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Aromatization of 1,3,5-Trisubstituted of 4,5-Dihydro-1*H*-Pyrazoles by *In-Situ* Generation of I^+ from Hydrogen Peroxide/Acids/Iodide Potassium or Sodium Systems

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A simple, green and cost-effective protocol was used for the aromatization of 1,3,5-trisubstituted-2-pyrazolines to the corresponding pyrazoles by in situ generation of iodine (I^+) from H_2O_2/AcOH or SSA or oxalic acid / KI or NaI system under thermal condition with moderate to good yields.

Key Words : 1,3,5-Trisubstituted-2-pyrazolines, Pyrazole, Acids, Hydrogen peroxide, Iodide sodium or potassium

Introduction

Pyrazoles and pyrazolines are important five-membered heterocyclic compounds, with a long history of applications in the pharmaceutical and agrochemical industries due to their herbicidal, fungicidal, insecticidal, analgesic, antipyretic, antitumor, antidiabetic, antidepressant, antibacterial and anti-inflammatory properties.[1-8]

There have been many attempts to develop alternative methods for pyrazoles synthesis.[9] The most important methodology for synthesis of pyrazoles is oxidative aromatization of 1,3,5-trisubstituted-2-pyrazoline[10,11] to their corresponding pyrazole.

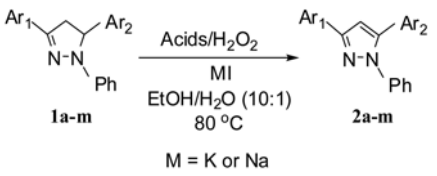
Therefore, oxidative aromatization of pyrazolines with oxidizing reagents should provide an efficient method for the preparation of pyrazole derivatives. Various oxidants have been examined for this process which include: human hemoglobin (HbA)/H_2O_2,[12] molecular oxygen using catalytic amount of *N*-hydroxyphthalimide and cobalt diacetate,[13] I_2O_5 or HIO_3/KBr,[14] nitric oxide,[15] Pd/C/AcOH,[16] $Zr(NO_3)_4$,[17] Co(II)/O_2,[18] iodobenzenediacetate,[19] $Pb(OAc)_4$,[20] MnO_2,[21] K MnO_4[22] and $Ag(NO_3)_2$.[23] However, many of these methods have one or more disadvantages such as high reaction temperature, use of microwave irradiation, prolonged reaction times, use of toxic and costly catalysts, and a need for hazardous and carcinogenic organic solvents. To avoid these drawbacks, the development of more simple, inexpensive, green and efficient protocols are highly demanded.

Result and Discussion

Previously, we developed more convenient and easily available reagents for the oxidative aromatization of 1,3,5-trisubstituted-2-pyrazolines to the corresponding pyrazoles, including 1,3-dibromo-5,5-dimethylhydantoin (DBH),[24,25] trichloroisocyanuric acid,[26,27] *N*-bromosulfonamides,[28-30] *N*-bromosuccinimide/SiO_2,[31] 4-(4-chlorophenyl)-1,2,4-triazole-3,5-dione,[32] poly(*N*,*N*′-dibromobenzene-1,3-disulfonamide-*N*,*N*′-1,2-ethanediyl) (PBBSE),[33] $Bi(NO_3)_4$. $5H_2O$/AcOH,[34] $NaNO_3$ or $NaNO_2$/AcOH[35] and silica-supported poly-1,3-dichloro-5-methyl-5(4-vinylphenyl)hydantoin,[36] Herein, we were prompted to examine the facile oxidation of substituted 1,3,5-trisubstituted-2-pyrazoline **1a-m** to corresponding pyrazoles **2a-m** by H_2O_2/Acids/KI or NaI/EtOH/H_2O as an easily accessible system (Scheme 1).

Acetic acid is an efficient and green acidic source which has been used for different organic transformation.[37-39] However, we preferred hydrogen peroxide as oxidant over other available oxidizing agents since it is cheap, operationally safe, environmentally friendly, easy to handle and produces only water as a by product, which reduces purification requirements.[40-43] The HI is highly toxic and corrosive as harmful as molecular iodine to the environment. The replacement of such reagents by non-toxic and more selective reagents is very desirable and represents an important goal in the context of clean synthesis.[44] We have designed a novel heterogeneous catalytic system to generate electrophilic iodine in situ from easily available KI or NaI as a iodine source and H_2O_2 as an oxidant for the aromatization as a possible alternative to solve the disadvantages describes in the earlier methods.

