



PDB Moderated Synthesis of Some 2-Substituted Aryl-5-Phenyl-1,3,4-Oxadiazole/5-Substituted Aryl-2-(Furan-2-yl)-1,3,4-Oxadiazole as Potential Pesticides

Akhilesh Kumar^{1*}, Arvind Kumar Pandey¹, Kamal Pratap Singh¹,
Nawseen Fatima Ansari¹, Shailendra Tiwari¹ and Manoj Kumar Shrivash²

1. Department of Chemistry, University of Allahabad, Allahabad 211002, **INDIA**

2. Centre of Biomedical Research, SGP GIMS, Lucknow 226014, **INDIA**

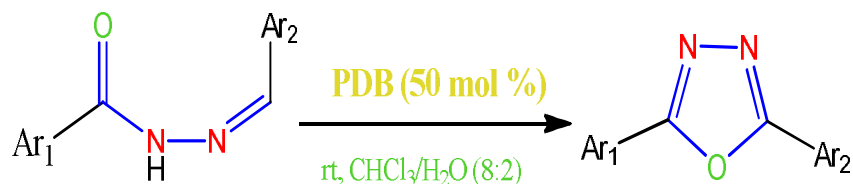
Email: aks.modanwal@gmail.com

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ABSTRACT

Novel, efficient and operationally improved method has been developed for one pot synthesis of several 2-substituted aryl-5-phenyl-1, 3, 4-oxadiazole / 5-aryl-2-(furan-2-yl)-1, 3, 4-oxadiazole. 1, 3, 4-Oxadiazole derivatives were prepared by stirring N^1 -aroyl- N^2 -arylidene hydrazines/ N^1 -aroyl- N^2 -furylidene hydrazines with PDB in $CHCl_3/H_2O$ (8:2) for 13-15 minute at room temperature. The reaction takes place smoothly and all the synthesized compounds were purified by column chromatography and then characterized by spectral analysis (1H NMR, ^{13}C NMR and Mass). All these compounds were screened for their antibacterial activity against two Gram-positive bacteria viz. *Bacillus subtilis* and *Bacillus pumilus* and three Gram-negative bacteria viz. *Salmonella typhi*, *Escherichia coli* and *Klebsiella pneumonia* antifungal activity against *Aspergillus niger*, *Pyricularia oryzae* and *Aspergillus fumigatus* and herbicidal activity against *Echinochloa oryzicola*, *Echinochloa crus-galli*, *Oryza sativa* and *Glycine max*.

Graphical Abstract:



Synthesis of 2,5 di-substituted 1,3,4-oxadiazole using PDB a mild catalyst.

Keywords: Chloroform; 4-oxadiazoles; PDB; pesticidal activity; Schiff's bases.

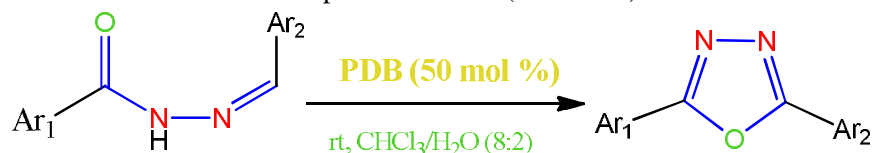
INTRODUCTION

Oxadiazole nucleus is considered to be highly efficient heterocyclic scaffold in world of agrochemical and pharmaceutical industry as Biozole [1] or 1,3,4-oxadiazole have efficient properties and it's their derivatives broadly used as antimicrobial [2], anti-inflammatory [3], analgesic [4], antihypertensive [5], anticonvulsant [6], antitumor activity [7], anticoagulant [8], muscle relaxant [9], antiHIV [10],

angiogenesis inhibitors [11], hypoglycemic [12], genotoxic [13], tyrosinase inhibitors [14] and plant growth regulators [15]. Its derivatives also have vibrant and exciting research attraction due to vast application in optoelectronic field of material [16-19].

Literature survey revealed that 1,3,4-oxadiazole ring has been synthesized using various conventional procedures like oxidative cyclisation [20] of corresponding derivative of aryl hydrazones /semicarbazone/thiosemicarbazide via various catalyst like Cu(II) [21], Pd-Catalyst [22], mercury salts [23], ceric ammonium nitrate [24], POCl₃ [25], Iodine based catalyst [26]. But these catalysts are hazardous and corrosive in nature and required a lot of safety protocols. Some irradiation technique [27,28] has been also used for the synthesis of oxadiazole motif but scale up production is difficult by irradiation method which is major drawback of the protocol.

