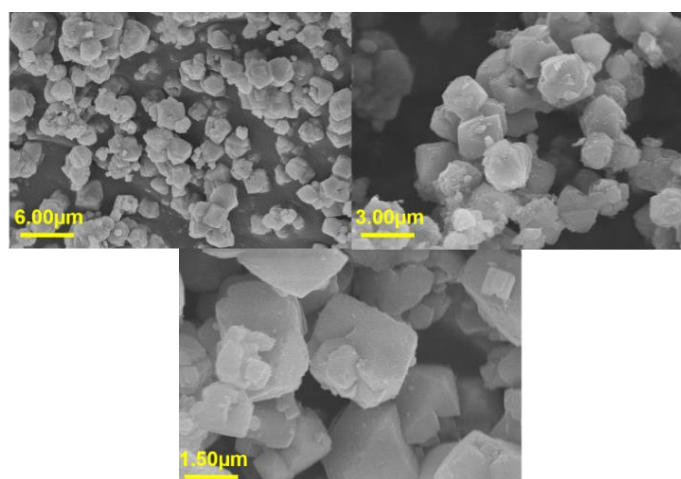
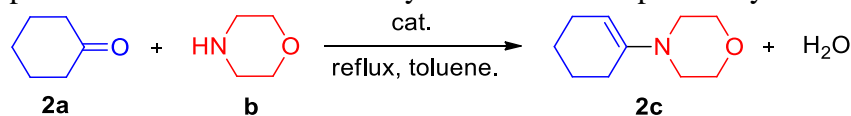


Figure5. SEM images of Y Zeolite.

SYNTHESIS OF 1-MORPHOLINOCYCLOHEXENE (2c):**Table 2.** Comparison between different catalysts toward 1-morpholinocyclohexene synthesis.

Entry	Catalyst	Reaction conditions				Time (h)	Yield (%)	Reference
		2a (mol)	b (mol)	Cat. (g)	Solvent			
1	None	0.12	0.13	-	Toluene ^a	7.5	88	This work
2	H-Y	0.12	0.13	0.5	Toluene^a	1.25	96	This work
3	Y	0.12	0.13	0.5	Toluene ^a	3.41	90	This work
4	PTSA	0.25	0.26	0.6	Toluene ^a	3	92	xxxxxiii
5	TiCl ₄	0.10	0.30	9.5	Hexane ^b	24	70	xxxxxvi
6	Molecular Sieve	0.10	0.20	40	Ether ^b	24	54	xxxxxvi
7	K-10 clay	0.25	0.26	2	Toluene ^a	3	95	xxxxxiii
8	MCM-41 ^c	0.12	0.13	0.5	Toluene ^a	2.25	81	This work
9	SBA-15 ^d	0.12	0.13	0.5	Toluene ^a	2.75	87	This work
10	Maghnite ^e	5.10 ⁻³	0.01	2	Solvent-free ^b	7	80	xxxxxvi

^aToluene refluxing under Dean-stark. ^broom temperature reaction. ^cxxxxxviii. ^dxxxxxix. ^exxxxxvii.

Table 2 shows a comparative study between different catalysts towards the synthesis of 1-morpholinocyclohexene. All these catalysts have shown interesting yields in different conditions for this reaction. According to Stork reports, this reaction without catalyst takes between 5 and 8 hours for cyclopentanone and cyclohexanone with morpholine or pyrrolidine, for large size rings, the reaction requires more than 24 h refluxing^{xix}. The use of homogeneous Bronsted or Lewis acid catalysts in this reaction is reported^{xxxxxiii} for PTSA and our group^{xxxxxvi} for TiCl₄. PTSA has accelerated the reaction to 3 h (Entry 4) however the use of TiCl₄ required 24 h at room temperature (Entry 5). Heterogeneous catalysis with clays has also been studied, Montmorillonite K-10 clay has decreased also the time of reaction to 3 h (Entry 7), the use of Algerian Montmorillonite clay Maghnite was tested in this reaction (Entry 10) with solvent-free at room temperature conditions for 7 h. The produced water in this reaction is adsorbed on these clays. Different porous solids were tested in the synthesis of 1-morpholinocyclohexene, Molecular sieve was used as a water adsorbent (Entry 6), a large amount of this catalyst was used in this reaction at room temperature for 24 h to give an average yield.

