Pyrazole derivatives, amongst five-membered heterocycles, are interesting heterocyclic compounds since they show a wide range of pharmacological properties including anti-inflammatory, anti-cancer, anti-bacterial, anti-viral, anti-diabetic, anti-microbial, and anti-fungal activities. Some pyrazoles display agrochemical properties (i.e., herbicidal and soil fungicidal activity) and have applications as pesticides and insecticides. 1,3,5-Trisubstituted pyrazoles can be easily obtained by oxidation of their corresponding pyrazolines produced by cyclization of chalcones with arylhydrazines. There is an obvious demand for oxidation of pyrazolines to pyrazoles due to their importance both as pharmacological targets and synthetic intermediates. A number of methods have been previously reported on the oxidation of pyrazolines using a variety of oxidants including Zr(NO₃)₄, carbon-activated oxygen, Pd/C/AcOH, Co(II)/O₂, iodobenzene diacetate, Pb(OAc)₄, MnO₂, KMnO₄, Ag(NO₃)₂, HgO, N-hydroxyphthalimide (NHPI) and I₂O₅/KBr. However, many suffer from certain drawbacks such as the use of expensive reagents, longer reaction times, low yields of products and toxicity of certain elements embodied in these reagents. These limitations necessitate further demand for new environmentally benign and easily accessible reagents for conversion of 2-pyrazolines to pyrazoles.

In this article, as part of our ongoing efforts to develop more robust methods for oxidative aromatization of various heterocycles including pyrazolines, we describe the use of silica-sulfuric acid-activated
poly-1,3-dichloro-5-methyl-5(4’-vinylphenyl)hydantoin (PDCVH) as a new and efficient system for aromatization of 1,3,5-trisubstituted 4,5-dihydro-1H-pyrazoles, under microwave irradiation. In this approach, we have observed that the coupling of microwave irradiation with the use of PDCVH,\textsuperscript{22} activated by silica sulfuric acid, provides smooth conversion of 2-pyrazolines (1\textit{a-m}) to 2-pyrazoles (2\textit{a-m}) in EtOH with special attributes such as enhanced reaction rates, higher yields of products and improved ease of manipulation (Scheme 1). The reactions were conducted under microwave irradiation as well as conventional thermal heating. The results (summarized in Table 1) display the superiority of microwave irradiation to thermal heating in providing enhanced reaction rates and improved yields.

It is interesting to know that, the reagent PDCVH can only affect the conversion of pyrazolines to pyrazoles if a suitable promoter is used in the reaction either under microwave irradiation or thermal conditions. Several acids including AcOH, TsOH and silica-sulfuric acid have been examined to activate the reagent to release Cl\textsuperscript{+} cation. It is noticed that, silica-sulfuric acid appears as the most effective activator providing highest yields and least reaction times. In addition, when the reactions are allowed to run in the absence of PDCVH with using solely silica-sulfuric acid in the reaction mixture, no oxidation of pyrazolines is resulted. This evidence substantiates the role of PDCVH as the main species acting as oxidant, and any involvement of silica sulfuric acid as the oxidant is ruled out. According to the experimental results shown in Table 1, more efficient conversion of 2-pyrazolines occurs under microwave irradiation in EtOH to yield the corresponding pyrazoles in shorter reaction times and higher yields (78-98\%) when compared with the yields obtained under thermal conditions at room temperature (68-90\%). The actual role of PDCVH is not clear at this time. However, a plausible explanation is that PDCVH might act as a source for Cl\textsuperscript{+}, which in turn activates silica sulfuric acid for further reaction with pyrazolines.

In conclusion, we have developed a new and mild procedure for oxidation of 2-pyrazolines to 2-pyrazoles utilizing poly-1,3-dichloro-5-methyl-5(4’-vinylphenyl)hydantoin (PDCVH) as a cheap, non-toxic and easily recoverable reagent which operates both under microwave irradiation and conventional thermal conditions at rt.
EXPERIMENTAL

IR spectra were recorded using a Shimadzu 435-U-04 spectrophotometer (KBr pellets) and NMR spectra were obtained using 90 MHz JEOL FT NMR spectrometer. Microwave-assisted reactions were conducted in a commercial Black & Decker model MX30PG1000 watt microwave oven. 4,5-Dihydro-1H-pyrazoles were all prepared according to our previously reported procedure. Poly-1,3-dichloro-5-methyl-5(4'-vinylphenyl)hydantoin was provided by Halosource Company in USA. 2-Pyrazoles were characterized on the basis of their melting points and IR, 1H NMR, and 13C NMR spectral analysis and compared with the reported data.

Aromatization of 1,3,5-trisubstituted pyrazolines with silica sulfuric acid-activated PDCVH;

General Procedure:
Poly-1,3-dichloro-5-methyl-5(4'-vinylphenyl)hydantoin (0.45g) and silica-sulfuric acid-activated poly-1,3-dichloro-5-methyl-5(4'-vinylphenyl)hydantoin (PDCVH) in EtOH under both microwave irradiation and thermal conditions at rt.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>R¹</th>
<th>R²</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>Mp (°C)</th>
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<tbody>
<tr>
<td>1a</td>
<td>2a</td>
<td>Ph</td>
<td>Ph</td>
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<td>82 (82)</td>
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<tr>
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<td>2b</td>
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<tr>
<td>1c</td>
<td>2c</td>
<td>Ph</td>
<td>4-NO₂C₆H₄</td>
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<td>84 (90)</td>
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<td>1d</td>
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<td>Ph</td>
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<td>1e</td>
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<td>4-CIC₆H₄</td>
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<td>2-CIC₆H₄</td>
<td>165 (2)</td>
<td>70 (80)</td>
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<td>2j</td>
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<td>3-CIC₆H₄</td>
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<td>68 (82)</td>
<td>92-94</td>
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<tr>
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</table>

The reaction data obtained under microwave irradiation are given in parentheses. All the isolated products were characterized on the basis of their physical properties and IR, 1H NMR and 13C NMR spectral analysis and by direct comparison with authentic materials. Isolated yields.

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REFERENCES