Bearing the above drawbacks in mind we designed a novel strategy, were mild oxidizing polymeric DABCO bromine salt (PDB) has been used for the synthesis of target nuclei. This efficiently transform organic Schiff's base to important boistere 2,5-disubstituted 1,3,5-oxadiazole. Some of the elegant features of PDB are stable towards light, air or water, it is a non-corrosive, homogeneous stable amorphous yellow solid with no hygroscopic nature, having selective catalytic properties. It is a source of bromine having structure made up of alternating 1,4-diazabicyclo [2,2,2]octane and bromonium, with Br₃⁻ counter ion. After careful literature investigations we observed that tribromide based organic salt are very useful in many oxidative processes like benzothiazoles synthesis, benzyl cyanides coupling, dithioacetal's deprotection, bromination of phenols and aryl amines, and in synthesis of carbonyl compounds, disulfides, sulfoxides [29-33]. With this in mind, we set out to study the reactivity of the PDB system under biphasic reaction condition and plan to explore the utility of PDB for the synthesis of oxadiazole derivatives with an atom economy, non-corrosive and eco-compatible fashion (Scheme 1).



Scheme 1. Synthesis of 2,5 di-substituted 1,3,4-oxadiazole using PDB a mild catalyst.

MATERIALS AND METHODS

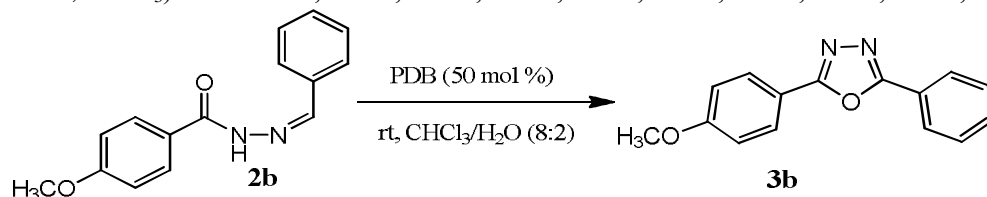
Melting points were taken in Riechart thermover instrument and are uncorrected. The IR spectra were recorded on Perkin Elmer RXI spectrometer in KBr, ¹H NMR on Bruker DRX 400 MHz using tetramethylsilane (TMS) as the internal standard and DMSO-d₆/CDCl₃ as solvent. The purity of the compounds was checked by thin layer chromatography (TLC).

Synthesis of Compounds

N¹-aroyl-N²-arylidene hydrazines (2b, R = 4-OCH₃): It was prepared according to the known method [34]. A mixture of 4-methoxybenzohydrazide (0.02mol) and benzaldehyde (0.02mol) was refluxed in methanol using glacial CH₃COOH as a catalyst for 3-4h. The mixture was cooled and poured in to water. The solid product was obtained, which was filtered, washed and recrystallized from aqueous ethanol.

4-substituted aryl-5-phenyl-1,3,4-oxadiazole (3b, R = 4-OCH₃): It was prepared by N¹-4-methoxy benzoyl-N²-benzylidene hydrazine Schiff's base (1mmol) stirred with PDB (0.55mmol) in CHCl₃/H₂O (8:2) for 13-15 min. The reaction progressed smoothly and cleanly under mild reaction conditions without any parallel reactions were observed (Scheme 2). The crude products thus obtained were purified column chromatography. The m.p. of the product were checked and found 160⁰C, yield 93%, White solid, m.p.151 °C; IR (KBr): 3012, 2954, 2840, 1617, 1502, 1316, 1264, 1180, 1075, 831, 742, 681; ¹H NMR (400 MHz,

CDCl_3): $\delta = 8.12-8.09$ (m, 2H), 8.09-8.06 (m, 2H), 7.53-7.49 (m, 3H), 7.05-7.02 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 164.54, 164.0, 162.3, 131.3, 129.2, 128.5, 126.8, 124.2, 116.3, 114.4, 55.5$.



Scheme 2. Synthesis of 2-(4-methoxyphenyl)-5-phenyl-1,3,4-oxadiazole (3b) using PDB a mild catalyst