To find the best catalytic conditions for the aromatization of 1,3,5-trisubstituted-2-pyrazolines, a combination of H_2O_2/AcOH/KI was examined and the results are summarized in (Table 1). As a test case, 1,3,5-triphenyl-2-pyrazolines (**1a**, 1 mmol) was chosen as a model substrate and the reaction was studied by using H_2O_2/AcOH/KI system. We initiated our studies by subjecting catalytic amount of H_2O_2/AcOH/KI in various solvent in various thermal conditions (entry 1-5). Then, this reaction was carried out under solvent-free con-



Scheme 1. Aromatization of 1,3,5-trisubstituted-2-pyrazoline.

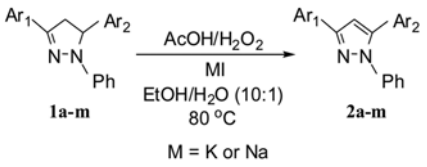
Table 1. Optimization of the reaction conditions[a]

Entry	$AcOH/H_2O_2/KI$ [b]		Solvent	Temperature (°C)	Time (min)	Yield[c] (%)
	I (II)	III				
1	1 (1)	1	EtOH	rt	60	60
2	1 (1)	1	MeOH	rt	60	54
3	1 (1)	1	H_2O	rt	300	42
4	1 (1)	1	EtOH/H_2O 10:1	rt	40	72
5	1 (1)	1	EtOH/H_2O 10:1	80	15	80
6	1 (1)	1	Neat	rt	100	42
7	1 (1)	1	Neat	70	20	-[d]
8	0.3 (0.3)	0.3	EtOH/H_2O 10:1	80	120	60
9	0.6 (0.5)	0.5	EtOH/H_2O 10:1	80	45	68
10	1 (–[e])	1	EtOH/H_2O 10:1	80	40	-[f]
11	1 (1)	1[g]	EtOH/H_2O 10:1	80	15	78
12	1 (1)	1[h]	EtOH/H_2O 10:1	80	50	52

[a]1,3,5-Triphenyl-2-pyrazoline is 1 mmol; [b]AcOH (mL), H_2O_2 (mL) and KI (mmol). [c]Isolated yields. [d]Reaction did not complete and two spots was observed on the TLC. [e]In absence of H_2O_2. [f]No reaction. [g]In the presence of NaI. [h]In the presence of KBr.

dition with H_2O_2/AcOH/KI system under thermal condition (entry 6-7). To effect the reaction, various amounts of KI, AcOH and H_2O_2 were screened in EtOH/H_2O (10:1) at 80 °C (entry 8-9). No reaction was detected when AcOH and KI were used in the absence of H_2O_2 (entry 10).

Then, we screened the reaction condition by taking different oxidants in the presence of H_2O_2/AcOH. Interestingly, almost the same yields were achieved when NaI was used as oxidant (entry 11).



Scheme 2. Aromatization by acetic acid/hydrogen peroxide/iodide potasium or sodium.

Similary, by adopting optimized reaction conditions, the various pyrazoles were prepared by aromatization of 1,3,5-trisubstituted-2-pyrazolines using H_2O_2/AcOH/KI/EtOH/H_2O under thermal condition (Scheme 2, Table 2).

Silica sulfuric acid (SSA) is another eco-friendly, versatile solid acid which has recently found much interest in various organic transformations as a catalyst.[45-55] The salient catalytic activities attributed to silica sulfuric acid have encouraged us, in the second part of the present paper, to use various solvents like CH_3CN, MeOH, H_2O, EtOH, EtOAc, CH_2Cl_2 and CCl_4 used for aromatization of 1,3,5-triphenyl-2-pyrazolines (**1a**) as model reaction, EtOH:H_2O (10:1, v/v) was the solvent of choice as best results in terms of the yield was obtained using SSA (0.02 g), H_2O_2 (1 mL) and KI (0.016 g) for 1 mmol of 1,3,5-triphenyl-2-pyrazolines when the reaction was run at 80 °C for 15 min in 90% yield (Table 3).

