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Ultrasound-promoted synthesis of (4 or 5)-aryl-2-aryloyl-(1H)-imidazoles in water

Behzad Khalili[a*] and Mehdi Rimaz[b]

[a]*Department of Chemistry, Faculty of Siences, Guilan University, P.O. Box 41335-1914, Rasht, Iran*
[b]*Department of Chemistry, Payame Noor University, P.O. Box 19395-3697, Tehran, Iran*

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A B S T R A C T

A green and efficient method for the synthesis of (4 or 5)-aryl-2-aryloyl-(1H)-imidazoles via self-condensation reaction of arylglyoxal hydrates in the presence of ammonium acetate using water as solvent under ultrasonic irradiation was reported. The reactions proceeded in high yields and very short reaction time. Introduced procedure is completely ecofriendly and don't need any toxic organic solvent in all performing steps. In addition, we use computational chemistry for acquiring some information about the thermochemistry and geometrical structure of these imidazole derivatives.

1. Introduction

The imidazole heterocyclic ring is present in a wide range of naturally occurring molecules.[1] It is a common scaffold in highly significant biomolecules, including biotin, the essential amino acid histidine, and histamine.[2] The use of imidazoles and their derivatives in chemical processes, especially in pharmaceuticals is becoming increasingly important, because of the possibility of hydrogen bond formation.[3] The biological importance of the imidazole ring system has made it a common structure in numerous synthetic compounds, such as fungicides,[4] herbicides,[4] plant growth regulators[5] and therapeutic agents.[6] There are many methods existed in the literature for the synthesis of imidazoles, such as hetero-cope rearrangement,[7] four component condensation of aryl glyoxals, primary amines and etc.[8]

Ultrasonic irradiation is widely used in organic chemistry especially for shortening of the reaction times and enhancing of the product yields.[9-11] In addition every year many of published papers

* Corresponding author.
E-mail addresses: b.khalili@guilan.ac.ir (B. Khalili)

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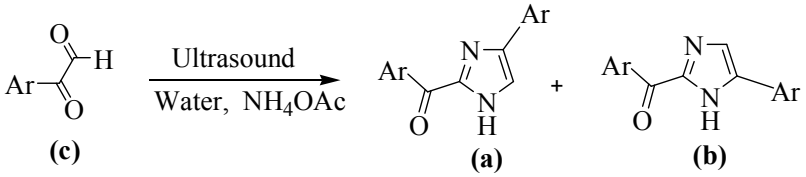
includes application of ultrasonic irradiation which indicates that ultrasonic irradiation has a main role in the synthesis and functionalizing of a wide range of organic compounds.

Many of the publications about the construction of imidazole heterocycles suffer from one or more problems such as long reaction times, problems according to reaction work up and environmental problems due to using organic solvents. Therefore, development of new routes including higher yields, shorter reaction time and milder conditions for these important heterocycles could receive considerable attention.

In this paper, we describe an efficient, environmentally benign, simple and very fast procedure for the synthesis of (4 or 5)-aryl-2-aryloyl-(1*H*)-imidazoles (**a** or **b**) by the reaction of various substituted phenylglyoxal hydrates and ammonium acetate under US irradiation in aqua's media. (Scheme 1)

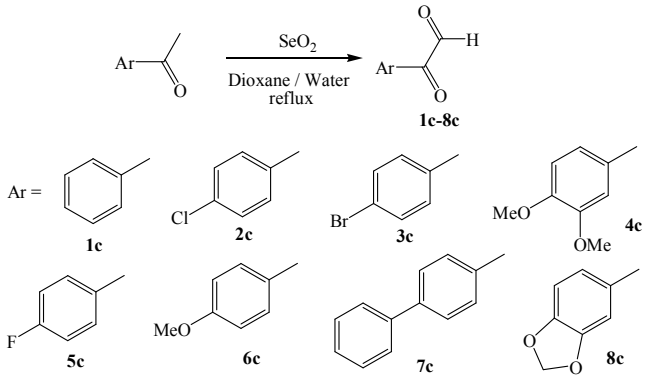


(c) (a) (b)

Scheme 1. Synthesis of (4 or 5)-aryl-2-aryloyl-(1*H*)-imidazole under ultrasonic irradiation

2. Results and Discussion

Recently, glyoxals have made much attention in heterocyclic synthetic chemistry.[12] They can be prepared from the corresponding acetophenones via oxidation by SeO_2 in dioxane at reflux conditions[13] (Scheme 2).