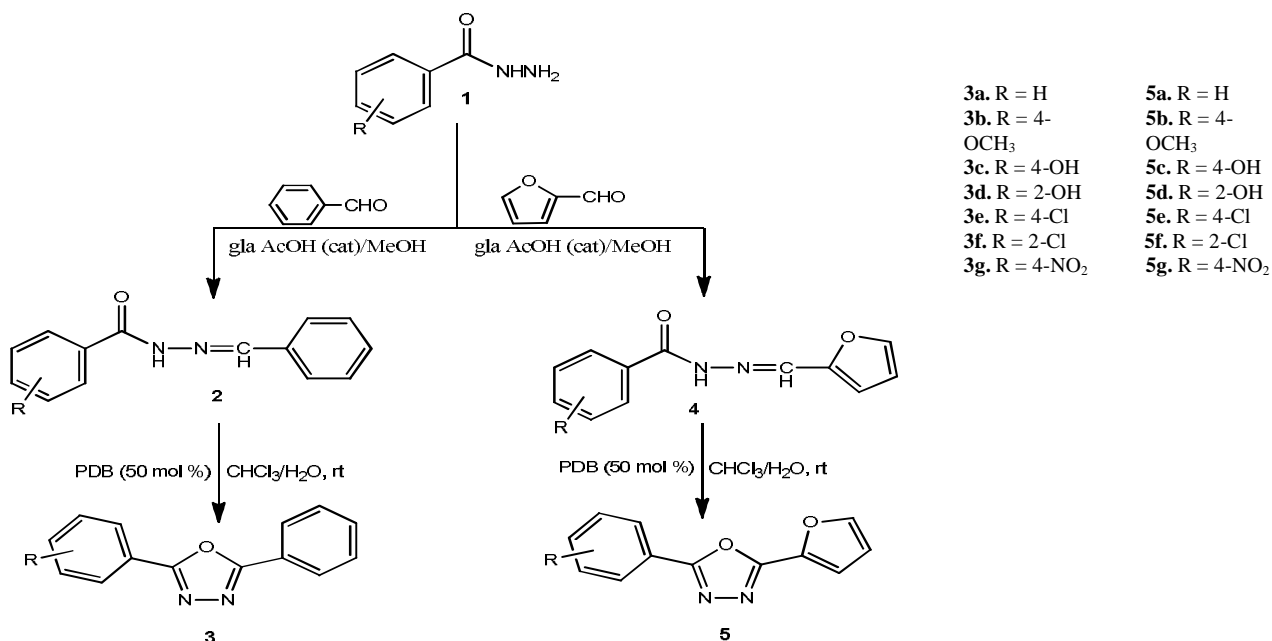
Other such compounds were also prepared in a similar way and their characterization data are given in Table 3.

2,5-Diphenyl-1,3,4-oxadiazole (3a): White solid, m.p. 190 °C; IR (KBr): 3055, 3006, 2998, 1602, 1550, 1484, 1442, 1266, 1066, 785, 711, 684; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.15-8.12$ (m, 4H), 7.53-7.52 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 164.4, 131.7, 129.1, 126.8, 123.8$.

2-(2-Chlorophenyl)-5-phenyl-1,3,4-oxadiazole (3f): White solid, m.p. 197 °C; IR (KBr): 3066, 2920, 1594, 1549, 1492, 1455, 1435, 1088, 778, 731, 688 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.16-8.16$ (m, 2H), 8.11 (dd, $J = 7.5, 1.6$ Hz, 1H), 7.58-7.41 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 165.2, 163.1, 133.1, 132.3, 131.9, 131.3, 131.3, 129.2, 127.1, 127.3, 123.6, 23.2$

2-(4-Nitrophenyl)-5-phenyl-1,3,4-oxadiazole (3g): Yellow solid, m.p. 225°C; IR (KBr): 3221, 3074, 2845, 1608, 1554, 1515, 1340, 1076, 858, 718, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.41$ (d, $J = 8.8$ Hz, 2H), 8.36 (d, $J = 8.8$ Hz, 2H), 8.18-8.16 (m, 2H), 7.61-7.56 (m, 3H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): $\delta = 165.3, 163.2, 149.5, 132.7, 129.8, 129.3, 128.5, 127.3, 125.0, 123.5$.

2-(Furan-2-yl)-5-phenyl-1,3,4-oxadiazole (5a): White solid, m.p. 105 °C IR (KBr): 3142, 3112, 2920, 1635, 1521, 1492, 1452, 1174, 1080, 897, 776, 688; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.12-8.08$ (m, 2H), 7.68-7.65 (m, 1H), 7.55-7.50 (m, 3H), 7.24 (d, $J = 3.2$ Hz, 1H), 6.65 (dd, $J = 3.1, 1.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 163.6, 157.5, 145.8, 139.4, 131.7, 129.2, 127.3, 123.6, 114.2, 112.5$.



Scheme 2.

RESULTS AND DISCUSSION

After having reaction condition in hand we then tried to shape the methodology with better reaction optimization for the synthesis of useful 1,3,4-oxadiazoles from starting materials, N¹-4-hydroxy benzoyl-N²-benzylidene hydrazine Schiff's base (1.0mmol) stirred with 50mol% of different similar type catalyst (Chloramine T, DMP, DIB, PhI(OAc)₂, PDB) in CHCl₃/H₂O (8:2) for 13min at room temperature among these catalyst, PDB was best reagent observed (table 1, entry 10) During the course of optimization of reaction under water free conditions reactivity is very slow is analysed while under biphasic conditions, water as assumes the role of Bronsted base which enhanced reactivity of PDB in order to further improve the yield of the reaction, optimization of the reaction with a variety of solvents under biphasic (EtOH/H₂O, DCM/H₂O, DMSO/H₂O, CHCl₃/H₂O, Toluene/H₂O, Hexane/H₂O, CCl₄/H₂O) and examined the results. Solvent optimization shows that CHCl₃/H₂O in reflux is the best reaction condition (Table 1, entry 10).

