SYNTHESIS OF SOME NEW ARYL THIOCARBAMIDES, RESPECTIVE BENZYLIDENE DERIVATIVESAND CHARACTERIZATION

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Abstract: Thioureas have great medicinal applications as well as non-medicinal activities in industry, analytical chemistry and metallurgy. New thiourea derivatives and their structures have received attention of several research groups because of their complexation capacity. Thiourea and its derivatives represent well-known important group of organic compounds due to the diverse application in fields.

Several aryl thiocarbamides were synthesized by the interaction of aryl isothiocyanates and *o*-phenylenediamine. While these thiocarbamides on further reaction with benzaldehyde gives respective benzylidene derivatives. The identities of these newly synthesized compounds were established on the basis of usual chemical transformations, IR, ^{1}H NMR and Mass spectral studies.

***Keywords*:** Aryl thiocarbamides, aryl isothiocyanates, benzylidene aryl thiocarbamides.

INTRODUCTION:

New thiourea derivatives and their structures have received attention of several research groups because of their complexation capacity. Some derivatives are biologically active, such as antifungal, antitumour, antiviral, antibacterial, pharmacological, herbicidal, and insecticidal properties. In addition, some of the research groups have reported thermal behaviour and the acidity constants of ligands of some benzoylthiourea derivatives and their metal complexes[1].

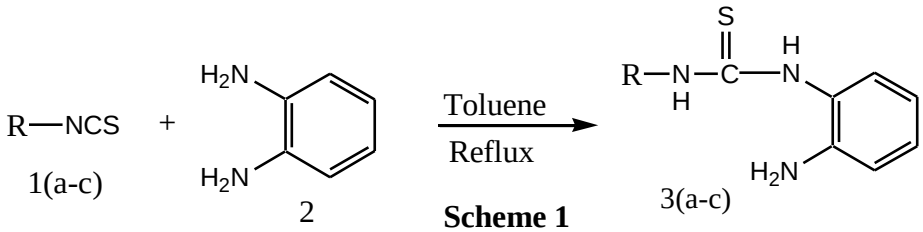
Thiourea and its derivatives represent well-known important group of organic compounds due to the diverse application in fields such as medicine, agriculture, coordination, and analytical chemistry[2]. They also can be used as selective analytical reagents, especially for the determination of metals in complex interfering materials[3-5].

Schiff bases have received a considerable amount of attention from many researchers owing to their importance in exhibiting thermochromism and photochromism[6–9]. Thiourea compounds works as building blocks in the synthesis of heterocyclic compounds. Substituted thioureas have recently gained much interest in the preparation of wide variety of biologically active compounds[10,11].

In view of the advantage conferred by thiourea and benzylidene derivatives, it was interesting to carry out synthesis of various thiocarbamides and benzylidenederivatives by the interaction of aryl isothiocyanate with*o*-phenylenediamine and further with benzaldehyde. (**Scheme 1 and Scheme 2**).

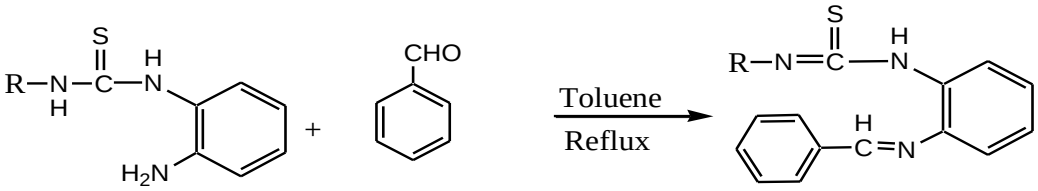
EXPERIMENTAL

All melting points are uncorrected and were obtained in capillary using paraffin bath. Specific rotations of the newly synthesized compounds were measured on an Equip-Tronic digital polarimeter model no. EQ 801 at 30^{0}C in $CHCl_3$. IR spectra were recorded on a Shimatzu FTIR spectrophotometer, ^{1}H NMR on a Bruker DRX-300 (300 MHz FT) NMR spectrometer in $CDCl_3$ solution with TMS as an internal reference. The Mass spectra were recorded on a Jeol SX -102 FAB mass spectrometer. Purity of the compound was checked by thin layer chromatography using merck silica gel-coated aluminium plates and petroleum ether: ethyl acetate as eluent and iodine vapours as a visualizing agent.