Similarly, to illustrate the scope and usefulness of this methodology, a number of reactions were conducted (Scheme

Table 2. Oxidative aromatization of 1,3,5-trisubstituted-4,5-dihydro-1H-pyrazoles **1a-m** (1 mmol) to their corresponding pyrazoles using H_2O_2/AcOH/KI or NaI

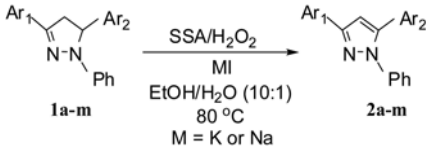
Product	Ar_1	Ar_2	Time (min)	Yield[a] (%)	mp (°C)	
					Found	Reported[b]
2a	Ph	Ph	15 (15)[c]	80 (78)[c]	136-138	138-139
2b	2-naphtyl	2-MeC_6H_4	20	74	142-143	139-141
2c	4-$MeOC_6H_4$	Ph	20	78	138-140	139-140
2d	4-ClC_6H_4	Ph	20	72	141-143	143-145
2e	Ph	4-BrC_6H_4	20 (25)[c]	70 (70)[c]	127-128	129-130
2f	2-naphtyl	4-ClC_6H_4	20	68	134-135	130-133
2g	Ph	3-ClC_6H_4	25	76	90-92	93-95
2h	4-MeC_6H_4	3-MeC_6H_4	30	74	102-103	100-102
2i	4-MeC_6H_4	4-MeC_6H_4	30	68	114-116	115-116
2j	Ph	4-MeC_6H_4	25	72	117-118	115-116
2k	4-ClC_6H_4	4-$MeOC_6H_4$	25	74	113-114	111-1112
2l	4-ClC_6H_4	4-ClC_6H_4	30	68	141-142	138-140
2m	Ph	4-$MeOC_6H_4$	15 (15)[c]	76 (72)[c]	79-80	77-78

[a]Isolated yield. [b]Literature data.[12-36] [c]In the presence of NaI.

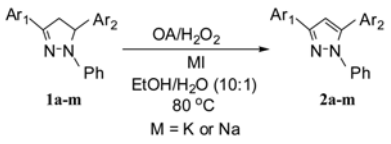
Table 3. Oxidative aromatization of 1,3,5-trisubstituted-4,5-dihydro-1H-pyrazoles **1a-m** (1 mmol) to their corresponding pyrazoles using H_2O_2/SSA/KI or NaI

Product	Ar_1	Ar_2	Time (min)	Yield[a] (%)	mp (°C)	
					Found	Reported[b]
2a	Ph	Ph	15	90	137-139	138-139
2b	2-naphtyl	2-MeC_6H_4	20	82	141-142	139-141
2c	4-$MeOC_6H_4$	Ph	15 (15)[c]	80 (76)[c]	140-141	139-140
2d	4-ClC_6H_4	Ph	15	78	141-143	143-145
2e	Ph	4-BrC_6H_4	15 (15)[c]	78 (80)[c]	129-130	129-130
2f	2-naphtyl	4-ClC_6H_4	20	80	134-135	130-133
2g	Ph	3-ClC_6H_4	20	80	92-93	93-95
2h	4-MeC_6H_4	3-MeC_6H_4	25	82	101-102	100-102
2i	4-MeC_6H_4	4-MeC_6H_4	20	84	114-115	115-116
2j	Ph	4-MeC_6H_4	25	80	116-117	115-116
2k	4-ClC_6H_4	4-$MeOC_6H_4$	20	90	110-112	111-1112
2l	4-ClC_6H_4	4-ClC_6H_4	25	76	140-141	138-140
2m	Ph	4-$MeOC_6H_4$	15 (15)[c]	84 (80)[c]	78-80	77-78

[a]Isolated yield. [b]Literature data.[12-36] [c]In the presence of NaI.



Scheme 3. Aromatization by silica sulfuric acid/hydrogen peroxide/iodide potasium or sodium.



Scheme 4. Aromatization by oxalic acid/hydrogen peroxide/iodide potasium or sodium.

Table 4. Oxidative aromatization of 1,3,5-trisubstituted-4,5-dihydro-1H-pyrazoles **1a-m** (1 mmol) to their corresponding pyrazoles using H_2O_2/OA/KI or NaI