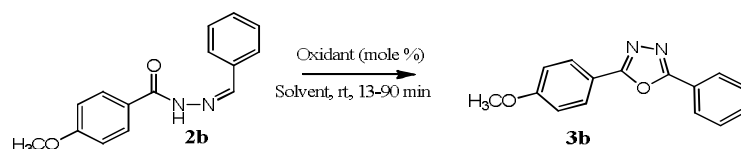
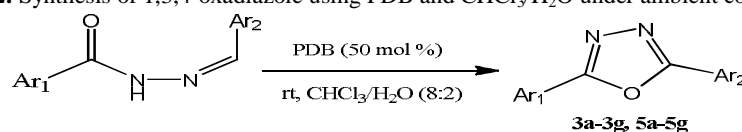


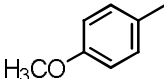
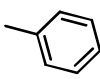
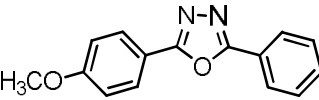
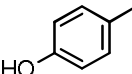
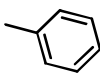
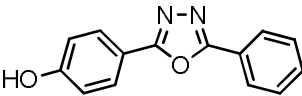
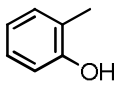
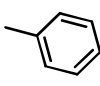
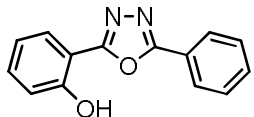
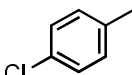
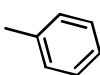
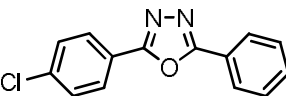
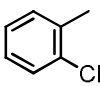
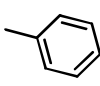
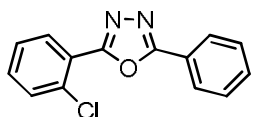
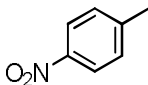
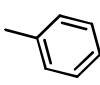
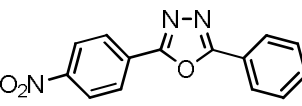
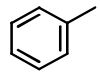

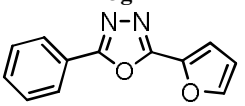
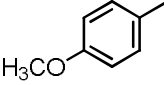

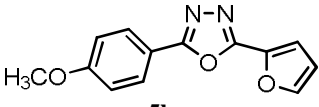
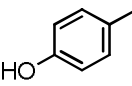

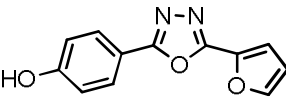
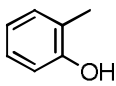

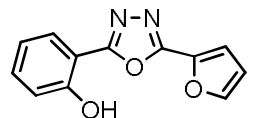
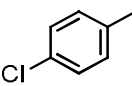

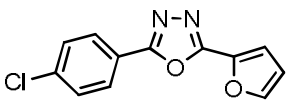
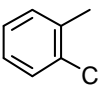

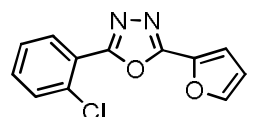
Table 1: Synthesis of 1,3,4 oxadiazole derivatives under various conditions.

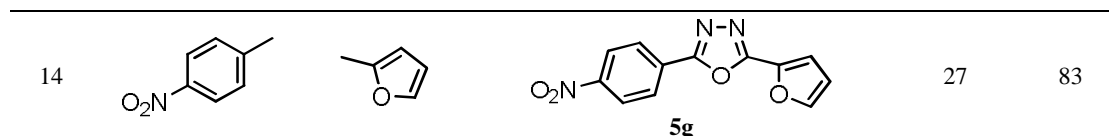
| Entry | Reagent | Solvent | Time (min) | Yield (%) |
|-----------|------------------------------------|---|------------|-----------|
| 1 | Chloramin T (50 mol %) | CHCl ₃ /H ₂ O | 13 | 48 |
| 2 | DMP (50 mol %) | CHCl ₃ /H ₂ O | 13 | 45 |
| 3 | DIB (50 mol %) | CHCl ₃ /H ₂ O | 13 | 43 |
| 4 | PhI (OAc) ₂ (50 mol %) | CHCl ₃ /H ₂ O | 13 | 50 |
| 5 | PDB (50 mol %) | C ₂ H ₅ OH/H ₂ O | 13 | 42 |
| 6 | PDB (50 mol %) | DCM/H ₂ O | 13 | 47 |
| 7 | PDB (50 mol %) | DMSO/H ₂ O | 13 | 48 |
| 8 | PDB (50 mol %) | CHCl ₃ | 90 | 11 |
| 9 | PDB (40 mol %) | CHCl ₃ /H ₂ O | 20 | 35 |
| 10 | PDB (50 mol %) | CHCl₃/H₂O | 13 | 93 |
| 11 | PDB (60 mol %) | CHCl ₃ /H ₂ O | 13 | 81 |
| 12 | PDB (50 mol %) | Hexane/H ₂ O | 13 | 45 |
| 13 | PDB (50 mol %) | Toluene/H ₂ O | 13 | 40 |
| 14 | PDB (50 mol %) | CCl ₄ /H ₂ O | 13 | 45 |

