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دانشگاه بو علی سینا

Bu-Ali Sina University

Faculty of Chemistry

Thesis

**Submitted in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy (Ph.D.)**

in

Organic Chemistry

Title

**Synthesis and Characterization of Azole
Heterocycles**

Under Supervision of

Professor Davood Azarifar

Advisor

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By

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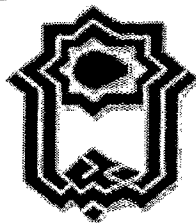
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Dedicated to

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Abstract

Azoles are an important group of five-membered heterocyclic compounds including pyrazolines, pyrazoles, 2-arylbenzothiazoles and 2-aryl-1-arylmethyl-1*H*-benzoimidazoles that have been studied in this thesis. In some cases in this work, the intermediate chalcones were first prepared from aldol condensation between the aromatic aldehydes and ketones in ethanolic NaOH solution. These chalcones were then reacted with nucleophilic reagent, like phenyl hydrazine in solvent-free under microwave irradiation in presence SiO₂ to yield the corresponding 2-pyrazolines upon cyclization. The aromatization of 2-pyrazolines to their pyrazoles by oxidation is a well known reaction in organic chemistry. A good range of 1,3,5-trisubstituted 2-pyrazolines were subjected to aromatization in the presence of various reagents such as *N,N,N',N'*-tetrabromo-benzene-1,3-disulfonamide [TBBDAs], *N,N'*-dibromo-*N,N'*-1,2-ethanediybis(*p*-toluenesulfonamide) [BNBTS], silica-supported *N*-bromosuccinimide [NBS], trichloroisocyanuric acid [TCCA], silica sulfuric acid-activated poly-1,3-dichloro-5-methyl-5(4'-vinylphenyl)hydantoin [PDCVH], silica sulfuric acid-activated poly-1-bromo-5-methyl-5(4'-vinylphenyl)hydantoin [PBVH], bismuth(III) nitrate pentahydrate, Bi(NO₃)₃.5H₂O, sodium nitrite or sodium nitrate in acetic acid, ZrCl₄/WetSiO₂/NaNO₂, silica sulfuric acid/WetSiO₂/NaNO₂ or NaNO₃ and 4-(*p*-chloro)phenyl-1,2,4-tiazole-3,5-dione. 2-Arylbentothiazoles have been synthesized by condensation of 2-aminothiophenol with aldehydes in various acids such as: acetic acid or silica sulfuric acid, bismuth(III) nitrate pentahydrate, Bi(NO₃)₃.5H₂O, ZrCl₄, and trichloroisocyanuric acid [TCCA], both under microwave irradiation (MW) and thermal conditions. Also, 2-aryl-1-arylmethyl-1*H*-benzoimidazoles were prepared from the reaction between *o*-aminaniline and aldehydes using oxalic acid or acetic acid under microwave irradiation and thermal heating.

In conclusion, the advantages of the methods presented in this thesis are as follows:

(i) the use of the inexpensive, readily available and non-toxic catalysts, (ii) easy workup of the products, (iii) improved yields and reduce time of the products, (iv) the use of relatively environmentally benign solvents such as: ethanol, acetic acid and water, (v) the experimental procedure is simple, and (vi) reduced pollution (formation of reactions in solid state).

Abbreviation

| | |
|-----------------------------|---|
| IBD..... | Iodobenzendiacetate |
| NHPI..... | <i>N</i> -hydroxyphthalimide |
| DBH..... | 1,3-dibromo-5,5-dimethylhydantoin |
| TCCA..... | Trichloroisocyanuric acid |
| TBBDA..... | <i>N,N,N',N'</i> -tetrabromo-benzen-1,3-disulfonamide |
| BNBTS..... | <i>N,N'</i> -dibromo- <i>N,N'</i> -1,2-ethanediylbis (<i>p</i> -toluenesulphonamide) |
| NBS..... | <i>N</i> -bromosuccinimide |
| NCS..... | <i>N</i> -chlorosuccinimide |
| NIS..... | <i>N</i> -iodosuccinimide |
| PDCVH..... | Poly-1,3-dichloro-5-methyl-5 (4'-vinylphenyl)hydantoin |
| PBVH..... | Poly-1-bromo-5-methyl-5 (4'-vinylphenyl)hydantoin |
| BNP..... | Bismuth(III) nitrate pentahydrate |
| PBBS..... | Poly(<i>N</i> -bromobenzene-1,3-disulfonamide) |
| TADs..... | 4-Substituted-1,2,4-triazoles-3,5-dione |
| SSA..... | Silica-sulfuric acid |
| MWI..... | Microwave irradiation |
| DMF..... | Dimethylformaldehyde |
| [PmIm]Br..... | 1-Phenyl-3-methylimidazolium bromide |
| BTA..... | Benzothiazoles |
| PET..... | Positron emission tomography |
| OATB..... | Organic ammonium tribromide |
| [Hbim]BF ₄ | 1-Butylimidazolium tetrafluoroborate |
| [bbim]BF ₄ | 1,3-Di- <i>n</i> -butylimidazolium tetrafluoroborate |
| SCE..... | Sister chromatid exchange |
| K-10..... | Montmorillonite |
| SA..... | Sulfamic acid |
| SA..... | Sulfamic acid |
| <i>o</i> -PD..... | Ortho-phenylenediamine |
| [Hmim]BF ₄ | 1-Methylimidazolium tetrafluoroborate |

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