Scheme 2. Synthesis of arylglyoxals

At first, we started with the reaction of phenylglyoxal and ammonium acetate to find optimal reaction conditions. The solvent selection and reaction time optimization were performed (**Table 1**).

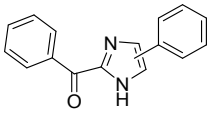
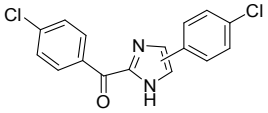
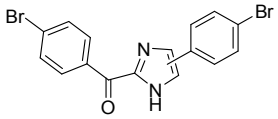
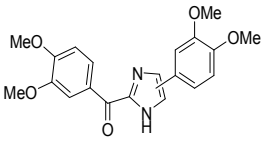
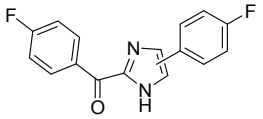
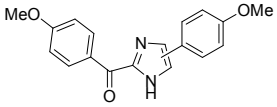
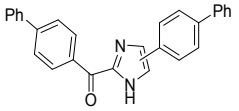
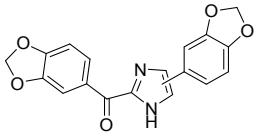
Table 1. Optimization of reaction conditions

Entry	Solvent	Time (min)	Yield (%)
1	Acetonitril	3	65
		4	67
		5	70
2	Ethanol	3	86
		4	94
		5	93
3	Methanol	4	83
4	Water	3	85
		4	95
		5	95
5	Diethyl ether	4	62
6	Chloroform	4	86
7	Dichloromethane	4	79

Thus, we have found that ethanol, methanol, chloroform and water could be suitable solvent for this reaction. Among these solvents because of simplicity of work up and from the ecofriendly point of view, we chose the water. The results of the reaction of phenylglyoxal and ammonium acetate in water for different reaction times presented in **Table 1, entry 4** indicate that optimal time for this reaction promoted by ultrasonic irradiation is four minutes.

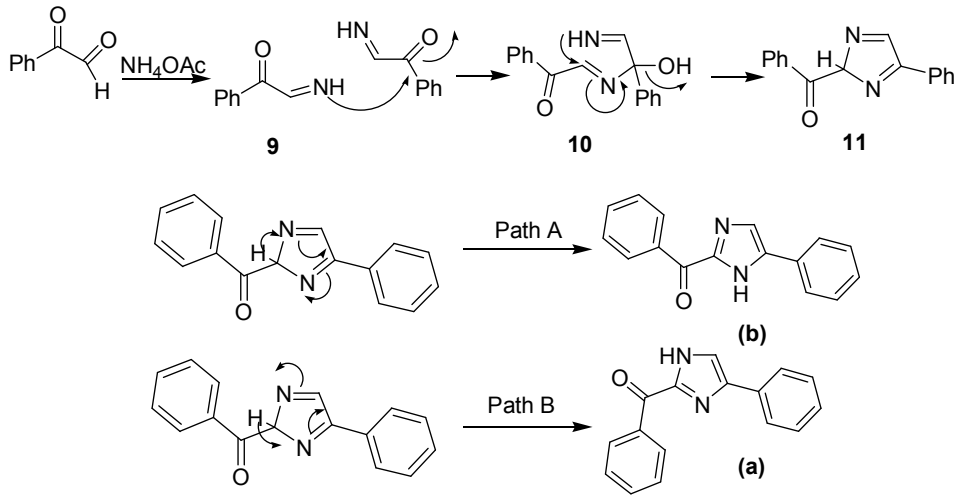
Then the reactions of arylglyoxals **(1c-8c)** with ammonium acetate run in the selected conditions yielded corresponding (4 or 5)-aryl-2-aryloyl-(1*H*)-imidazoles in high yields. The results are summarized in **Table 2** and indicated that application of ultrasounic irradiation causes shorter reaction times and higher yields in comparison with classic conditions.