In this paper, we were interested to evaluate the catalytic effect of some micro and mesoporous materials in the synthesis of cyclic enamines. MCM-41 (Entry 8) and SBA-15 (Entry 9) mesoporous materials give a good result, we note an acceleration of the reaction time, which decreased to 2.25 h for MCM-41 and 2.75 h for SBA-15 with good yields. Y zeolite (Entry 3) microporous material give also a good effect catalytic, time and yield were also optimized. Reaction time is the contrast between both these homogeneous, heterogeneous catalysts and the H-Y zeolite. Indeed 0.5 g of Y zeolite protonated has accelerated the reaction between morpholine and cyclohexanone, decreasing the time of the reaction from 7.5 h (Entry 1) without catalyst at 1.25 h (Entry 2), and the yield mildly increased. According to this study, we find that the use of zeolite H-Y which exhibits both Bronsted and Lewis acidity as catalyst have accelerated this reaction.

SYNTHESIS OF CYCLIC ENAMINES:

Table 3. Synthesis of cyclic enamines catalyzed by H-Y zeolite.

$$\text{1-4a} + \text{b} \xrightarrow[\text{reflux, toluene.}]{\text{H-Y}} \text{1-4c} + \text{H}_2\text{O}$$

Entry	Product	Time	Yield
1		1c 1.33 h	94%
2		2c 1.25 h	96%
3		3c 1.5 h	98%
4		4c 26 h	97%

n=1,2,3,4

0.12 mol of cyclic ketones, 0.13 mol of morpholine and 0.5 g of H-Y zeolite in toluene refluxing under Dean-stark.

After showing that the best result in the synthesis of cyclic enamines was using zeolite H-Y (**Table 2.**), we were interested to synthesize other cyclic enamines by varying cyclic ketones with morpholine under the same reaction conditions. The obtained results are illustrated in Table 3. In all cases, cyclic enamines were obtained with excellent yields after simple filtration to remove the catalyst and distillation of the residue. We arrived to reduce the reaction time, all of **1c**, **2c**, **3c** were obtained by our group in 3 hours using Montmorillonite K-10 as catalyst and **4c** in 36 h but with H-Y zeolite we had reduced the time to 1.33 h-1.5 h for **1c**, **2c**, **3c** and 26 h for **4c**.

The water molecule that formed during the reaction adsorbs on the surface of the zeolite. As a result, zeolite H-Y has two roles: a proton donor and a water molecule sensor (**See Fig. 6**).

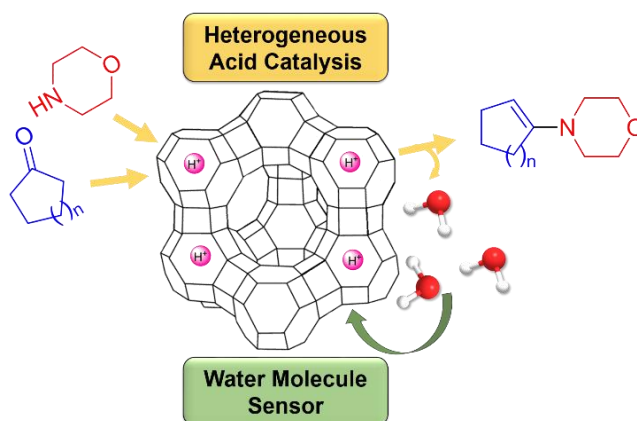


Figure6. Action of zeolite H-Y during formation of cyclic enamines.

RECYCLING:

It is important to examine recoverability and reusability of heterogeneous catalyst, **Fig. 7** shows the evolution of the product yield and the time of reaction based on the number of reuse.