Table 2: Synthesis of 1,3,4-oxadiazole using PDB and CHCl₃/H₂O under ambient conditions.



| Entry | Ar ₁ | Ar ₂ | Product 2 | Time (min) | Yield (%) |
|-------|-----------------|-----------------|-----------|------------|-----------|
| 1 | | | | 15 | 85 |

| | | | | | |
|----|---|---|---|----|----|
| 2 |  |  |  3b | 13 | 93 |
| 3 |  |  |  3c | 14 | 91 |
| 4 |  |  |  3d | 15 | 88 |
| 5 |  |  |  3e | 20 | 88 |
| 6 |  |  |  3f | 21 | 87 |
| 7 |  |  |  3g | 25 | 84 |
| 8 |  |  |  5a | 16 | 86 |
| 9 |  |  |  5b | 12 | 92 |
| 10 |  |  |  5c | 13 | 91 |
| 11 |  |  |  5d | 15 | 90 |
| 12 |  |  |  5e | 20 | 90 |
| 13 |  |  |  5f | 19 | 88 |



The Variety of Schiff's bases have been employed in order to obtain library of compounds. With these reaction conditions in hand the structure activity relationship was fully investigated. It has been observed that compounds bearing electron donating groups gave products with marginally greater yields and those with electron withdrawing groups gave corresponding products with lower yield (Table 2).

Table 3. Characterization data of compounds 3a-g and 5a-g.

| Compounds | Molecular formula | m.p. °C | Found (%) calcd. | | |
|-----------|--|---------|------------------|----------------|------------------|
| | | | C | H | N |
| 3a | C ₁₄ H ₁₀ N ₂ O | 190 | 75.66 (75.86) | 4.54 (4.68) | 12.60 (12.77) |
| 3b | C ₁₅ H ₁₂ N ₂ O ₂ | 151 | 71.42 (71.27) | 4.79 (4.65) | 11.10 (11.07) |
| 3c | C ₁₄ H ₁₀ N ₂ O ₂ | 160 | 70.58 (70.39) | 4.23 (4.11) | 11.76 (11.48) |
| 3d | C ₁₄ H ₁₀ N ₂ O ₂ | 169 | 70.58 (70.83) | 4.23 (4.37) | 11.76 (11.89) |
| 3e | C ₁₄ H ₉ ClN ₂ O | 210 | 65.51 (65.47) | 3.53 (3.32) | 10.91 (10.77) |
| 3f | C ₁₄ H ₉ ClN ₂ O | 197 | 65.51 (65.41) | 3.53 (3.40) | 10.91 (10.79) |
| 3g | C ₁₄ H ₉ N ₃ O ₃ | 225 | 62.92 (62.71) | 3.39 (3.15) | 15.72 (15.63) |
| 5a | C ₁₂ H ₈ N ₂ O ₂ | 105 | 67.92 (67.59) | 3.80 (3.60) | 13.20 (13.04) |
| 5b | C ₁₃ H ₁₀ N ₂ O ₃ | 190 | 64.46 (64.33) | 4.16 (4.13) | 11.56 (11.34) |
| 5c | C ₁₂ H ₈ N ₂ O ₃ | 175 | 63.16 (63.37) | 3.53 (3.70) | 12.28 (12.41) |
| 5d | C ₁₂ H ₈ N ₂ O ₃ | 165 | 63.16 (63.23) | 3.53 (3.73) | 12.28 (12.53) |
| 5e | C ₁₂ H ₇ ClN ₂ O ₂ | 170 | 58.43 (58.37) | 2.86 (2.99) | 11.36 (11.63) |
| 5f | C ₁₂ H ₇ ClN ₂ O ₂ | 160 | 58.43 (58.23) | 2.86 (2.59) | 11.36 (11.19) |
| 5g | C ₁₂ H ₇ N ₃ O ₄ | 230 | 56.04 (56.23) | 2.74 (2.63) | 16.34 (16.53) |

Oxadiazole derivatives exhibit various types of biological activities such as anti-helminthic, antihistaminic, antifungal, antibacterial and pesticidal. Guided by these observations and in continuation of our work we synthesized the title compounds. The structure of these compounds was established by the IR, ¹HNMR spectral data and elemental analysis. The results of the elemental analysis (C,H,N) were within ±0.4% of the calculated amounts (Table 3).

