JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

MICROWAVE SOLVENT FREE SYNTHESIS OF ANALOGS OF 4-THIOCARBAMIDONAPTHOLS

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Abstract:

Recently in this laboratory we synthesized analogues of 4-thiocarbamidonapthols by microwave solvent free green synthesis. In this synthesis interactions of 4-amino-1-naphthol were carried out with *p*-chlorophenylisothiocynate, *p*-tolylisothiocynate, *o*-tolyliso- thiocynate and *m*-tolylisothiocynate in microwave irradiations to obtained 4-substituted- thiocarbamido-1-naphthols. Characterization of newly synthesized compounds was done on the basis of elemental analysis, chemical characteristics and spectral studies. This is solvent free synthesis and yields obtained were good and remarkable by obtaining purity of the products.

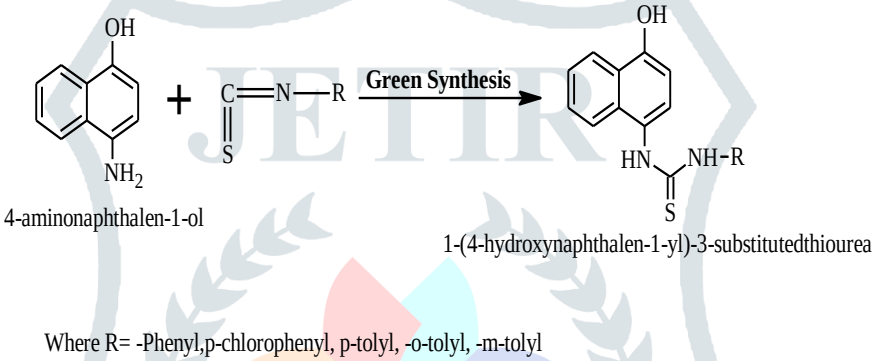
Key words: Green synthesis, 4-substitutedthiocarbamidonaphthols and microwave irradiations.

Introduction:

Now-a-days, special attention gained by chemist towards the electromagnetic energy in the range of microwaves have as regards the most various fields of utilization such as the alimentary (domestic ovens), analytical (small ovens devoted to the mineralization) and that one of bio-medical applications[1]. Various article and book have been explained numerous organic reaction assisted by microwave heating[2-3]. In the field of synthetic chemistry, a certain delay has been suffered either in the base research for the clear improvements which can lead to higher yields of cleaner products, minor energy consumption and environmental compatibility. This delay can however be rapidly reduced by use of electromagnetic energy caused by microwaves. Thus microwave energy can be used and is been used as an activating agent in chemistry for the

synthesis of a large variety of compound. In organic synthesis thiocarbamates are versatile reagent and their derivatives also show strong antimicrobial activity [4]. Although they have been known from long ago to be biologically active[5-7]. Thiocarbamido molecules have biological features and are still of great scientific interest and showed anti-tuberculosis, anti-cancer, anti-tumor, anti-pyretic activities[8-9]. Thiocarbamides, heterocyles and derivatives have their own individuality shown by several modern theories and concept concerning to the physical as well as chemical study [10-14]. Thiocarbamide nucleus containing compounds also show remarkable biological activity and significances[15-22].

Considering all these things present research work is carried out solvent free green synthesis to synthesized new series of substitutedthiocarbamidonaphthols by the interaction of 4-amino-1-naphthol with *p*-tolylisothiocynate, *o*-tolylisothiocynate, *m*-tolylisothiocynate, phenylisothiocynate and *p*-chlorophenylisothiocynate, in microwave irradiations respectively which are hither to unknown. Scheme of synthesis is given in **Scheme-I**.



4-aminonaphthalen-1-ol

1-(4-hydroxynaphthalen-1-yl)-3-substitutedthiourea

Where R= -Phenyl,p-chlorophenyl, p-tolyl, -o-tolyl, -m-tolyl

Scheme-I

Experimental Part

Glassware: All glassware used throughout the research work are of Borosil make.

Chemicals: All chemicals were used of AR grade of Merck and Aldrich India make.

IR Spectra were recorded on Perkin-Elmer spectrum RXI FTIR and ^{1}H NMR were recorded in $CDCl_3$ on Bruker DRX-300 spectrometer operating at 300 MHz at SAIF, Chandigarh, Punjab.

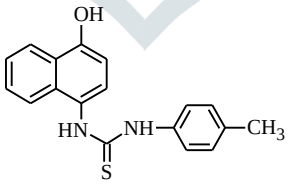
Microwave reactions were carried out in Brand-META-LAB, Model Number MSI-1, Temperature Range 50-250ºCat Department of chemistry Government Vidarbha Institute of Science and Humanities, Amravati.

Brand-META-LAB Microwave Oven

1) 4-(*p*-Methyl)phenylthiocarbamido-1-naphthol:

A mixture of 4-aminonapthol (0.05 M) and *p*-tolylisothiocynate (0.05 M) was irradiated in microwave for 65 seconds, then the reaction mixture was poured on ice cube with vigorous stirring, ivory colure crystalline product was obtained and recrystalised by ethanol. Yield is 97.1% and melting point is 203-204°C.