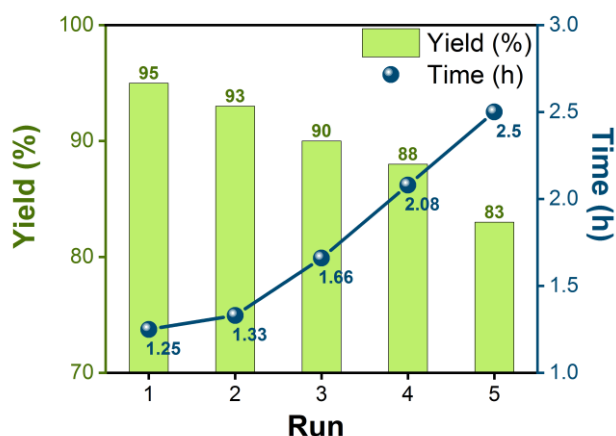


Figure7. Recycling of H-Y in the synthesis of 1-morpholinocyclohexene

H-Y zeolite can be reused five times in the reaction between cyclohexanone and morpholine under the same reaction conditions without a significant loss of catalytic activity. Between each run, there is a minor decline in yield and a slight increase in reaction time. The catalyst is recovered by simple filtration, washed by toluene to remove all products and then dried before use for the next cycle.

CONCLUSION:

The solid catalyst H-Y was prepared by hydrothermal method, structure and texture properties of Y zeolite were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), nitrogen sorption at 77 K, and scanning electronic microscopy (SEM). We have shown the potential of zeolite H-Y in the synthesis of cyclic enamines, compared to other heterogeneous or homogeneous catalysts. Easy to prepare, handle, recover, and recycle, H-Y offers an interesting alternative to more conventional homogeneous catalysts in the synthesis of enamines. A variety of possible future studies using the same experimental setup are apparent. It would be interesting to assess the effects of zeolite Y catalyst on other reactions.

ACKNOWLEDGEMENTS:

The authors are very grateful to Prof D. El Abed, Oran-1 University (Algeria), for his help and "Direction Générale de la Recherche Scientifique et du Développement Technologique" DGRSDT for financial support.

CONFLICT TO INTEREST: The authors declare that there is no conflict of interest.

ANALYTICAL DATA FOR COMPOUNDS:

Spectra of the final products were recorded on a Bruker Avance-300 spectrometer for NMR (300 MHz and 75 MHz for ^1H and ^{13}C respectively) in CDCl_3 . Chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the external reference. Coupling constants (J) are reported in Hertz. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet).

1-morpholinocyclopentene (1a). Colorless liquid. b.p. 108-109 °C / 18 mmHg; Yield 94% ; ^1H NMR (300 MHz, CDCl_3) δ ppm: 1.78-1.88 (m, 2H), 2.26-2.33 (m, 4H), 2.83 (dt, $J = 9.8$; $J = 0.9$ Hz, 4H), 3.68 (dt, $J = 9.8$; $J = 0.9$ Hz, 4H), 4.40 (s, 1H) ; ^{13}C NMR(300 MHz, CDCl_3) δ ppm: 27.8, 35.5, 35.7, 47.1, 66, 98.9, 150.7 ; IR (ATR) cm^{-1} : 1630 (C=C).

1-morpholinocyclohexene (2c). Colorless liquid. b.p 118-120 °C / 18 mmHg; Yield 96% ; ^1H NMR (300 MHz, CDCl_3) δ ppm: 1.49-1.57 (m, 2H), 1.62-1.70 (m, 2H), 2.01-2.08 (m, 4H), 2.71 (t, $J = 4.9$ Hz, 4H), 3.71 (t, $J = 4.9$ Hz , 4H), 4.65 (t, $J = 3.4$ Hz , 1H) ; ^{13}C NMR(300 MHz, CDCl_3) δ ppm : 22.2, 23.8, 26.2, 36.0, 47.9, 66.7, 99.5, 144.8 ; IR (ATR) cm^{-1} : 1644 (C=C).

