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

"A NOVEL SYNTHESIS OF 1,4- BIS (3,3-DI-SUBSTITUTED)THIOCARBAMIDOBENZENE"

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Abstract-

Recently in this laboratory the synthesis of 1,4- Bis (3,3-disubstituted) thiocarbamidobenzene were carried out by the interactions of1,4dichlorobenzene (I) with various thiourea (2a-e) in 1:2 proportion in isopropanol medium for 4 hours. The synthesized compounds were characterized on the basis of elemental analysis, chemical characteristics and spectral data.

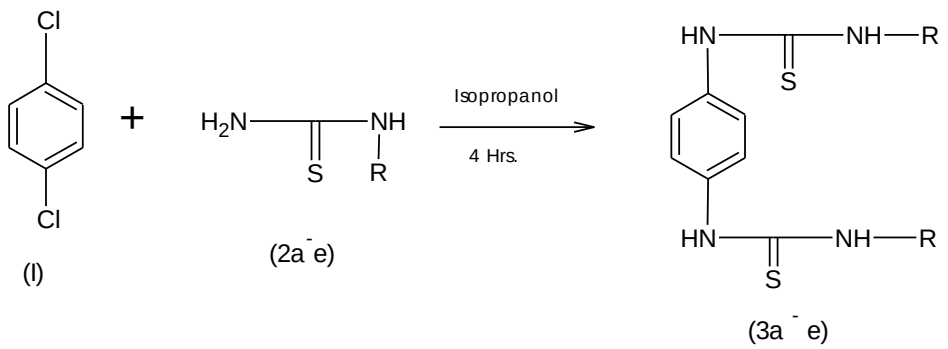
Keywords- 1,4-dichlorobenzene, substituted thioureas, isopropanol, etc.

INTRODUCTION-

The literature survey of 1,4-dichlorobenzene this compound is generally use as fumigant and disinfectant agent having side effect. The literature survey of thiocarbamide also shows that the thiocarbamido nucleus containing drug have their own importance in pharmaceutical chemistry because thus drugshow antiemetic, analgesic, anti-emetic anti-pyretic, anti-ulcer, anti-malarial properties[1-10].

The clinical uses, adverse effect, physiochemical properties and the chemistry of 1,4-dichlorobenzene were studied insufficient details. Thiocarbamide nucleus containing molecules shows various medicinal and pharmaceutical applications[11-17].

As wider program of this laboratory in the synthesis of nitrogen and sulphur containing heterocycles and their cyclisation into 5,6, and 7 membered heterocyclic and to investigate their medicinal, pharmaceutical parameters, it was thought interesting to carry out the interactions of 1,4-dichlorobenzenewith different thiocarbamides in isopropanol medium to isolate a new series of heterocyclic drugs having benzene and thiocarbamide nucleus in the same drug. This may enhance the potency of drug and may also introduce new type of drug activity. This type of reaction is heither to unknown. This synthetic approach will become a milestone and open a new path in pharmaceutical, biochemical, medicinal and drug chemistry. Taking all these things into consideration the interactions of 1,4- dichlorobenzene (1) and various thiocarbamide (2a-e) were carried out in isopropanol medium (**Scheme-I**)



RESULT AND DISCUSSION

Synthesis of 1, 4-Dithiocarbamidobenzene (3a) –

A mixture 1, 4-dichlorobenzene (I) and thiocarbamide (2a) in 1:2 proportions in isopropanol medium were refluxed for 4 hours on water bath. During boiling 1, 4-dichlorobenzene and thiocarbamide went into the solution and the new product was formed i.e. 1, 4 dithiocarbamidobenzene to be gradually separated out which on basification with dilute ammonium hydroxide afforded crystals. It was filtered in hot condition and crystallized with aqueous ethanol to obtain yield 92% and melting point 145^0C.

Properties of 3a –

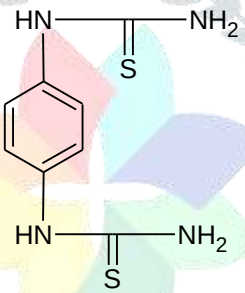
The compound is white and crystalline in nature and having melting 145^0C. It contains nitrogen and sulphur. It did not give test for chlorine it means that chlorine is removed duringrefluxed. Desulphurised with alkaline plumbite solution. It form picrate having melting point 173^0C. From analytical data the molecular formula found to be $C_8H_{10}N_4S_2$.

IR Spectra[16-18]:- The IR spectra was carried out in KBr pellets and reproduced on IR plate number **DSS-1**. The important absorption can as N-H stretching amine at 3391.97 cm^{-1}, N-H stretching Imine at 3397.15 cm^{-1}, [C=C] stretching at 1607.74 cm^{-1}, benzene C-H Stretching at 2927.10 cm^{-1}, in benzene C-N at 1310.69 cm^{-1}, -C=S at 1225.82 cm^{-1} and -C-N-C Stretching at 1087.90 cm^{-1}.