Compounds 3a-g and 5a-g were screened for their herbicidal activity against *Echinochloa oryzicola*, *Echinochloa crus-galli*, *Oryzae sativa*, and *Glycine max* antifungal activity against *Aspergillus niger*, *Pyricularia oryzae* and *Aspergillus fumigatus* whereas antibacterial activity against *Bacillus subtilis*, *Bacillus pumilus* (Gram-positive) and *Salmonella typhi*, *Escherchia coli*, *Klebsiella pneumoniae* (Gram-negative). Among these the most active compounds are 3b, 3c, 5b, 5c for herbicidal compounds 3b, 3g, 5b and 5g for fungicidal activity whereas compounds 3g and 5g showed highly antibacterial activity.

APPLICATIONS

Biological Activity: Antibacterial and antifungal activities of the synthesized compounds were completed by the disk diffusion method by halo zone test. The minimum inhibitory concentration (MIC) of synthesized compounds against bacterial and fungal strains was performed by macro dilution test and results were observed visually and spectrophotometrically.

Antibacterial activity: The newly prepared compounds were screened for their antibacterial activity against two Gram-positive bacteria viz. *Bacillus subtilis* and *Bacillus pumilus* and three Gram-negative bacteria viz. *Salmonella typhi*, *Escherichia coli* and *Klebsiella pneumoniae* bacterial strains by disk diffusion method [34]. Ciprofloxacin was used as reference standard for comparing the results. The antimicrobial activity seemed to be dependent on the nature of heterocyclic moieties. The antibacterial activity of the oxadiazole derivatives are shown in fig.1 for plates 1-9 and the zone of inhibition values are given in table 2. Among the tested compounds 3c, 3e, 3g, 5c, 5e and 5g showed more potent bactericidal activity against all bacterial strains against Gram-positive and Gram-negative pathogenic organism. Thus, the substituents place a vital role in imparting enhanced antibacterial activity to the compounds. The screening results indicate that compounds 3c and 5c was found to be active against *S. typhi* and *K. pneumoniae* compounds 3g and 5g were found to be active against *S. typhi*, *E. coli*, *K. pneumoniae*, *B. subtilis* and *B. pumillus*. Whereas 3b, 3c, 5b, 5c were found to be inactive against *B. pumillus*. The minimum inhibitory concentrations of the strongly active compounds were also measured. In the present study DMSO is used as control. While ciprofloxacin used as standard for antibacterial strain. Antibacterial activity of all active synthesized compounds was measured by serial dilution method and the MICs are presented in table 4.

Table 4. Antibacterial activity of compounds having promising biological activity, cup diameter = 0.5 cm.

| Compounds | Gram-positive bacteria | | Gram-negative bacteria | | |
|---------------|------------------------|------------------|------------------------|---------------|---------------------|
| | <i>B.subtilis</i> | <i>B.pumilus</i> | <i>S.typhi</i> | <i>E.coli</i> | <i>K.pneumoniae</i> |
| 3b | — | 05.0±0.2 | — | — | — |
| 3c | — | 15.0±0.4 | — | — | — |
| 3e | — | — | 25.0±0.2 | — | 15.0±0.2 |
| 3g | 25.0±0.4 | 35.0±0.2 | 35.0±0.3 | 45.0±0.2 | 65.0±0.2 |
| 5b | — | 05.0±0.2 | — | — | — |
| 5c | — | 15.0±0.4 | — | — | — |
| 5e | — | — | 25.0±0.4 | — | 15.0±0.3 |
| 5g | 25.0±0.3 | 35.0±0.2 | 35.0±0.2 | 45.0±0.2 | 65.0±0.1 |
| Ciprofloxacin | Δ | Δ | Δ | Δ | Δ |

Less active 1-1.5 cm, moderately active 1.5-2 cm, highly active 2-3 cm and very high active = Δ = 3-4.5 cm

