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SYNTHESIS AND ABSORPTION SPECTRA OF 4-PHENYL SUBSTITUTED -2-AMINOTHIAZOLES INTERMEDIATES FOR ORGANIC SYNTHESIS

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ABSTRACT

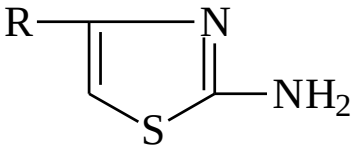
A series of4-aryl-2-aminothiazole derivatives were synthesized with an objective to develop novel and potent coupling components of synthetic origin as well as in dye synthesis. The required derivatives of 4-phenylsubstituted-2-aminothiazole were synthesized via a multicomponent condensation between thiourea, acetophenone and iodine. The intermediates were obtained using acetophenone and various substitute daldehydes to synthesize the intermediates which on cyclization with sulphur yielded the final products. Synthesized compounds were purified, characterized and evaluated for their spectra properties. All the synthesized intermediates exhibited moderate to significant properties. They were found to possess good coupling properties as well as high degree of brightness and a colour deepening effect compared to other heterocyclic couplers obtained from aniline and anthraquinone dyes.

Keywords: *4-phenyl-2-aminothiazole, synthesis, acetophenone, heterocyclic and condensation.*

I. INTRODUCTION

Thiazole nucleus has been established as the potential entity in the largely growing chemical world of heterocyclic compounds possessing promising characteristics. Substituted thiazoles and their biheterocycles have received considerable attention during last two decades as they are endowed with wide range of therapeutic properties (Ananthanarayan ,2006). A number of thiazole derivatives have been reported to possess significant and diverse biological activities such as antimicrobial [Koti, 2006], analgesic, antinflammatory, antioxidant[singh, 2011] andantiallergic activities(Ishaet al, 2012)**.** Various pesticides possessinga thiazole nucleus are well known in agriculture. Large numbers of thiazole derivatives have emerged as active pharmaceutical ingredients in several drugs for their potential anti-inflammatory (baur,1996) anti-tumour (Azam,2007), anti-hyperlipidemic, anti-hypertensive and several other biological properties. Besides, thiazoles are also synthetic intermediates and common substructures in numerous biologically active compounds (Cruikshank, 1975). Thus, the thiazole nucleus has beenmuch studied in the field of organic and medicinal chemistry (Aoyama, 2006)

In continuation to these efforts and with an objective to develop potent heterocyclic intermediates of synthetic origin, it was decided to synthesize certain amino thiazole derivatives and evaluate them for their coupling potential in dye synthesis. The synhesis fromacetophenone, thiourea and iodine as well as the absorption spectra of these intermediates are discussed.



2-amino-4-arylthiazole

II. MATERIALS AND METHOD

All the chemicals for the synthesis were purchased from approved vendors of different make like Aldrich, Dayang chemicals, Ievakluga, Synquest laboratory and King scientific and all chemicals were of laboratory grade.

Completion of reaction were confirmed using physical constant determination (Sharp or narrow melting ranges). Melting points were determined using melting point apparatus in open capillaries and are uncorrected.

Further the compounds synthesized were proceeded for TLC wherein single spots (1st TLC run) were observed, indicating completion of reaction. After work-up was completed, (unreacted starting materials were removed by washing with ether), the products were subjected to purification by recrystallization process. Again TLC was run to find out exact Rf value. TLC plates used for final recrystallized product were pre-coated silica gel G plates. Solvent systems were developed using trial and error method by use of appropriate solvents of different polarity until the use of diethylether : ethanol (75%: 25%) solvent mixture was established. The Visible absorption spectra were measured using CARY 630 UV-visible spectrophotometer. Model: agilent technology . The infra-red spectra were carried out on FTIR Nexus 670 spectrophotometer in KBr disc (thermo nicolet) and absorption bands are expressed in cm^{-1}.

III. SYNTHESIS OF 2-AMINO-4-PHENYL THIAZOLE DERIVATIVES AII

3.1 Preparation of the 2- amino-4-phenylthiazole AII_1
Resublimed iodine (7.6g,0.03mol) was added to the slurry of the corresponding ketone (acetophenone and its para substituents- chloro, 2,4-dichloro, 3,4-dibromo, methyl, and bromo)(0.03mol) and thiourea (4.5g, 0.06mol) in toluene and the mixture was heated in an oil bath at 130ºC - 140ºC overnight. After cooling, the reaction mixture was diluted with distilled water (50ml) and heated to dissolve most of the solid, again cooled to ambient temperature. The aqueous solution was treated with 25% aqueous ammonium hydroxide(to pH 9-10). The precipitated thiazole wasfiltered, washed successively with water, collected and purified by crystallization from hotethanol (Kamaljit et al, 2002).