Table 2. Synthesis of (4 or 5)-aryl-2-aryloyl-(1*H*)-imidazoles

Entry	Aryl glyoxal	Imidazole	Overall Yield (%)(*) [12d]
1	1c	 1a,1b	95 (69)
2	2c	 2a,2b	91 (75)
3	3c	 3a,3b	87 (59)
4	4c	 4a,4b	95 (86)
5	5c	 5a,5b	86 (55)
6	6c	 6a,6b	93 (79)
7	7c	 7a,7b	72 (48)
8	8c	 8a,8b	89 (76)

(*)Reaction carried out without sonication for up to 45 min in water.

The proposed mechanism for this transformation involves an attack of (*in-situ)* generated aldimine **9** onto another aldimine molecule with the elimination of one H_2O molecule from formed intermediate **10** to give compound **11** (**Scheme 3**).[12d]



Scheme 3. Plausible mechanism for imidazole synthesis

According to paths **A** and **B** after a [1,5]-hydrogen shift, compounds (**a**) and (**b**) can be generated respectively. Isomers (**a**) and (**b**) possess very similar properties and therefore had not been separated.

In progress we calculate the optimized geometry and thermochemical data for some of the products,[14,15] and summarized the results in **Table 3**. For the computation was used Density functional theory (B3LYP) and 6-311++G(d,p) basis set incorporated in a computer program Gaussian 03.[16] This basis set was selected for all of the calculations because it contains both diffuse functions and polarized basis set. Diffuse functions are important in the case of some systems particularly where electrons are relatively far from the nucleus including molecules with lone pairs such as molecules with oxygen and nitrogen atoms in the structure.[17-19]

Computed Gibbs free energy of the products gives us important information about stability of both isomers **(a** and **b)** and equilibrium constant between them which can be used for assigning of ^{1}H NMR spectra. Peaks with lower intensity correspond to isomer, which has lower stability or higher Gibbs free energy. Obtained results showed that in all of the products isomer (**a)** has a higher thermodinamical stability than isomer **(b)**, for example $\Delta G = - RTLnK_{eq} = G_a - G_b$ (kcal) in the case of compound **1** is -0.43 that corresponds to the ratio of isomers **1a / 1b** in a mixture (**Table 3**).

Table 3. Selected computed thermochemical data.

Entry	Compound	Eelec (Hartree)		$E_{elec+ZPE}$ (Hartree)		$\Delta G = G_a - G_b$ (kcal/mol)	K_{eq} = [a]/[b]
		Isomer (a)	Isomer (b)	Isomer (a)	Isomer (b)		
1	1	-801.880791	-801.880501	-801.638624	-801.638203	-0.434	2.08
2	2	-1721.126822	-1721.125853	-1720.903868	-1720.902800	-0.87	4.38
3	6	-1030.996464	-1030.996453	-1030.689849	-1030.689651	-0.337	1.77

As shown in **Fig. 1** all the signals in ^{1}H NMR spectra of mixture isomers (**a**) and (**b**) are repeated, respectively. Thus, isomers of 4-methoxyphenyl imidazole derivative (**6a** and **6b**) were assigned based on assumption that the peaks with higher intensity are related to the isomer with lower Gibbs free energy.

