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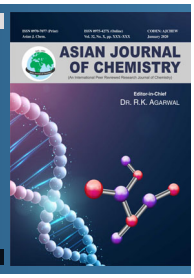

Ultrasound Assisted Synthesis of 1,5-Disubstituted Pyrazole using Cu(I) Catalyst

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A new efficient and convenient approach towards the synthesis of pyrazole is described. The α,β-unsaturated cyanoesters were obtained from substituted benzaldehyde and ethyl cyanoacetate by reported methods. 1,5-Disubstituted pyrazoles were synthesized from α,β-unsaturated cyanoester and phenyl hydrazine using sodium ethoxide as a base in the presence of 10 mol % Cu(I) catalyst in high yields within 75-90 min under ultrasound irradiation at 60 ºC. The reaction rate is enhanced tremendously under ultrasound irradiation as compare to conventional methods with improved yields are recorded.

Keywords: Cyanoester, Cu(I) catalyst, Phenyl hydrazine, Pyrazole, Ultrasound irradiation.

INTRODUCTION

Now-a-days, ultrasonic irradiation technique is widely used in organic synthesis. Ultrasonic irradiation technique reduces the time of reaction. Ultrasonic technique is widely used for simple experimental procedure, increased yield and selectivity of the products. The pyrazole ring emerged as a powerful scaffold used extensively in the design of compounds targeted to block the cell cycle progression in cancer cells. Pyrazole is a five membered heterocyclic compounds having two adjacent nitrogen atoms and exists in natural product [1] and synthetic biologically active compounds [2], such as cyclooxygenase-2 [3], protein kinase [4], and HIV-I reverse transcriptase [5] inhibitors, as well as antibacterial and antifungal compounds [6]. Various substituted pyrazole derivatives act as an antitumor [7], antitubercular, antiviral, antiparasitic, antifungal, antibacterial and insecticidal agents [8-16]. Some pyrazole derivatives show antidiabetic, anti-inflammatory, analgesic and anesthetic properties [17-20]. An I_2-catalyzed metal free procedure has been developed for synthesis of various substituted pyrazole from conjugated aldehydes or ketones and hydrazine in the presence of EtOH [21]. In ambient temperature, different pyrazole derivatives were prepared using Lewis acid catalyst [22]. In the literature survey, pyrazole derivatives were prepared using iron oxide-supported copper oxide nanoparticles [23], 3-aryl-1-phenyl-1*H*-pyrazole-4-carbaldehydes [24], chalcones and hydrazine in EtOH [25], in glacial acetic acid [26], *p*-sulfamyl phenyl hydrazine in EtOH [27], *N*-alkylated tosylhydrazones and terminal alkynes in *t*-BuOK [28], rhodium-catalyzed addition cyclization [29], in MeOH [30], 1,3-diols *via* hydrogen transfer catalysis [31], amberlyst A21 in EtOH [32] and starch solution [33]. A hypervalent iodine catalyzed synthesis of 3-trifluoro methyl pyrazole has been developed *via* trifluoroethylation/cyclization of α,β-alkynic hydrazones [34] under conventional method. But these methods also suffer some drawbacks such as long reaction time, low yield and expensive reagents. Microwave assisted pyrazoles were also reported using formic acid [35], sodium acetate in EtOH [36] and $POCl_3$ in DMF [37].

Thus development of facile and efficient, mild, faster and greener methods is to be required. Therefore, it is essential to produce effective and environmental procedure for synthesis of novel pyrazole derivatives using sodium ethoxide in the presence of nitrato*bis*(triphenyl phosphine)copper(I) as catalyst and EtOH as a solvent.