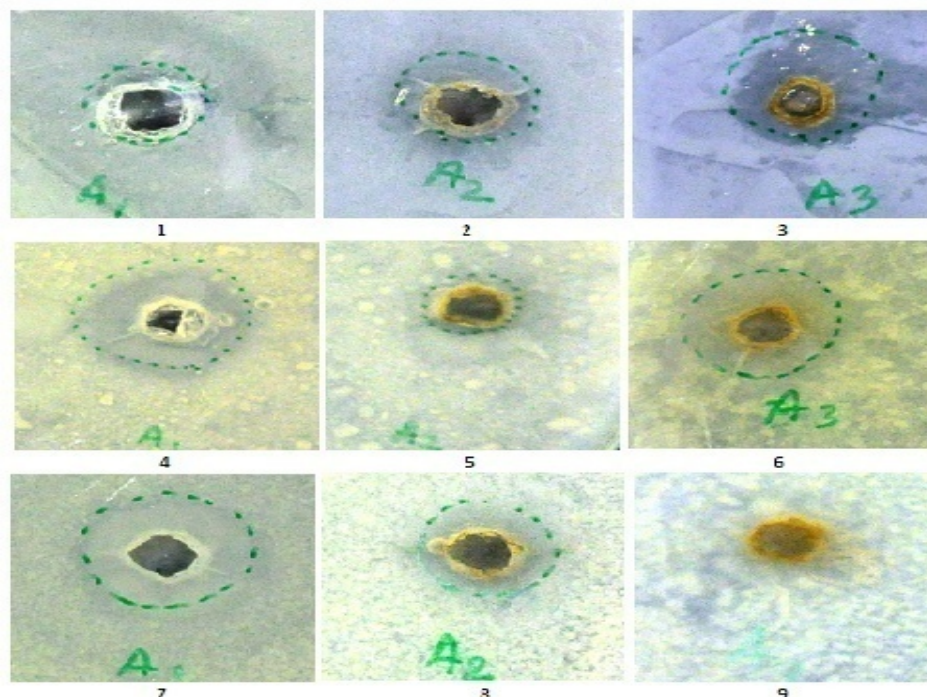


Figure 1. Plates 1-9 showing antibacterial activity of compounds 3b, 3c, 3e, 3g, 5b, 5c, 5e, 5g

Antifungal activity: Antifungal activity was also done by disk diffusion method. For assaying antifungal activity *Aspergillus niger*, *Pyricularia oryzae* and *Aspergillus fumigatus* were recultured in DMSO by agar diffusion method [35-36]. The inhibitory results are presented in Table 5 and 6.

The antifungal screening data showed good to moderate activity. Compounds 3b, 3g, 5b and 5g showed good fungicidal activity against *A. niger*, *P. oryzae* and *A. fumigatus* fungal strains. Among the tested compounds 3g and 5g showed more potent fungicidal activity all fungal strains (MIC 12.5 $\mu\text{g/mL}$). The MFC of the compounds was found to be two-, three- or four folds higher than the corresponding MIC results.

Thus, the nature of heterocycles and basic skeleton of molecule have significant influence on the extent of antibacterial and antifungal activities. A comparative study of the activity results with standard drugs (ciprofloxacin and carbendazim) revealed that none of the compounds exceeds the activity of commercial drugs. However, compounds have produced the marked enhancement in the potency of these analogous as antibacterial and antifungal agents.

Table 5: Antifungal activity of compounds 3b, 3g, 5b and 5g.

| Compounds | Diameter of zone of inhibition(mm) | | |
|-----------|------------------------------------|-----------------|--------------------|
| | <i>A.niger</i> | <i>P.oryzae</i> | <i>A.fumigatus</i> |
| 3b | 18.1 \pm 0.2 | 15.7 \pm 0.2 | 18.3 \pm 0.6 |
| 3g | 26.2 \pm 0.3 | 22.1 \pm 0.1 | 18.4 \pm 0.2 |
| 5b | 23.1 \pm 0.4 | 20.3 \pm 0.2 | 16.8 \pm 0.4 |

| | | | |
|----------|----------|----------|----------|
| 5g | 22.9±0.5 | 20.7±0.2 | 19.1±0.3 |
| Standard | 30.0±0.2 | 27.0±0.2 | 24.0±0.3 |
| DMSO | — | — | — |

Positive control (carbendazim) and negative control (DMSO) measured by the halo zone test (unit: mm)

Table 6. MIC and MFC of compounds 3b, 3g, 5b and 5g.

| Compounds | <i>A.niger</i> | | <i>P.oryzae</i> | | <i>A.fumigatus</i> | |
|-----------|----------------|------|-----------------|------|--------------------|------|
| | MIC | MFC | MIC | MFC | MIC | MFC |
| 3b | 24 | 100 | 24 | 50 | 24 | 50 |
| 3g | 12.5 | 25 | 12.5 | 25 | 12.5 | 50 |
| 5b | 12.5 | 50 | 12.5 | 50 | 12.5 | 50 |
| 5g | 25 | 50 | 25 | 50 | 25 | 50 |
| Standard | 25 | 12.5 | 12.5 | 6.25 | 25 | 12.5 |

MIC($\mu\text{g/mL}$) minimum inhibitory concentration, i.e. the lowest concentration of the compounds to inhibit the growth of fungus completely, MFC($\mu\text{g/mL}$) minimum fungicidal concentration, i.e. the lowest concentration of the compound for killing the fungus completely.

Herbicidal activity: The compounds 3b, 3c, 3e, 3g, 5g, 5b, 5c, 5e and 5g were subjected to primary post and pre-emergent herbicidal evaluation [37] at the rate of 8.0, 4.0 and 0.5 kg ha^{-1} . The test species are *Echinochloa oryzicola*, *Echinochloa crus-galli*, *Oryza sativa* and *Glycine max*. The detailed data on title compounds having promising herbicidal activity are given in Table 6.

