Journal Homepage: - www.journalijar.com
INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)
Article DOI: 10.21474/IJAR01/2581
DOI URL: http://dx.doi.org/10.21474/IJAR01/2581
ISSN NO. 2320-5407

RESEARCH ARTICLE

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

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Manuscript Info

Manuscript History

Received: 27 October 2016
Final Accepted: 25 November 2016
Published: December 2016

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-substitutedthiocarbamidophenol and p-substitutedthiocarbamidophenol 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[1-3]. These methods involve design, development and implementation of performance criterion with selectivity in current synthesis[4]. These methods are low cost, facile, safe and reproducible experimental procedures. In microwave and sonochemical methods time duration decreases by evading undesired by-products[5-12]. Hence, microwave irradiation (MWI) [13-14] technique has gained popularity in past decade as a powerful tool for rapid, economic and efficient synthesis of variety of compounds[15]. Microwave irradiation is well-known to promote synthesis of a variety of compounds [16]. Literature survey reveals example of specific reactions, which do not occur under conventional conditional heating, but could be possible by microwave irradiation[17]. Synthesis of 1-phenyl amidinothiocarbamide was successfully carried out[18,19]. Literature survey also reveals that thiocarbamido nucleus showed strong antimicrobial activity and is also versatile reagent in organic synthesis[20]. Although they have been known from long ago to be biologically active[21-23], their varied biological features are still of great scientific interest. Some derivatives of these possess anti-tuberculosis, anti-tumor, anti-cancer, anti-pyretic activites[24,25].

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

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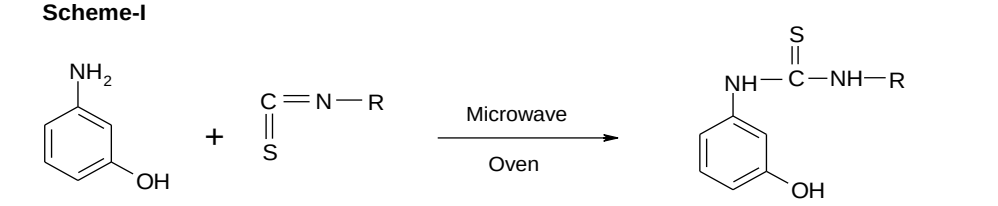
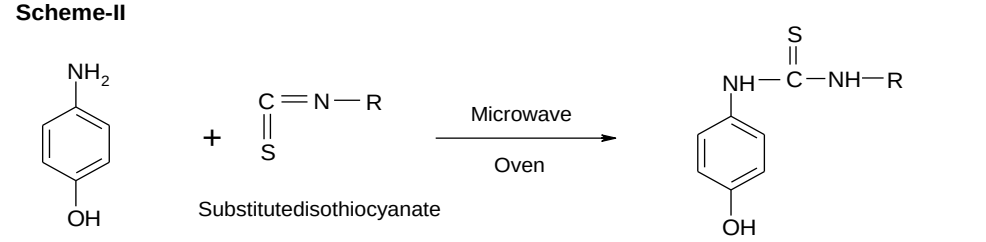
Scheme-I



m-Aminophenol Substitutedisothiocyanate m-Substitutedthiocarbamidophenol

Where R = -Phenyl

Scheme-II



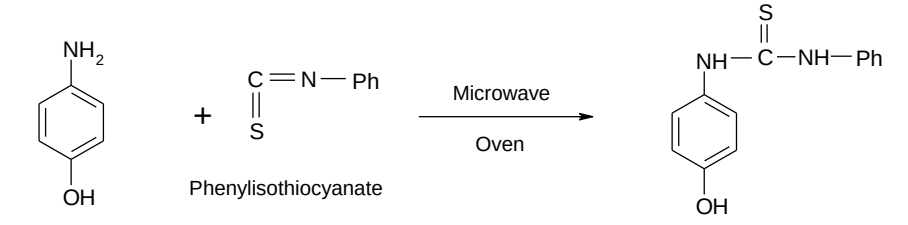
p-Aminophenol Substitutedisothiocyanate p-Substitutedthiocarbamidophenol

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

Synthesis of m-phenylthiocarbamidophenol: m-Phenylthiocarbamidophenol was synthesized by interacting m-aminophenol with phenylisothiocynate in microwave oven for two minutes. Faint yellow crystals were obtained; these were washed several times with ether, recrystalised from ethanol. Yield 96%, melting point 168^{0C}.

The probable reaction for the formation of is depicted below,

Reaction:-



p-Aminophenol Phenylisothiocyanate p-Phenylthiocarbamidophenol

Properties: $C_{13}H_{12}N_2O_1S_1$, Faint yellow crystalline solid, melting point 168^0C. 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 155^0C. % 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). **^{1}H NMR (400 MHz $CDCl_3$ 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-substitutedthiocarbamidophenols and p-substituted thiocarbamidophenols were synthesized by interaction of m-aminophenol and p-aminophenol with methylisothiocyanate, ethylisothiocyanate, tertbutylisothiocynate and p-chlorophenylisothiocynate respectively by above mentioned method and enlisted in **Table No. 1.**

Table No. 1:-

Sr.No.	m-**Substituted**thiocarbamidophenols p-**Substituted**thiocarbamidophenols	Yield	m.p.
1	**m-Methyl----------**	89	152
2	**m-Ethyl----------**	82	130
3	**m-Tertbutyl----------**	84	132
4	**m-(4-Chlorophenyl)------**	93	147
5	**p-Phenyl----------**	96	168
6	**p-methyl----------**	93	127
7	**p-Ethyl----------**	88	190
8	**p-Tertbutyl----------**	86	178
9	**p-(4-Chlorophenyl)------**	94	174

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, recrystalised from ethanol. Yield 96%, melting point 168^0C.

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