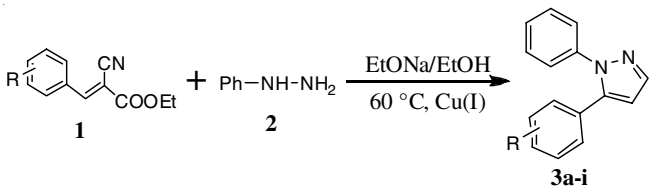
EXPERIMENTAL

The melting points of the compounds were determined in open capillaries and are uncorrected. Purity of the compounds

was checked by TLC aluminum sheets precoated with silica gel. IR spectra were determined on a Shimadzu Miracle 10 ATR instrument. NMR spectra were recorded on a Bruker 500 MHz spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. ^{13}C NMR spectra were recorded on Bruker 125 MHz spectrometer with $CDCl_3$ as the solvent. Column chromatography was conducted on silica gel (70-230 mesh) by using pet-ether:ethyl acetate as 7:3. Ultrasound irradiation was performed in an ultrasonic cleaner with frequency of 33 KHz and a output power of 250 W. Elemental analysis was performed on a CHN elemental analyzer. The reaction flasks were located in the maximum energy area of the cleaner.

Synthesis of nitrato*bis*(triphenyl phosphine)copper(I): A 0.04 mol triphenylphosphine (10.5 g) and $Cu(NO_3)_2{\cdot}2H_2O$ (0.01 mol, 2.45 g) was added to 100 mL hot methanol. Immediately, Cu(II) dissolves and white suspension formed. This suspension was refluxed for 10 min and cooled to ambient temperature. After filtration, washed with ether, ethanol and dried. Recrystallization from methanol gave colourless solid. m.p.: 232 ºC, soluble in common organic solvents. IR (ν_{max}, cm^{-1}): 3047, 2924, 1538, 1479, 1464, 1384, 1295, 1096, 810, 741, 693.

Synthesis of 1,5-disubstituted pyrazole: The α,β-cyanoesters were prepared from ethyl cyanoacetate and aromatic aldehydes by reported method [38]. Pyrazole derivatives were prepared by dissolving α,β-cyanoesters (5 mmol) and phenyl hydrazone (5 mmol) in alcoholic sodium ethoxide (0.5 g EtONa in 20 mL ethanol) in a 100 mL conical flask. Then $Cu(PPh_3)_2{\cdot}NO_3$ catalyst (10 mol % *i.e*. 31 mg) was added in the reaction mixture. The mixture was irradiated in the water bath of an ultrasonic cleaner at 60 ºC for the period. After completion of the reaction, the mixture was poured in ice water and filtered. The crude product was purified using column chromatography (silica gel 70 % peteroleum ether/30 % EtOAc) to afford pure compound (**Scheme-I**). Details of the synthesis of substituted pyrazoles under ultrasonic irradiation are summarized in Table-1.



Scheme-I: Synthesis of 1,5-disubstituted pyrazole

Spectral data of compounds 3a-i

5-(4-Methoxyphenyl)-1-phenyl-1*H*-pyrazole (3a): Brown solid, TLC R_f = 0.77 (PE:EtOAc = 10:2); IR (KBr, ν_{max}, cm^{-1}): 1595, 1496, 1242, 1126, 941, 819, 650; ^1H NMR (500 MHz, $CDCl_3$) δ ppm: 3.88 (s, 3H), 6.86 (d, *J* = 7 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.36 (m, 1H) 7.60 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 160.0, 146.0, 144.9, 142.2, 137.4, 129.2, 128.1, 127.5, 119.8, 114.3, 112.6, 55.3. Anal. calcd. (%) for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found (%): C, 76.80; H, 5.62; N, 11.18.

5-(4-Nitrophenyl)-1-phenyl-1*H*-pyrazole (3b): Brown solid, TLC R_f = 0.71 (PE:EtOAc = 10:2); IR (KBr, ν_{max}, cm^{-1}): 1585, 1494, 1340, 1261, 1143, 1068, 748, 667; ^1H NMR (500 MHz, $CDCl_3$) δ 6.94 (d, *J* = 7 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 8.22 (d, *J* = 8.5 Hz, 2H), 7.31 (m, 1H) 7.77 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 144.6, 137.3, 135.3, 130.2, 129.3, 128.6, 126.4, 120.1, 119.8, 113.0, 112.5. Anal. calcd. (%) for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84. Found (%): C, 67.95; H, 4.16; N, 15.81.