1-morpholinocycloheptene (3c). Colorless liquid. b.p. 138-140 °C / 18 mmHg ; Yield 98% ; ^1H NMR (300 MHz, CDCl_3) δ ppm: 1.31-1.42 (m, 4H), 1.59-1.57 (m, 2H), 1.96-2.02 (m, 2H), 2.14 (t, $J = 4.8$ Hz , 2H), 2.61 (t, $J = 4.5$ Hz , 4H), 3.63(t, $J = 4.5$ Hz , 4H), 4.78 (t, $J = 6.9$ Hz, 1H) ; ^{13}C NMR(300 MHz, CDCl_3) δ ppm :26.13, 26.57, 27.83, 31.43, 32.46, 49.73, 66.80, 106.73, 154.07; IR (ATR) cm^{-1} : 1645 (C=C).

1-morpholinocyclooctene (4c). Colorless liquid. b.p. 156-157 °C / 18 mmHg ; Yield 97% ; ^1H NMR (300 MHz, CDCl_3) δ ppm: 1.42-1.50 (m, 8H), 2.04-2.07 (m, 2H), 2.21-2.25 (m, 2H), 2.72-2.75 (m, 4H), 3.64-3.67 (m, 4H), 4.50 (td, $J = 8.2$ Hz ; $J = 3.7$ Hz , 1H) ; ^{13}C NMR(300 MHz, CDCl_3) δ ppm: 25.6, 26, 26.4, 26.9, 29.5, 30.3, 49, 66.8, 103.2, 148.7 ; IR (ATR) cm^{-1} : 1641 (C=C).

REFERENCES:

- i. Gilbert Cook; A. Enamines: Synthesis, Structure, and Reactions; Marcel Dekker.; New York, 1988.
- ii. Hamadouche, M.; Belkheira, M.; El Abed, D.; Use of enamins in organic synthesis leading bioactive molecules; Phys. Chem. News.; 2007, **37**, 83–106.
- iii. Notz, W.; Tanaka, F.; Barbas, F.C.; Enamine-Based Organocatalysis with Proline and Diamines: The Development of Direct Catalytic Asymmetric Aldol, Mannich, Michael, and Diels–Alder Reactions; Acc. Chem. Res.; 2004, **37**, 580–591.
- iv. List, B.; Enamine Catalysis Is a Powerful Strategy for the Catalytic Generation and Use of Carbanion Equivalents; Acc. Chem. Res.; 2004, **37**, 548–557.
- v. Pihko, P.M.; Majander, I.; Erkkilä, A.; Enamine Catalysis. In Asymmetric Organocatalysis; List, B., Ed.; Topics in Current Chemistry; Springer: Berlin, Heidelberg; 2009; pp. 145–200.
- vi. Belkheira, M.; El Abed, D.; Pons, J.-M.; Bressy, C.; Organocatalytic Synthesis of 1,2,3-Triazoles from Unactivated Ketones and Arylazides.; Chem. Eur. J.; 2011, **17**, 12917–12921.