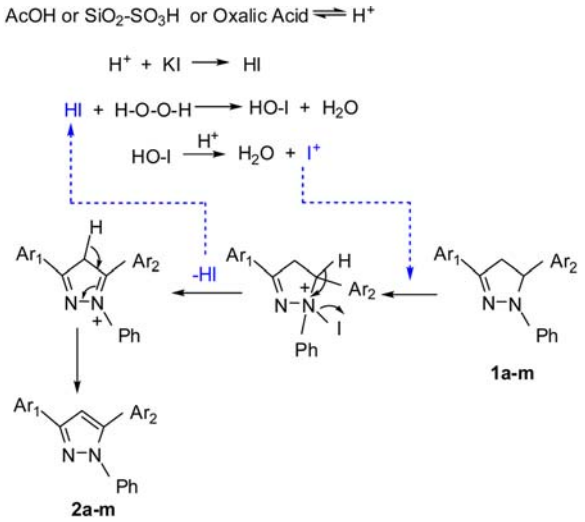
Product	Ar_1	Ar_2	Time (min)	Yield[a] (%)	mp (°C)	
					Found	Reported[b]
2a	Ph	Ph	15	86	138-140	138-139
2b	2-naphtyl	2-MeC_6H_4	20	88	141-142	139-141
2c	4-$MeOC_6H_4$	Ph	15	80	140-141	139-140
2d	4-ClC_6H_4	Ph	20	78	145-146	143-145
2e	Ph	4-BrC_6H_4	10 (15)[c]	74 (72)[c]	129-130	129-130
2f	2-naphtyl	4-ClC_6H_4	15	82	134-135	130-133
2g	Ph	3-ClC_6H_4	20	78	92-93	93-95
2h	4-MeC_6H_4	3-MeC_6H_4	20	75	101-102	100-102
2i	4-MeC_6H_4	4-MeC_6H_4	20	80	113-115	115-116
2j	Ph	4-MeC_6H_4	25	86	114-115	115-116
2k	4-ClC_6H_4	4-$MeOC_6H_4$	20	82	112-113	111-1112
2l	4-ClC_6H_4	4-ClC_6H_4	25	72	139-140	138-140
2m	Ph	4-$MeOC_6H_4$	15 (15)[c]	80 (80)[c]	79-80	77-78

[a]Isolated yield. [b]Literature data.[12-36] [c]In the presence of NaI.

3). The isolated products are summarized in Table 3. A comparison of the experimental results, summarized in Table 2, with those given in Table 3 indicates a general increase in reaction rates and also, in some cases, slight improvement of the yields when silica sulfuric acid (SSA) is used as a catalyst.

Finally, in search for other more robust and efficient acidic catalysts for the aromatization of 1,3,5-trisubstituted-2-pyrazoline, we chose oxalic acid as another solid acid. Oxalic acid (15 mol %) appeared as the most effective catalyst in catalyzing the oxidation of 1,3,5-triphenyl-2-pyrazoline (**1a**) with H_2O_2 (1 mL) and KI (0.016 g) as a model reaction.

Oxalic acid (OA) is the most acidic among the simple dicarboxylic acids having a first pKa value of 1.27. Application of oxalic acid as a catalyst was previously reported for one-pot synthesis of 2-aryl-1-arylmethyl-1*H*-benzimidazoles and 2,4,5-triaryl-1*H*-imidazoles,[56] dealumination of zeolite,[57] and synthesis of quinoxalines.[58]



Scheme 5. Proposed mechanism.

In order to study the generalizability of this procedure, the applicability of the OA/H_2O_2/KI system was then examined for the aromatization of 1,3,5-trisubstituted-2-pyrazoline under the optimized reaction condition (Scheme 4, Table 4).

Regarding the mechanism of the reaction,[24-58] it may be proposed that the liberated H^+ from AcOH or SSA or OA react with KI to generate HI. Then, HI reacts with H_2O_2 to generate HOI. Subsequently, the oxidation may be initiated by I^+ ion. Thus *in situ* generated iodine (I^+) reacts with 1,3,5-trisubstituted-2-pyrazolines to generate species which on elimination of HI to gives a desired product as shown in Scheme 5.

Conclusions

In conclusion, an efficient one-pot procedure was developed for the synthesis of pyrazoles *via* aromatization of 1,3,5-trisubstituted-2-pyrazolines catalyzed by H_2O_2/acids/KI or NaI/EtOH/H_2O system. Mild and simple experimental, green work up, isolation procedure, green aspects avoiding hazardous solvents, use of eco-friendly and less toxic reagents, shorter reaction times and high yields of the products are among the advantages of the present procedure.

Experimental. Solvents, reagents, and chemical materials were obtained from Aldrich (United States), Merck (Germany) and Fluka (Switzerland) chemical companies and purified prior to use. Melting points were determined in open capillary tubes in a Stuart BI Branstead Electrothermal Cat No: IA9200 apparatus and uncorrected. Nuclear magnetic resonance spectra were recorded on JEOL FX 90Q using tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer (KBr).

Typical Experimental Procedure for the Oxidation of 1,3,5-Trisubstituted-2-Pyrazolines.