1,5-Diphenyl-1*H*-pyrazole (3c): Brown solid, TLC R_f = 0.71 (PE:EtOAc = 10:2); IR (KBr, ν_{max}, cm^{-1}): 1591, 1494, 1442, 1257, 1134, 1066, 927, 748, 634; ^1H NMR (500 MHz, $CDCl_3$) δ ppm: 6.86 (d, *J* = 7 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.45 (m, 1H), 7.59 (m, 1H) 7.63 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 144.6, 137.3, 135.3, 133.7, 129.5, 128.6, 126.4, 120.1, 119.8, 113.0, 112.7. Anal. calcd. (%) for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found (%): C, 81.81; H, 5.50; N, 12.69.

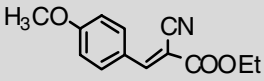
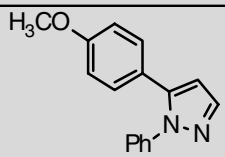
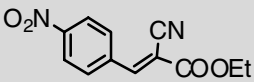
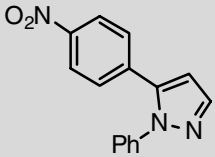
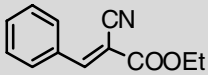
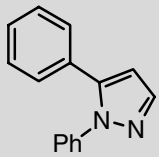
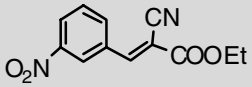
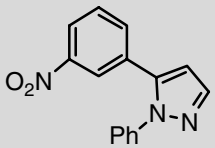
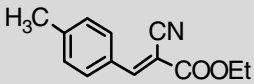
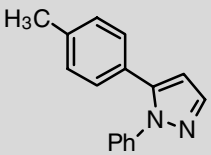
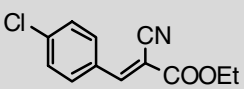
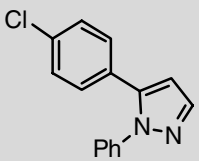
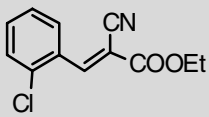
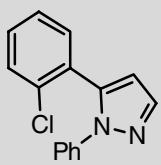
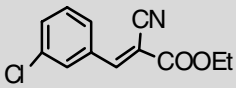
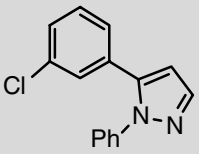
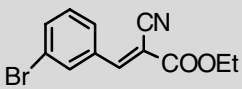
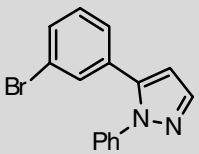
5-(3-Nitrophenyl)-1-phenyl-1*H*-pyrazole (3d): Brick red solid, TLC R_f = 0.63 (PE:EtOAc = 10:2); IR (KBr, ν_{max}, cm^{-1}): 1595, 1568, 1512, 1489, 1320, 1265, 1143, 1107, 848, 750, 644; ^1H NMR (500 MHz, $CDCl_3$) δ ppm: 6.91 (d, *J* = 7 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.50 (m, 1H), 7.53 (m, 1H), 8.09 (d, 8.5 Hz, 1H) 8.10 (d, *J* = 8.5 Hz, 1H), 8.11 (s, 1H) 8.11 (d, *J* = 7 Hz, 1H), ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 148.7, 143.8, 137.3, 133.8, 131.4, 130.1, 129.5, 129.4, 129.0, 128.5, 122.5, 120.9, 112.9. Anal. calcd. (%) for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84. Found (%): C, 67.91; H, 4.17; N, 15.86.