NMR Spectra:- The spectrum was carried out in $CDCl_3$. This spectrum distinctly displayed the signals **DSS-1** due to Ar-H protons at δ 7.2599 ppm, - NH_2 protons at δ 1.1891-1.3099, -NH at δ 1.4235-1.5506 ppm.

Mass spectrum:- The Mass analysis of the compound was carried out and reproduced on Mass Plate No. **DSS-1.** The fragmentation occurs during the analysis is given in Mass spectrum.

From the above properties and the spectral analysis the compound (**3a**) was assigned the structure as 1, 4-dithiocarbamidobenzene acid.



(3a)

Synthesis of 1,4- bis (3,3-diphenyl)thiocarbamidobenzene (3e)–

A mixture 1, 4-dichlorobenzene (I) and phenylthiocarbamide (2e) in 1:2 proportions in isopropanol medium were refluxed for 4 hours on water bath. During refluxing 1, 4-dichlorobenzene and phenylthiocarbamide went into the solution and the new product was formed i.e. 1,4- bis (3,3- diphenyl)thiocarbamidobenzene to be gradually separated out which on basification with dilute ammonium hydroxide afforded crystals. It was filtered in hot condition and crystallized with aqueous ethanol to obtain yield 87% and melting point 102^0C.

Properties of 3e –

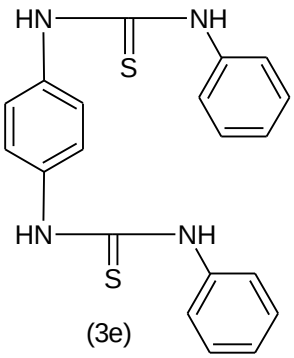
The compound is white and crystalline in nature and having melting 157^0C. It contains nitrogen and sulphur. It did not give test for chlorine it means that chlorine is removed during refluxed. Desulphurised with alkaline plumbite solution. It form picrate having melting point 169^0C. From analytical data the molecular formula found to be $C_{20}H_{18}N_4S_2$.

IR Spectra[16-18]:- The IR spectra was carried out in KBr pellets and reproduced on IR plate number **DSS-2**. The important absorption can as N-H stretching Imine at 3421.87 cm^{-1}, [C=C] stretching in benzene at 1606.77 cm^{-1}, C-H Stretching in benzene at 3012.94 cm^{-1}, -C=S at 1155.41cm^{-1} and -C-N-C Stretching at 1071.50 cm^{-1}.

NMR Spectra:- The spectrum was carried out in $CDCl_3$. This spectrum distinctly displayed the signals **VRA-3** due to Ar-H protons at δ 7.9250-6.6478 ppm, - NH protons at δ 3.8952-3.8888 ppm.

Mass spectrum:- The Mass analysis of the compound was carried out and reproduced on Mass Plate No**. DSS-2**. The fragmentation occurs during the analysis is given in Mass Spectrum.

From the above properties and the spectral analysis the compound (**3e**) was assigned the structure as 1,4- bis (3,3-diphenyl)thiocarbamidobenzene.



(3e)

Similarly, 1,4- bis (3,3-dimethyl)thiocarbamidobenzene (3b), 1,4- bis (3,3-diethyl)thio- carbamidobenzene (3c) and 1,4- bis (3,3-diallyl)thiocarbamidobenzene (3d) were synthesized by refluxing 1,4-dichlorobenzene (I) with methyl thiourea (2b), ethyl thiourea (2c) and allyl thiourea (2d) respectively in 1:2 proportion in isopropanol medium for 4 hours as shown in **table number-I**

Table No.-I

Sr.No.	Experiment No.	1,4- bis (3,3-disubstituted) thiocarbamidobenzene	Yield	Melting Point (^{0}C)
3	2	------dimethyl-------	82	178
4	3	------diethyl-------	78	163
5	4	------diallyl-------	76	169

EXPERIMENTAL

The melting point of all the synthesized compounds was recorded using hot paraffin bath. IR spectra were recorded on Shemadzu spectrometer in the range 4000-400 cm^{-1} in KBr pellet's. PMR spectra were recorded Bruker AC - 500F spectrometer with TMS as internal standard using $CDCl_3$ and DMSO as solvent. The purity of compounds was checked on Silica-gel-g plates by TLC within the layer thickness of 0.3 mm. All used were of AR Grade.

Acknowledgment:

The authors thank to the Prof. Dr. D.T.Tayade, G.V.I.S.H., Amravati for guidance and thanks to Principal J.M.V., Achalpur (City) for granting permission for research facility for kind cooperation.

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