Scheme 1

Where R= 1.Phenyl 2. p-tolyl 3. p-chloro phenyl



3(a-c) 4 **Scheme 2** 5(a-c)

Characterization data of compounds 3(a-c) and 5(a-c) Table-1

Compound	% yield	M.P. (^{O}C)
3a	76	204
3b	67	198
3c	80	236
5a	79	186
5b	65	223
5c	82	205

Preparation of aryl thiocarbamides3(a-c)

These have been prepared by the interaction of various aryl isocyanates which were prepared by earlier known method, interaction of aryl isothiocyanatesand *o*-phenylenediamine in boiling toluene medium.(**Scheme 1**)

Preparation of 1-phenyl-[*o*-benzylidene amino]-3-aryl thiocarbamide5(a-c)

To 1-phenyl-*o*-amino-3-phenylthiocarbamide **(3a)**benzaldehyde **(4)** was added in toluene as solvent and the reaction mixture was gently refluxed for 3h. Reaction was monitored by TLC. After the completion of reaction solvent was distilled off and the resultant mass was triturated several times with light petroleum (60-80^{O}C) to afford a pale yellow solid.

The product was found to be desulphurizable when boiled with alkaline plumbite solution. m.p. 186°C. (**Scheme 2**)

All other aryl thiocarbamides**(3b-f)** and arylbezylidenethiocarbamides (5a-c) were prepared in a similar manner.

IR[12-17] and ^{1}H NMR[18-22] Spectral studies:

1-phenyl(o-amino)-3-phenyl thiocarbamide(3a):

IR (KBr) ν cm^{-1} : 3332, 3369 (N-H str.), 3016 (Ar. C-H str.), 2970 (Ali. C-H str.), 1361 (Ar. C-N str.),

1-phenyl(*o*-amino)-3-p-tolyl thiocarbamide(3b):

IR (KBr) ν cm^{-1}: 3430, 3310 (N-H str.), 2965 (Ali. C-H str.), 1372 (Ar. C-N str.), 1210 (C=S str.) ; **^{1}H NMR** in $CDCl_3$ at δ ppm: 2.88 (3H, s, CH_3), 5.05 (2H, s, NH), 3.65 (1H, s, NH), 3.75 (1H, s, NH), 6.98-7.54 (8H, m, Ar-H);

1-phenyl(*o*-amino)-3-p-chlrophenyl thiocarbamide(3c):

IR (KBr) ν cm^{-1} : 3370, 3310 (N-H str.), 2955 (Ali. C-H str.), 1371 (Ar. C-N str.), 1230 (C=S str.); **^{1}H NMR** in $CDCl_3$ at δ ppm: 3.71 (3H, s, CH_3), 5.15 (2H, s, NH), 4.05 (1H, s, NH), 3.75 (1H, s, NH), 7.31-7.77 (8H, m, Ar-H);

1-pheny(*o*-benzylidene amino)-3-phenyl thiocarbamide 5(a)

IR (KBr) ν cm^{-1} : 3340, 3389 (N-H str.), 3012 (Ar. C-H str.), 2960 (Ali. C-H str.), 1210 (C=S str.), ; **^{1}H NMR** in $CDCl_3$ at δ: 3.65 (1H, s, NH), 3.75 (1H, s, NH), 6.98-7.54 (14H, m, Ar-H);

1-pheny(*o*-benzylidene amino)-3-p-tolylthiocarbamide 5(b)

IR (KBr) ν cm^{-1} : 3440, 3370 (N-H str.), 2945 (Ali. C-H str.), 1209 (Ar. C-N str.), 1230 (C=S str.) ; **^{1}H NMR** in $CDCl_3$ at δ ppm: 2.88 (3H, s, CH_3), 5.45 (1H, s, NH), 4.51 (1H, s, NH) 7.28-7.64 (13H, m, Ar-H);

1-pheny(*o*-benzylidene amino)-3-p-chloro phenylthiocarbamide (5c):

IR (KBr) ν cm^{-1} : 3380, 3290 (N-H str.), 3035 (Ar. C-H str.), 1169 (C=S str.), **^{1}H NMR** in $CDCl_3$ at δ ppm: 4.58 (1H, s, NH), 4.01 (1H, s, NH), 7.53-8.01 (13H, m, Ar-H);

ANTIMICROBIAL ACTIVITY:

These newly synthesized compounds were screened for their microbial activity against different pathogenic microbes for their antibacterial and antifungal activities using well method. The compounds were screened for antibacterial activity against E. coli, S. aureus, P. vulgaris and for antifungal activity against C. albicancs and A. niger in potato dextrose agar medium.

Procedure for antimicrobial screening:

Media used (Nutrient broth) : Peptone – 10 g, NaCl – 10 g and yeast extract 5 g, Agar 20 g in 1000 ml of distilled water. Initially, the stock culture of bacteria were revived by inoculating in broth media and grown at 37 ^{0}C for 18 h. The agar plates of the above media were prepared and wells were made in the plate. Each plate was inoculated with 18 h old culture (100 µL, 10^4cfu) and spread evenly on the plate. After 20 min. the wells were filled with different concentrations of samples. The control wells were filled with Gentamycin. All the plates were incubated at 37 ^{O}C for 24 h and the diameter of inhibition zones were noted in mm. The activity was quantitatively assessed on the basis of inhibition zone.

Most of the compound showed strong to moderate activity while some showed poor activity against the tested microorganisms.

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