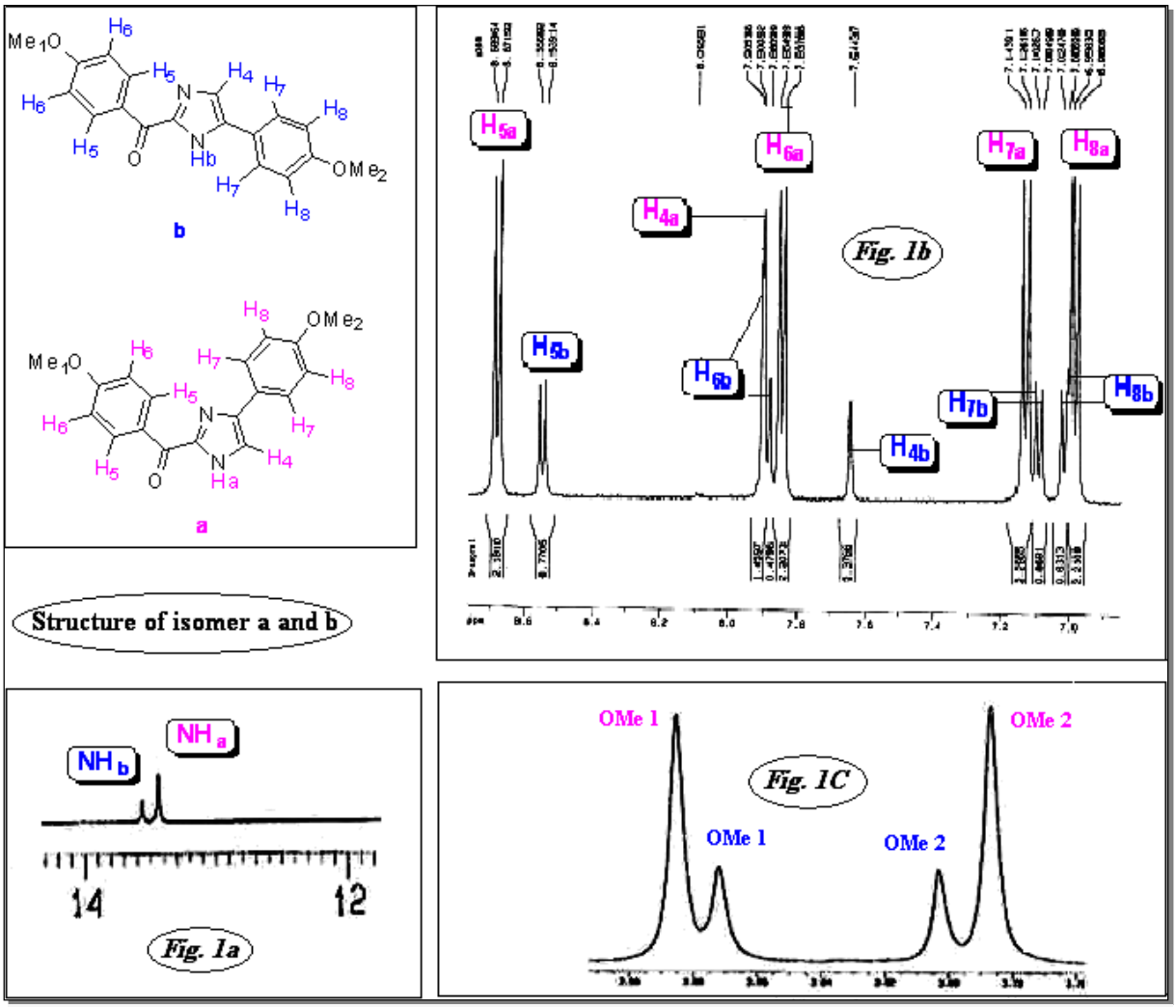


Fig. 1. ^{1}H NMR spectra of 4-Methoxyphenyl-[4-(4-methoxyphenyl)-1*H*-imidazol-2-yl]ketone (**6a**) and 4-Methoxyphenyl-[5-(4-methoxyphenyl)-1*H*-imidazol-2-yl]ketone (**6b**)

3. Conclusions

In conclusion, we have developed a simple, facile and environmentally benign procedure for the synthesis of (4 or 5)-aryl-2-aryloyl-(1*H*)-imidazoles using ultrasonic irradiation in water as solvent. Easy work up, high yields, short reaction times, mild reaction conditions, and green procedure are some of the advantageous of our described procedure.