Table 6. Herbicidal activity of compounds 3b, 3c, 3e, 3g, 5b, 5c, 5e and 5g.

| Compounds no. | Application rate kgha^{-1} | Post-emergence species | | | | Post-emergence species | | | |
|---------------|-------------------------------------|------------------------|-------------|-------------|--------------|------------------------|-------------|-------------|--------------|
| | | <i>E.or</i> | <i>E.cr</i> | <i>O.sa</i> | <i>G.max</i> | <i>E.or</i> | <i>E.cr</i> | <i>O.sa</i> | <i>G.max</i> |
| 3b | 8.0 | 4 | 4 | 4 | 4 | 5 | 4 | 4 | 5 |
| | 4.0 | 5 | 4 | 4 | 4 | 4 | 5 | 5 | 5 |
| | 1.0 | 3 | 2 | 2 | 3 | 2 | 2 | 2 | 3 |
| | 0.5 | 1 | 2 | 1 | 1 | 2 | 2 | 1 | 1 |
| 3c | 8.0 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| | 4.0 | 4 | 5 | 4 | 5 | 5 | 4 | 4 | 5 |
| | 1.0 | 4 | 4 | 4 | 3 | 3 | 4 | 3 | 4 |
| | 0.5 | 4 | 3 | 3 | 3 | 3 | 4 | 3 | 3 |
| 3e | 8.0 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| | 4.0 | 4 | 3 | 3 | 3 | 4 | 3 | 4 | 4 |
| | 1.0 | 4 | 3 | 2 | 1 | 3 | 2 | 2 | 2 |
| | 0.5 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 3g | 8.0 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| | 4.0 | 4 | 5 | 5 | 4 | 4 | 5 | 4 | 4 |
| | 1.0 | 2 | 3 | 2 | 3 | 3 | 3 | 2 | 2 |
| | 0.5 | 1 | 2 | 1 | 2 | 2 | 2 | 1 | 1 |
| 5b | 8.0 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| | 4.0 | 5 | 4 | 5 | 4 | 4 | 5 | 5 | 4 |
| | 1.0 | 3 | 2 | 2 | 3 | 2 | 2 | 3 | 2 |
| | 0.5 | 1 | 2 | 1 | 1 | 2 | 2 | 1 | 1 |
| 5c | 8.0 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |

| | | | | | | | | | |
|----|-----|---|---|---|---|---|---|---|---|
| | 4.0 | 4 | 5 | 4 | 5 | 5 | 4 | 4 | 4 |
| | 1.0 | 4 | 4 | 3 | 3 | 3 | 4 | 3 | 3 |
| | 0.5 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| 5e | 8.0 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| | 4.0 | 4 | 5 | 4 | 5 | 4 | 4 | 4 | 4 |
| | 1.0 | 4 | 3 | 1 | 2 | 2 | 3 | 3 | 3 |
| | 0.5 | 1 | 2 | 1 | 2 | 1 | 1 | 1 | 1 |
| 5g | 8.0 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| | 4.0 | 4 | 5 | 4 | 5 | 4 | 5 | 4 | 4 |
| | 1.0 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| | 0.5 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 |

CONCLUSIONS

In summary, we have synthesized 2-substituted aryl-5-phenyl-1,3,4-oxadiazole / 5- aryl-2-(furan-2-yl)-1,3,4-oxadiazole from corresponding Schiff bases as potential pesticides. Some important features of the method is sustainability, eco-compatible, noncorrosive and the reaction was carried through one-pot heterocyclization via metal-free PDB catalyst which has no offensive odor of bromine or amine. The applied protocol will be very effective for industrial use as it is simple, efficient and metal free. All these compounds have assayed for their pesticidal activities. Some of them have shown excellent pesticidal activities.

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AUTHORS' ADDRESSES

1. Akhilesh Kumar

Department of Chemistry
University of Allahabad, Allahabad 211002, India
Mob: 8565916521, Email: aks.modanwal@gmail.com

2. Arvind Kumar Pandey

Department of Chemistry
University of Allahabad, Allahabad 211002, India
Mob: 9452708012, Email: arvind010pandey@gmail.com

3. **Kamal Pratap Singh**
Department of Chemistry
University of Allahabad, Allahabad 211002, India
Mob: 8726733272, Email: kamalpratapsingh8587@gmail.com
4. **Nawseen Fatima Ansari**
Department of Chemistry
University of Allahabad, Allahabad 211002, India
Mob: 9169661983, Email: nfsnrau@gmail.com
5. **Shailendra Tiwari**
Department of Chemistry
University of Allahabad, Allahabad 211002, India
Mob: 9452368452, Email: drshailendratiwari@gmail.com
6. **Manoj Kumar Shrivash**
Centre of Biomedical Research
SGPGIMS, Lucknow 226014, India
Mob: 8004433399, Email: manojshrivash@gmail.com