1-Phenyl-5-(*p*-tolyl)-1*H*-pyrazole (3e): Orange solid, TLC R_f = 0.66 (PE:EtOAc = 10:2); IR (KBr, ν_{max}, cm^{-1}): 1595, 1494, 1442, 1255, 1132, 1070, 1049, 815, 669; ^1H NMR (500 MHz, $CDCl_3$) δ ppm: 2.43 (s, 3H), 6.85 (d, *J* = 7 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.26 (m, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.53 (d *J* = 8.5 Hz, 2H) 7.99 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 144.8, 138.4, 137.5, 132.5, 130.2, 129.9, 127.3, 126.1, 125.6, 113.8, 112.7, 21.7. Anal. calcd. (%) for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found (%): C, 82.04; H, 6.03; N, 11.93.

5-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazole (3f): Brown solid, TLC R_f = 0.76 (PE:EtOAc = 10:2); IR (KBr, ν_{max}, cm^{-1}): 1598, 1519, 1487, 1442, 1257, 1134, 1082, 914, 819, 747, 693; ^1H NMR (500 MHz, $CDCl_3$) δ ppm: 6.88 (d, *J* = 7 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.27 (m, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.33 (d *J* = 8.5 Hz, 2H) 7.58 (d, *J* = 8.5 Hz, 2H) 7.61 (d, *J* = 7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 144.8, 138.4, 137.5, 132.5, 130.2, 129.9, 127.3, 126.1, 125.6, 113.8, 112.7, 21.7. Anal. calcd. (%) for $C_{15}H_{11}N_2Cl$: C, 70.73; H, 4.35; N, 11.00. Found (%): C, 70.70; H, 4.37; N, 10.98.

5-(2-Chlorophenyl)-1-phenyl-1*H*-pyrazole (3g): Brown solid, TLC R_f = 0.79 (PE:EtOAc = 10:2); IR (KBr, ν_{max}, cm^{-1}): 1600, 1494, 1471, 1438, 1255, 1138, 1049, 1029, 692; ^1H NMR (500 MHz, $CDCl_3$) δ ppm: 6.88 (d, *J* = 7 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.23 (m, 1H), 7.25 (m, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.32 (d *J* = 8.5 Hz, 2H) 8.06 (d, *J* = 7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 144.3, 135.2, 132.7, 131.0, 130.4, 129.2, 128.0, 127.2, 126.6, 125.8, 118.4, 113.1, 112.8. Anal. calcd. (%) for $C_{15}H_{11}N_2Cl$: C, 70.73; H, 4.35; N, 11.00. Found (%): C, 70.71; H, 4.34; N, 11.02.

TABLE-1
PREPARATION OF SUBSTITUTED PYRAZOLES UNDER ULTRASOUND IRRADIATION

Compound	Substrate	Product	Time (min)	m.p. (°C)	Yield (%)
3a			90	116-117	97
3b			75	144-146	96
3c			85	158-160	95
3d			75	118-119	97
3e			90	96-98	92
3f			75	130-131	93
3g			90	80-82	92
3h			80	126-127	94
3i			75	146-147	95

5-(3-Chlorophenyl)-1-phenyl-1*H*-pyrazole (3h): Brown solid, TLC R_f = 0.79 (PE:EtOAc = 10:2); IR (KBr, ν_{max}, cm^{-1}): 1578, 1514, 1477, 1253, 1141, 1074, 921, 885, 792, 632; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 6.89 (d, *J* = 7 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.27 (m, 1H), 7.30 (m, 1H), 7.48 (d, *J* = 8.5 Hz, 2H) 7.59 (d, *J* = 7 Hz, 1H), 7.66 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 144.2, 137.2, 135.3, 134.6, 129.8, 129.3, 129.1, 128.2, 125.7, 124.3, 120.5, 112.8. Anal. calcd. (%) for $C_{15}H_{11}N_2Cl$: C, 70.73; H, 4.35; N, 11.00. Found (%): C, 70.74; H, 4.33; N, 11.02.