4. Experimental

All chemicals were purchased from Merck, Aldrich and Fluka companies. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AMX (500 MHz) spectrometer using DMSO-*d6* as solvent and Bandeline sonoplus (GM 2200) used for preparing ultrasonic irradiation.

4.1. General procedure for the synthesis of (4or5)-aryl-2-aryloyl-(1H)-imidazole derivatives:

To arylglyoxal compound (1 mmol) in water (10 mL), was added ammonium acetate (3 mmol), the resultant mixture was irradiated with ultrasound, after 4 minutes the reaction mixture was solidified. The obtained solid was then filtered. The filtrate washed with water (3-10 mL), and the crude material

was purified by crystallization from ethanol. The products were known compounds, and their authenticity was established by their ^{1}H NMR, ^{13}C NMR and IR spectroscopy data compared with that reported in literatures.[12d]

4.2. Computational details:

First of all, we start from search of minima on the potential energy surface for both imidazole isomers (**a** and **b**) at the relative energy range of 10 kcal/Mol by MMFF(Merck Molecular Force Field) level using Spartan software.[20] The most stable conformer of each molecule were optimized using density functional theory (DFT) calculations with a nonlocal hybrid B3LYP (Becke- Lee-Parr) exchange-correlation functional[21,22] employing 6-311++G(d,p) basis set. Energy minimizations and harmonic vibrational calculations were performed on the same theoretical level. Vibration frequencies are calculated in all cases to confirm that all the stationary points correspond to true minima on the potential energy surface. Thermochemical data were extracted from the results of the frequency calculations on the same theoretical level and basis set for all studied molecules. Gaussian 03 program package used for all DFT computations.[16]

4.3. Selected spectroscopic data:

*Phenyl-(5-phenyl-1H-imidazol-2-yl)ketoneand (**1a**) Phenyl-(4-phenyl-1H-imidazol-2-yl)ketone (**1b**) (Table 2 entry1):* a yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.80 (0.25 H, s, NH), 13.63 (1 H, s, NH), 8.60 (2 H, d, J = 7.76 Hz), 8.47 (0.5 H, d J = 7.7 Hz), 8.08 (1 H, s), 7.97 (0.5 H, d, J = 7.95 Hz), 7.94 (2 H, d, J = 7.64 Hz), 7.79 (0.25 H, s), 7.69 (1 H, t, J = 7.1 Hz), 7.66 (0.25 H, t, J = 7.6 Hz), 7.60 (2 H, t, J = 7.6 Hz), 7.57 (0.5 H, t, J = 8.1 Hz), 7.47 (0.5 H, t, J = 7.55 Hz), 7.42 (2 H, t, J = 7.7 Hz), 7.37 (0.25 H, t, J = 7.1 Hz), 7.28 (1 H, t, J = 7.3 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 181.6, 179.2, 146.6, 145.5, 143.7, 137.0, 136.8, 136.6, 134.5, 133.9, 133.7, 131.5, 131.4, 129.8, 129.5, 129.1, 129.0, 128.0, 126.5, 125.7, 119.5. IR (neat, cm^{-1}): 3270, 1621, 1454, 1280, 1164, 906, 771, 687.

