RESEARCH ARTICLE

ECO-FRIENDLY SYNTHESIS OF m-SUBSTITUTED THIOCARBAMIDOPHENOLS AND p-SUBSTITUTED THIOCARBAMIDOPHENOLS.

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Abstract

Solvent free synthetic methods are resourceful for increasing speed and course of number of organic reactions with elevated selectivity to produce high yield removing lower quantities of by-products. These methods are easy and not time consuming. Hence, in this laboratory series of m-substituted thiocarbamidophenol and p-substituted thiocarbamidophenol were synthesized by interactions of m-aminophenol and p-aminophenol with different isothiocynates by using microwave technique. Structure determination of products was established on the basis of usual elemental analysis, chemical transformations and spectral studies.

Introduction:

In recent years, methods for a synthesis of compounds by eco-friendly techniques were developed. These methods are environmentally and diminish impact of environmental pollution in green chemistry. These methods involve design, development and implementation of performance criterion with selectivity in current synthesis. These methods are low cost, facile, safe and reproducible experimental procedures. In microwave and sonochemical methods time duration decreases by evading undesired by-products. Hence, microwave irradiation (MWI) technique has gained popularity in past decade as a powerful tool for rapid, economic and efficient synthesis of variety of compounds. Microwave irradiation is well-known to promote synthesis of a variety of compounds. Literature survey reveals example of specific reactions, which do not occur under conventional conditional heating, but could be possible by microwave irradiation. Synthesis of 1-phenyl amidinothiocarbamide was successfully carried out. Literature survey also reveals that thiocarbamido nucleus showed strong antimicrobial activity and is also versatile reagent in organic synthesis. Although they have been known from long ago to be biologically active, their varied biological features are still of great scientific interest. Some derivatives of these possess anti-tuberculosis, anti-tumor, anti-cancer, anti-pyretic activities.

Considering all these facts and in view of our interest in synthesis of nitrogen and sulphur containing benzenoides we here report synthesis of m-substituted thiocarbamidophenols and p-substituted thiocarbamidophenols by using microwave irradiation technique (Scheme-I and Scheme-II).
Scheme-I

\[
\begin{align*}
&\text{m-Aminophenol} + \text{Substituted disothiocyanate} \\
&\xrightarrow{\text{Microwave Oven}} \text{m-Substituted thiocarbamidophenol}
\end{align*}
\]

Where R = -Phenyl

Scheme-II

\[
\begin{align*}
&\text{p-Aminophenol} + \text{Substituted disothiocyanate} \\
&\xrightarrow{\text{Microwave Oven}} \text{p-Substituted thiocarbamidophenol}
\end{align*}
\]

Where R = -Phenyl, -p-Cl-phenyl, -p-tolyl.

**Synthesis of m-phenylthiocarbamidophenol:** m-Phenylthiocarbamidophenol was synthesized by interacting m-aminophenol with phenylisothiocyanate in microwave oven for two minutes. Faint yellow crystals were obtained; these were washed several times with ether, recrystallised from ethanol. Yield 96%, melting point 168°C.

The probable reaction for the formation of is depicted below,

**Reaction:**

\[
\begin{align*}
&\text{p-Aminophenol} + \text{Phenylisothiocyanate} \\
&\xrightarrow{\text{Microwave Oven}} \text{p-Phenylthiocarbamidophenol}
\end{align*}
\]

**Properties:** C_{13}H_{12}N_{2}O_{1}S_{1}, Faint yellow crystalline solid, melting point 168°C. It gave positive test for nitrogen and sulphur. Desulphurised by alkaline plumbite solution which clearly indicate presence of C=S group. It gave positive test for phenol. It formed picrate, melting point 155°C. % Composition- Found (Calculated) C: 62.73 (63.94), H: 03.92 (04.91), N:11.47 (11.47), S:13.09 (13.11). **FTIR (KBr)** ν cm^{-1}: 3361.4 (OH stretching), 3296 (NH stretching), 2752.13 (Ar-H stretching), 1603.3 (N-C-N stretching), 1504.20 (N-C=S stretching), 1258.4 (C=S stretching), 1178.4 (C-N stretching). **^1H NMR (400 MHz CDCl₃ δ ppm)**: phenolic -OH proton at δ 8.7998 ppm, Ar-H protons at δ 6.8050-6.0006 ppm and -NH protons at δ 3.6005-2.4876 ppm.

Similarly, other m-substituted thiocarbamidophenols and p-substituted thiocarbamidophenols were synthesized by interaction of m-aminophenol and p-aminophenol with methylisothiocyanate, ethylisothiocyanate, tertbutylisothiocyanate and p-chlorophenylisothiocyanate respectively by above mentioned method and enlisted in Table No. 1.
References:


Table No. 1:-

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>m-Substituted thiocarbamidophenols</th>
<th>p-Substituted thiocarbamidophenols</th>
<th>Yield</th>
<th>m.p.</th>
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<tbody>
<tr>
<td>1</td>
<td>m-Methyl--------------------------</td>
<td></td>
<td>89</td>
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<td>2</td>
<td>m-Ethyl---------------------------</td>
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<td>3</td>
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<td>4</td>
<td>m-(4-Chlorophenyl)-----------------</td>
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<td>5</td>
<td>p-Phenyl---------------------------</td>
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<td>6</td>
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<td>9</td>
<td>p-(4-Chlorophenyl)-----------------</td>
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<td>174</td>
</tr>
</tbody>
</table>

Experimental:-

Synthesis of p-phenylthiocarbamidophenol: A reaction mixture of m-aminophenol (0.1M) and phenylisothiocynate (0.1M) was taken in 50 ml beaker and kept in microwave oven for irradiation for two minutes then the reaction mixture was poured on ice cubes then faint yellow crystals were obtained; these were washed several times with ether, recrystallised from ethanol. Yield 96%, melting point 168°C.

References:

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