(i) Aromatization with H_2O_2/AcOH/KI/EtOH/H_2O System. To a stirred solution of 1,3,5-trisubstituted-2-pyrazolines (**1a-m**, 1 mmol) in EtOH/H_2O (10:1, 5 mL), acetic acid (2 mmol), H_2O_2 (10 mmol) and KI (1 mmol) were added at room temperature. Then, the mixture was stirred under refluxing at 80 °C and the progress of the reaction was monitored by TLC using *n*-hexane/EtOAc (2:8). After the completion of the reaction, the solvent was evaporated and washed with water to give the crude products. Then, the residue was recrystallized from EtOH (96%, 5 mL) to afford the pure product (**2a-m**).

(ii) Aromatization with H_2O_2/SSA/KI/EtOH/H_2O System. To a stirred solution of 1,3,5-trisubstituted-2-pyrazolines (**1a-m**, 1 mmol) in EtOH/H_2O (10:1, 5 mL), SSA (0.02 g), H_2O_2 (10 mmol) and KI (1 mmol) were added at room temperature. Then, the mixture was stirred under refluxing at 80 °C and the progress of the reaction was monitored by TLC using *n*-hexane/EtOAc (2:8). After the complete conversion of the substrate, as indicated by TLC analysis, The insoluble silica sulfuric acid was then removed by filtration and washed with EtOH. The solvent was evaporated under reduced pressure to give the products **2a-m**, which were recrystallized from EtOH (96%).

(iii) Aromatization with H_2O_2/OA/KI/EtOH/H_2O System. To a stirred solution of 1,3,5-trisubstituted-2-pyrazolines (**1a-m**, 1 mmol) in EtOH/H_2O (10:1, 5 mL), OA (15 mol %), H_2O_2 (10 mmol) and KI (1 mmol) were added at room temperature. Then, the mixture was stirred under refluxing at 80 °C and the progress of the reaction was monitored by TLC using *n*-hexane/EtOAc (2:8). After the complete conversion of the substrate, Then, H_2O (5 mL) was added to the reaction mixture, and was allowed to stand at room temperature for 3-4 h. The residue of the product formed which were recrystallized from EtOH (96%).

All the isolated products were characterized based on their physical properties and IR, ^{13}C, ^1H-NMR and by direct comparison with authentic materials. All the synthesized compounds gave the expected spectral data. As a representative product, the spectroscopic data for 1,3,5-triphenyl-pyrazole (**2a**) and 5-(2-methylphenyl)-3-(2-naphthyl)-1-phenyl-2-pyrazole (**2b**) are given below.

Selected Spectral Data of the Products.

1,3,5-Triphenyl-Pyrazole (2a). FTIR spectrum (KBr) ν_{max}/cm^{-1}: 3020 (C-H stretching of aromatic ring), 1582 (C=N stretching of pyrazole ring), 1491 (C=C- stretching of aromatic ring), 964 (C-H bending); ^1H-NMR spectrum (90 MHz, $CDCl_3$): δ 6.93 (s, 1H, $CH_{pyrazole}$), 7.21-7.93 (m, 15H, Ar-H); ^{13}C-NMR spectrum (22.5 MHz, $CDCl_3$): δ 95.44, 121.1, 126.06, 128.06, 128.42, 128.71, 129.26, 129.86, 130.16, 131.99 (Ar-CH), 135.99, 138.80, 150.08 (Ar-C), 142.08 ($C=N_{pyrazole}$).

5-(2-Methylphenyl)-3-(2-Naphthyl)-1-Phenyl-2-Pyrazole (2b). FTIR spectrum (KBr) ν_{max}/cm^{-1}: 3010 (C-H stretching of aromatic ring), 1582 (C=N stretching of pyrazole ring), 1491 (C=C- stretching of aromatic ring), 964 (C-H bending); ^1H-NMR spectrum (90 MHz, $CDCl_3$): δ 2.22 (s, 3H, CH_3), 7.80 (s, 1H), 7.16-8.27 (m, 16H, Ar-H); ^{13}C-NMR spectrum (22.5 MHz, $CDCl_3$): δ 19.49 (CH_3), 95.12, 120.86, 123.44, 124.56, 125.54, 126.23, 127.05, 127.69, 128.05, 128.46, 129.21, 129.95, 130.57 (Ar-CH), 131.92, 133.21, 137.71, 138.92, 149.28 (Ar-C), 142.5 ($C=N_{pyrazole}$).

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