4-Fluorophenyl-[5-(4-fluorophenyl)-1*H*-imidazol-2-yl]ketone (**5a**) and 4-Fluorophenyl-[4-(4-fluorophenyl)-1*H*-imidazol-2-yl]ketone (**5b**) *(Table 2 entry 5):* a yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.81 (0.2 H, s, NH), 13.64 (1H, s, NH), 8.70 (2 H, dd, J = 8.64, 5.89Hz), 8.58 (0.4 H, dd, J = 8.07, 5.15Hz), 8.07 (1 H, s), 8.01 (0.4 H, dd, J = 8.16, 5.01Hz), 7.95 (2 H, dd, J =, 8.31 5.74 Hz), 7.76 (0.2 H, s), 7.43 (2 H, t, J = 8.82 Hz), 7.39 (0.4 H, t, J = 8.83 Hz), 7.31 (0.4 H, t, J = 8.74 Hz), 7.25 (2 H, t, J = 8.8 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 179.9, 179.8, 166.9, 164.9, 163.3, 161.4, 145.3, 145.2, 142.8, 134.5, 134.5, 133.3, 131.0, 131.0, 128.7, 128.7, 127.6, 127.6, 119.4, 116.7, 116.4, 116.3, 116.2, 116.2. IR (neat, cm^{-1}): 3282, 3129, 3096, 1623, 1595, 1514, 1450, 1245, 1160, 906, 838, 774, 649.

*4-Methoxyphenyl-[5-(4-methoxyphenyl)-1H-imidazol-2-yl]ketone (**6a**) and 4-Methoxyphenyl-[4-(4-methoxyphenyl)-1H-imidazol-2-yl]ketone (**6b**) (Table 2 entry 6):*: a yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.52 (0.37 H, s, NH), 13.40 (1 H, s, NH), 8.67 (2 H, d, J = 9 Hz), 8.54 (0.74 H, d, J = 8.9 Hz), 7.90 (1 H, s), 7.89 (0.74 H, d, J = 8.16 Hz), 7.84 (2 H, d, J = 8.65 Hz), 7.64 (0.37 H, s), 7.13 (2 H, d, J = 8.9 Hz), 7.09 (0.74 H, d, J = 8.85 Hz), 7.01 (0.74 H, d, J = 8.9 Hz), 6.99 (2 H, d, J = 8.75 Hz) 3.88 (3 H, s), 3.87 (1.11 H, s), 3.80 (1.11 H, s), 3.78 (3 H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 179.9, 179.8, 164.1, 163.9, 161.0, 159.4, 146.4, 145.5, 143.5, 136.2, 133.9, 133.8, 129.7, 129.5, 128.5, 128.0, 127.3, 127.0, 122.1, 117.8, 115.2, 114.9, 114.5, 114.4, 56.4, 56.3, 56.0, 55.9. IR (neat, cm^{-1}): 3266, 1611, 1598, 1455, 1289, 1250, 1163, 1028, 905, 832, 774, 643.

*Benzo[d][1,3]dioxol-5-yl-[5-(benzo[d][1,3]dioxol-5-yl)-1H-imidazol-2 yl]ketone (**8a**) and Benzo[d][1,3]dioxol-5-yl-[4-(benzo[d][1,3]dioxol-5-yl)-1H-imidazol-2-yl]ketone (**8b**) (Table 2 entry 8):* a yellowish green solid, ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.52. (0.3 H, s, NH), 13.44 (1 H, s, NH), 8.45 (1 H, d, J = 8.19 Hz), 8.28 (0.3 H, d, J = 8.13 Hz), 8.16 (1 H, s), 8.01 (0.3 H, s), 7.94 (1 H,

s), 7.68 (0.3 H, s), 7.58 (0.3 H, s), 7.48-7.44 (2.3 H, m), 7.14 (1 H, d, J = 8.24 Hz), 7.10 (0.3 H, d, J = 8.22 Hz), 7.01-6.97 (1.3 H, m) 6.18 (2 H, s), 6.17 (0.6 H, s), 6.07 (0.6 H, s), 6.04 (2 H, s). ^{13}C NMR (125 MHz, DMSO-d_6): δ 182.2, 179.2, 152.4, 148.53, 148.25, 148.1, 147.2, 145.2, 143.4, 130.9, 128.8, 128.4, 128.1, 120.6, 119.2, 118.4, 110.7, 109.6, 109.4, 108.9, 108.7, 106.9, 106.2, 102.8, 102.1, 101.8. IR (neat, cm^{-1}): 3444, 3285, 1622, 1500, 1460, 1245, 1099, 1039, 935, 812, 770, 457.

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