- vii. Audran, G.; Adiche, C.; Brémond, P.; El Abed, D.; Hamadouche, M.; Siri, D.; Santelli, M.; Cycloaddition of Sulfonyl Azides and Cyanogen Azide to Enamines. Quantum-Chemical Calculations Concerning the Spontaneous Rearrangement of the Adduct into Ring-Contracted Amidines; *Tetrahedron Lett.*;2017, **58**, 945–948.
- viii. Ouasti, F.-Z.; Hamadouche, M.; Benmaati, A.; El Abed, D.; Facile and Efficient Microwave-Assisted Synthesis of Bicyclic Δ^2 (1,2,3)-Triazoline via 1,3 Dipolar Cycloaddition between Organic Azides and 1-Morpholinocyclopentene.; *Heterocycl.lett.*;2018, **18**,569-577.
- ix. Chenni, A.; Hamadouche, M.; El Abed, D.; Free Solvent Microwave-Assisted Synthesis of (1,2,3)-Triazolines.; *Heterocycl.lett.*;2018, **8**, 647-656.
- x. Ottinger, H.; Soldo, T.; Hofmann, T.; Systematic Studies on Structure and Physiological Activity of Cyclic α -Keto Enamines, a Novel Class of “Cooling” Compounds; *J. Agric. Food Chem.*;2001, **49**, 5383–5390.
- xi. Luzina, O.A.; Sokolov, D.N.; Pokrovskii, M.A.; Pokrovskii, A.G.; Bekker, O.B.; Danilenko, V.N.; Salakhutdinov, N.F.; Synthesis and Biological Activity of Usnic Acid Enamine Derivatives.; *Chem Nat Compd.*;2015, **51**, 646–651.
- xii. Holota, S.; Kryshchyn, A.; Derkach, H.; Trufin, Y.; Demchuk, I.; Gzella, A.; Grellier, P.; Lesyk, R.; Synthesis of 5-Enamine-4-Thiazolidinone Derivatives with Trypanocidal and Anticancer Activity; *Bioorg. Chem.*;2019, **86**, 126–136.
- xiii. Burcu Gürdere, M.; Aydin, A.; Yencilek, B.; Ertürk, F.; Özbek, O.; Erkan, S.; Budak, Y.; Ceylan, M.; Synthesis, Antiproliferative and Cytotoxic Activities, DNA Binding Features and Molecular Docking Study of Novel Enamine Derivatives; *Chem. Biodiversity*;2020, **17**:7.
- xiv. Xiao, Z.-P.; Fang, R.-Q.; Li, H.-Q.; Xue, J.-Y.; Zheng, Y.; Zhu, H.-L. Enamines as Novel Antibacterials and Their Structure–Activity Relationships; *Eur. J. Med. Chem.*;2008, **43**, 1828–1836.
- xv. Daskeviciene, M.; Paek, S.; Wang, Z.; Malinauskas, T.; Jokubauskaite, G.; Rakstys, K.; Cho, K.T.; Magomedov, A.; Jankauskas, V.; Ahmad, S.; et al.; Carbazole-Based Enamine: Low-Cost and Efficient Hole Transporting Material for Perovskite Solar Cells; *Nano Energy*; 2017, **32**, 551–557.
- xvi. Steponaitis, M.; La-Placa, M.-G.; Kaya, İ.C.; Bubniene, G.; Jankauskas, V.; Daskeviciene, M.; Sessolo, M.; Malinauskas, T.; Bolink, H.J.; Getautis, V.; Enamine-Based Hole Transporting Materials for Vacuum-Deposited Perovskite Solar Cells; *Sustain. Energy Fuels*;2020, **4**, 5017–5023.
- xvii. Mannich, C.; Davidsen, H.; Über einfache Enamine mit tertiär gebundenem Stickstoff. *Ber. dtsh. Chem. Ges.*;1936, **69**, 2106–2112.
- xviii. Stork, Gilbert; Terrell, R.; Szmuszkovicz, J.; A New Synthesis Of 2-Alkyl And 2-Acyl Ketone; *J. Am.Chem. Soc.*;1954, **76**, 2029–2030.
- xix. Stork, Gilbert.; Brizzolara, A.; Landesman, H.; Szmuszkovicz, J.; Terrell, R.; The Enamine Alkylation and Acylation of Carbonyl Compounds.; *J. Am. Chem. Soc.*;1963, **85**, 207–222.
- xx. Evans, D.A.; New Endocyclic Enamine Synthesis; *J. Am. Chem. Soc.*;1970, **92**, 7593–7595.
- xxi. Comi, R.; Franck, R.W.; Reitano, M.; Weinreb, S.M.; A Preparation of Enamines. *Tetrahedron Lett.*;1973, **14**, 3107–3109.
- xxii. Broekhof, N.L.J.M.; van Elburg, P.; Hoff, D.J.; van der Gen, A.; Enamine Synthesis Using the Horner-Wittig Reaction. Part 2. New Acyl Anion Equivalents Derived