Properties: Compound is ivory colour crystalline solid having melting point 187-188°C. It gave positive tests for nitrogen and sulphur. It gave positive alkaline plumbite test indicating presence of C=S group.Product was soluble in ethanol, acetone, benzene, dioxane, DMSO, $DMSOd_6$ and insoluble in water. **IR spectrum (cm^{-1}):** The IR spectrum of compound was carried out in KBr pallets. The important absorptions are correlated as: N-H stretching at 3295.52cm^{-1}, Phenolic-OH stretching at 1282.82 cm^{-1}, Aromatic C-H stretching at 3059.54 cm^{-1}, Aliphatic C-H stretching at 2969.54 cm^{-1}, N-C-N stretching at 1605.81 cm^{-1}, C-N stretching at 1520.94 cm^{-1}, C-C stretching at 1390.74 cm^{-1}, C-O stretching at 1282.72 cm^{-1}, N-C=S stretching at 1520.94 cm^{-1}, C=S stretching at 912.37 cm^{-1}. **PMR spectrum:** The spectrum of a compound was carried out in DMSO. This spectrum distinctly displayed the signals due to naphthol ring six protons at δ 8.2072- 7.0867 ppm,Ar-H protons at δ 6.9071- 6.6549 ppm, phenolic –OH proton at δ 5.4632-5.2534 ppm, NH protons at δ 3.3706 ppm, and CH_3 protons at 1.4823-1.2406.



1-(4-hydroxynaphthalen-1-yl)-3-(4-methylphenyl)thiourea

or

4-(p-Methyl)phenylthiocarbamido-1-naphthol

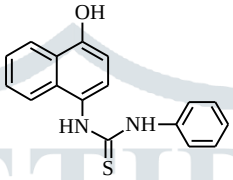
2) Synthesis of 4-phenylthiocarbamido-1-naphthol

A mixture of 4-aminonapthol (0.05 M) and *p*-tolylisothiocynate (0.05 M) was irradiated in microwave for 65 seconds, then the reaction mixture was poured on ice cube with vigorous stirring, ivory colure crystalline product was obtained and recrystalised by ethanol. Yield is 97.13% and melting point is 203-204°C.

Properties: Yellow needle shaped crystalline solid having melting point 203-204°C. It gave positive tests for nitrogen and sulphur are present. It gave positive alkaline plumbite test indicating presence of C=S group.

Product was soluble in ethanol, acetone, benzene, dioxane, DMSO, $DMSOd_6$ and insoluble in water. **IR spectrum (cm^{-1}):** The IR spectrum of compound was carried out in KBr pallets. The important absorptions are correlated as: N-H stretching at 3171.11 cm^{-1}, phenolic–OH stretching at 1598.09 cm^{-1}, aromatic C-H stretching at 2971.47 cm^{-1}, aliphatic C-H stretching at 2745.79 cm^{-1}, N-C-N stretching at 1598.09 cm^{-1}, C-N stretching at 1368.88 cm^{-1}, C-C stretching at 1598.09 cm^{-1}, C-O stretching at 1275.97 cm^{-1}, N-C=S stretching at 1275.97 cm^{-1}, C=S stretching at 1159.27 cm^{-1}.**PMR spectrum:** The spectrum of a compound was carried out in DMSO. This spectrum distinctly displayed the signals due to Ar-H protons at δ 6.9071- 6.6549 ppm, naphthol ring six protons at δ 8.2072- 7.0867 ppm, phenolic –OH proton at δ 5.4632-5.2534 ppm, NH protons at δ 3.3706 ppm, and CH_3 protons at 1.2406.

From the above chemical characteristics, elemental and spectral analysis, the compound was assigned the structure as 4-phenylthiocarbamido-1-naphthol.



1-(4-hydroxynaphthalen-1-yl)-3-phenylthiourea

4-phenylthiocarbamido-1-napthol

Similarly, solvent free interactions of 4-amino-1-naphthol with *o*-tolylisothiocynate and *m*-tolylisothiocynate, phenylisothiocynate and *p*-chlorophenylisothiocynate were carried out microwave irradiations and results obtained are given in **Table No.1**

Table No. 1

Sr. No.	**4-Substituted** thiocarbamido-1-naphthol	Time Required (Seconds)	Melting Point (°C)	Yield (%)
1	4-(***p*-Methyl)phenyl--**	65	187-188	97.15
2	4-(***o*-Methyl)phenyl--**	85	167-168	93.74
3	4-(***m*-Methyl)phenyl-**	73	175-176	95.40
4	4-**Phenyl--------**	70	203-204	97.13
5	4-(***p*-Chloro)phenyl--**	75	217-218	95.89

Conclusion

This work provides a new method for preparing analogs of 4-thiocarbamidonapthols. The microwave-assisted technique is preferable due to the yield enhancements attained, time saving, and environmental safety reactions. The newly prepared compounds were verified for spectral analysis. This is solvent free synthesis and yields obtained were good and remarkable yield by maintaining the purity of the products.

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