5-(3-Bromophenyl)-1-phenyl-1*H*-pyrazole (3i): Orange solid, TLC R_f = 0.81 (PE:EtOAc = 10:2); IR (KBr, ν_{max}, cm^{-1}): 1593, 1577, 1514, 1473, 1446, 1253, 1141, 1074, 923, 885, 788, 748; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 7.10 (d, *J* = 7 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.40 (m, 1H), 7.52 (m, *J* = 8.5 Hz, 1H) 7.56 (d, *J* = 7 Hz, 1H), 7.81 (s, 1H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ ppm: 144.2, 137.4, 135.2, 131.1, 131.0, 130.1, 129.5, 128.7, 124.8, 122.8, 120.5, 118.6, 112.8. Anal. calcd. (%) for $C_{15}H_{11}N_2Br$: C, 60.22; H, 3.71; N, 9.36. Found (%): C, 60.25; H, 3.70; N, 9.34.

RESULTS AND DISCUSSION

The effect of reaction conditions on the formation of 1,5-disubstituted pyrazole under ultrasound irradiation is summarized in Table-2. The reaction was initiated by the nucleophilic addition of phenyl hydrazine to α,β-unsaturated cyanoester resulting in different intermediates to form pyrazole **3**. Inspired by this result, a variety of reaction conditions in order to optimize the catalytic process was explored. When water was used as the solvent, product **3b** was not detected (Table-2, entry 1).

TABLE-2
SCREENING OF SOLVENT FOR SYNTHESIS OF COMPOUND **3b** UNDER ULTRASOUND IRRADIATION

Entry	Catalyst	Base	Solvent	Temp. (°)	Yield (%)
1	Catalyst free	EtONa	H_2O	60	–
2	$Cu(PPh_3)_2NO_3$	LiOH	EtOH	60	48
3	$Cu(PPh_3)_2NO_3$	K_2CO_3	EtOH	60	30
4	$Cu(PPh_3)_2NO_3$	EtONa	DMF	60	55
5	$Cu(PPh_3)_2NO_3$	EtONa	DCM	60	64
6	$Cu(PPh_3)_2NO_3$	EtONa	DMSO	60	62
7	$Cu(PPh_3)_2NO_3$	EtONa	CH_3CN	60	65
8	$Cu(PPh_3)_2NO_3$	EtONa	EtOH	60	96
9	$Cu(PPh_3)_2NO_3$	EtONa	EtOH	RT	22
10	$Cu(PPh_3)_2NO_3$	EtONa	EtOH	90	96

α,β-Unsaturated cyanoesters derived from benzaldehyde featuring electron-donating or withdrawing substituents in an aromatic ring gave the corresponding pyrazole derivatives in good to high yields, However, a lower yield was observed with bases such as LiOH and K_2CO_3 (Table-2, entry 2,3). Next, a variety of different solvents were also evaluated, however, use of DMF, DMSO and CH_3CN resulted in poor yields of compound **3b** (Table-2, entries 4-7). A controlled experiment confirmed that $Cu(PPh_3)_2{\cdot}NO_3$ catalyst was essential for the formation of pyrazoles. Notably, a reaction proceeded smoothly produced compound **3b** in 96% yield (Table-2, entry 8). To study the effect of temperature, we have performed the reaction at room temperature but reaction proceeded in low yield (Table-2, entry 9). To increase the reaction temperature upto 60 ºC, reaction was proceeded in excellent yield and above 60 ºC there was no effect on reaction time and yield (Table-2, entry-10). Polar aprotic solvents such as DMF, DMSO, DCM and CH_3CN forms complex with Cu(I) catalyst, so reaction rate went to be decrease.

In this work, during the reaction the oxidative transformations include the formation of C-N bond. Copper coordinates easily to heteroatoms and to π-bond and C-N cross coupling reactions were obtained. It is cleared that an oxidative addition and reductive elimination of Cu(I) can occurred, so it is possible that Cu(I) undergoes steps similar to Pd(0) in cross coupling reactions [39].

Conclusion

In the present investigation, a series of novel substituted pyrazole ring derivatives have been synthesized by using $Cu(PPh_3)_2NO_3$ as a catalyst under ultrasound irradiation. The short reaction time, easy workup and high yields made this protocol efficient by using $Cu(PPh_3)_2NO_3$ catalyst.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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