- from (Aminomethyl)Diphenylphosphine Oxides;Recl. Trav. Chim. Pays-Bas; 1984, **103**, 317–321.
- xxiii. Hamadouche, M.; El Abed, D.; Modes d'obtention Des Énamines;Journal de la Société Chimique de la Tunisie;1999, **IV**, 337–370.
- xxiv. Ning, Y.; Zhao, X.-F.; Wu, Y.-B.; Bi, X.; Radical Enamination of Vinyl Azides: Direct Synthesis of N -Unprotected Enamines;Org. Lett.;2017, **19**, 6240–6243.
- xxv. Angelov, P.; Ivanova, S.; Yanev, P.; Enamines of 3-Acyltetramic Acids from β -Enamino Amides and Amino Acids;Tetrahedron Lett.;2017, **58**, 4776–4778.
- xxvi. Carlson, R.; Nilsson, Å.; Strömquist, M.; Stenman, U.-H.; Rasmussen, P.B.; Lawesson, S.-O.; Williams, R.V.; Mahedevan, R.; Optimum Conditions for Enamine Synthesis by an Improved Titanium Tetrachloride Procedure;Acta Chem. Scand.; 1983, **37b**, 7–13.
- xxvii. Carlson, R.; Nilsson, Å.; Carlström, K.; Sköldefors, H.; Wilking, N.; Theve, N.O.; Improved Titanium Tetrachloride Procedure for Enamine Synthesis. II. Scope of the Reaction;Acta Chem. Scand.;1984, **38b**, 49–53.
- xxviii. Iimori, T.; Nii, Y.; Izawa, T.; Kobayashi, S.; Ohno, M.; Carbon-Carbon Bond Formation from Ethyl Cyanofornate and Active Methylene Compounds. ;Tetrahedron Lett.;1979, **20**, 2525–2528.
- xxix. Nazaré, M.; Schneider, C.; Lindenschmidt, A.; Will, D.W.; A Flexible, Palladium-Catalyzed Indole and Azaindole Synthesis by Direct Annulation of Chloroanilines and Chloroaminopyridines with Ketones;Angew. Chem. Int. Ed.;2004, **43**, 4526–4528.
- xxx. Beauvais, C.; Boutin, A.; Fuchs, A.H.; Adsorption of Water in Zeolite Sodium-Faujasite: A Molecular Simulation Study;C. R. Chim.;2005, **8**, 485–490.
- xxxi. Horňáček, M.; Hudec, P.; Nociar, A.; Smiešková, A.; Jakubík, T.; Activity and Regenerability of Dealuminated Zeolite Y in Liquid Phase Alkylation of Benzene with 1-Alkene;Chem. Pap.;2010, **64**, 469–474.
- xxxii. Masoudian, S.K.; Sadighi, S.; Abbasi, A.; Synthesis and Characterization of High Aluminum Zeolite X from Technical Grade Materials;Bull. Chem. React. Eng. Catal.;2013, **8**, 54–60.
- xxxiii. Takeuchi, M.; Hidaka, M.; Anpo, M.; Simple Evaluation of the Adsorption States of Benzene Molecule on the Hydroxyl, H⁺ and Na⁺ Sites of Y-Zeolite Surfaces by Using UV Absorption Spectroscopy.;Res Chem Intermed;2014, **40**, 2315–2325.
- xxxiv. Medina-Ramírez, A.; Trejo-García, A.J.; Ruiz-Camacho, B.; López-Badillo, C.M.; Minchaca-Mojica, J.I.; Martínez-Gómez, C.; Simple Synthesis of Hierarchically Structured X Zeolite from Geothermal Nanosilica and Its Evaluation in the Dehydration of Aqueous Solutions of Ethanol;Chem. Pap.;2021, **75**, 337-349.
- xxxv. Sasidharan, M.; Tatsumi, T.; Allylation of Aldehydes Catalyzed by Zeolites under Liquid Phase;Chem. Lett.;2003, **32**, 624–625.
- xxxvi. Parsapur, R.K.; Selvam, P.; Rational Design, Synthesis, Characterization and Catalytic Properties of High-Quality Low-Silica Hierarchical FAU- and LTA-Type Zeolites;Sci. Rep.;2018, **8**, 16291.
- xxxvii. Mekki, A.; Benmaati, A.; Mokhtar, A.; Hachemaoui, M.; Zaoui, F.; Habib Zahmani, H.; Sassi, M.; Hacini, S.; Boukoussa, B.; Michael Addition of 1,3-Dicarbonyl Derivatives in the Presence of Zeolite Y as an Heterogeneous Catalyst;J. Inorg. Organomet. Polym.;2020, **30**, 2323–2334.
- xxxiii. Schriider, K.-P.; Sauer, J.; Leslie, M.; Catlow, C.R.A.; Thomas, J.M.; Bridging Hydroxyl Groups in Zeolitic Catalysts: A Computer Simulation of Their Structure,

- Vibrational Properties and Acidity in Protonated Faujasites (H-Y Zeolites); *Chem. Phys. Lett.*; 1992, **6**, 188.
- xxxix. Parrillo, D.J.; Gorte, R.J.; Characterization of Acidity in H-ZSM-5, H-ZSM-12, H-Mordenite, and H-Y Using Microcalorimetry; *J. Phys. Chem.*; 1993, **97**, 8786–8792.
- xxxx. Farneth, W.E.; Gorte, R.J.; Methods for Characterizing Zeolite Acidity; *Chem. Rev.*; 1995, **95**, 615–635.
- xxxxi. Barrer, R.M. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; Academic Press.; London, 1978.
- xxxxii. Ahmedzeki, N.S.; Yilmaz, S.; Al-Tabbakh, B.A.; Synthesis and Characterization of Nanocrystalline Zeolite Y.; *ALKEJ*; 2016, **12**, 11.
- xxxxiii. Dewan, S. k; Varma, U.; Malik, S.D.; Synthesis of Enamines from Cycloalkanones and Secondary Cyclic Amines Using K-10 Montmorillonite Clay; *J. Chem. Res. (S)*; 1995, 21–26.
- xxxxiv. Bo, W.; Hongzhu, M.; Factors Affecting the Synthesis of Microsized NaY Zeolite; *Micropor. Mesopor. Mat.*; 1998, **25**, 131–136.
- xxxxv. Holmberg, B.A.; Wang, H.; Norbeck, J.M.; Yan, Y.; Controlling Size and Yield of Zeolite Y Nanocrystals Using Tetramethylammonium Bromide; *Micropor. Mesopor. Mat.*; 2003, **59**, 13–28.
- xxxxvi. Hamadouche, M.; Belkheira, M.; El Abed, D.; Préparation De La N-Cyclohexenylmorpholine: Etude Catalytique Et mécanistique.; *Annales de la Faculté des Sciences et Science de l'Ingénieur*; 2006, **1**, 21–24.
- xxxxvii. Belbachir, M.; Bensaoula, A. Composition and Method for Catalysis Using Bentonites. US Patent 2003/0069446A1. Apr. 10, 2003.
- xxxxviii. Kumar, D.; Schumacher, K.; du Fresne von Hohenesche, C.; Grün, M.; Unger, K.K.; MCM-41, MCM-48 and Related Mesoporous Adsorbents: Their Synthesis and Characterisation; *Colloid surf. A-physicochem. Eng. Asp*; 2001, **187–188**, 109–116.
- xxxxix. Brodie-Linder, N.; Dosseh, G.; Alba-Simonesco, C.; Audonnet, F.; Impéror-Clerc, M.; SBA-15 Synthesis: Are There Lasting Effects of Temperature Change within the First 10min of TEOS Polymerization?; *Mater. Chem. Phys.*; 2008, **108**, 73–81.

Received on February 2, 2021.