3.2 Preparation of the 2- amino,4-(p-chlorophenyl) thiazoleAII_2
The procedure is the same as in 3.1 above,except that the resublime iodine and thiourea were reacted with para-chloroacetophenone in toluene. The mixture was heated in an oil bath at 130ºC - 140ºC overnight. After cooling, the reaction mixture was diluted with distilled water (50ml) and heated to dissolve most of the solid, again cooled to ambient temperature. The aqueous solution containing the hydroiodide was treated with 25% aqueous ammonium hydroxide (to pH 9-10). The precipitated thiazole was filtered, washed successively with water, collected and purified by crystallization from aqueous ethanol (Kamaljit et al, 2002).

3.3 Preparation of the 2- amino,4-(p-aminophenyl) thiazole derivativeAII_3
The procedure is the same as in 3.1 above, except that the resublime iodine and thiourea were reacted with para-aminoacetophenone in tolueneand the mixture was heated in an oil bath at 130ºC - 140ºC overnight.

3.4 Preparation of the 2- amino-4-p(2,4-dichlorophenyl) thiazole derivativeAII_4
The procedure is the same as in 3.1 above, except that the resublime iodine and thiourea were reacted with 2,4-dichloroacetophenone in toluene. The mixture was heated in an oil bath at 130ºC - 140ºC overnight.

3.5 Preparation of the 2- amino-4-(p-bromophenyl) thiazole derivativeAII_5
The procedure is the same as in 3.1 above, except that the resublime iodine and thiourea were reacted with para-bromoacetophenone in toluene. and the mixture was heated in an oil bath at 130ºC - 140ºC overnight.

3.6 Preparation of the 2- amino-4-p(2,4-dibromophenyl) thiazole derivative AII_6
The procedure is the same as in 3.1 above, except that the resublime iodine and thiourea were reacted with 2,4-dibromoacetophenone in toluene. The mixture was heated in an oil bath at 130ºC - 140ºC overnight.
Scheme 1 ; Synthesis of 2-amino-4p(phenyl)thiazole derivatives

3.7 Recrystallization
All aminothiazole derivatives were purified by 3- 4 recrystallizations from hot ethanol. A known weight of the intermediate was dissolved in small quantity of ethanol and heated up.It was then filtered off using a Buchner funnel

with a sunction pump. The crystals were collected, washed severally with water and dried. After the recrystallization, the purity of each compound was checked by spotting on a thin layer chromatography plate

IV. RESULTS AND DISCUSSION

In a mixture of acetophenone and thiourea in toluene, iodine was added dropwisely with shaking. The mixture which was heated on an oil bath overnight at 130-140ºC afforded 2-amino-4-aryl-thiazole(1). Compound 1 on reaction with 4-chloroacetophenone give 1-{4-[(4-phenyl-1,3-thiazol-2-yl) amino] phenyl}ethanone (2) which on further stepwise reaction with various aromatic aldehydes afforded various 2-amino-4p-phenylthiazole derivatives respectively. The primary structural difference within the series involves the nature of various substituted aldehydes. Synthesized compounds were found to be crystalline in nature and easily soluble in ethyl acetate, benzene, DMSO and DMF but insoluble in hexane and toluene.

With the help of analytical techniques such as melting point,UV-visible spectrophotometer and FTIR, the synthesized derivatives were characterized. These compounds showed absorption band forC-S stretching of thiazole ring between 674-745cm^{-1} and 1028- 1088 cm-^{1} for C-N. All the compounds showed absorption peaks for different kinds of functional groups at their respective regions. All of them were found to be in full consignment with assigned structures.

For Compound AII$_1$: Yellow crystals were obtained;It was purified by recrystallization in hot ethanol. Melting point 144-147ºC, 74% yield which correspond to literature values148ºC, 80% yield(Prajapati,2010) . FTIR (KBr)/cm^{-1}):1624 (C=C), 847 (CH –Ar bend), 2283 (Ali C-H), 3435 (NH str),1483, 1532 (Ar C=C str), 1340 (C-C), 1039 (C-N), 691 (C-S), 3134 (Ar-H)

FOR COMPOUND AII$_2$: Off white crystals wereobtained.It was purified by recrystallization in hot ethanol. Melting point 173ºC, 67% yield 85% yield. FTIR (KBr)/cm^{-1}):1621 (C=C), 827, 741(CH –Ar bend, double), 2847 (Ali C-H), 3391(NHstr) . 1569 (Ar C=C str) ,1088 (C-N), 1196 (C-H) 741 (C-S), 827 (C-Cl), 3119 (Ar-H).

FOR COMPOUND AII$_3$: A deep YELLOW crystal was obtained. It was purified by recrystallization in hot ethanol. Melting point 187-188ºC, 52% yield. FTIR (KBr)/cm^{-1}):1610 (C=C), 831,738 (CH –Ar bend, double), 2776 (Ali C-H), 3410 (NH),1490,1427 (Ar C=C str), 1265(C-C) ,1043 (C-N), 685 (C-S), 3116 (Ar-H), 1539 (N-H Ali)

FOR COMPOUND AII$_4$: A brownish yellow crystal was obtained, It was purified by recrystallization in hot ethanol. Melting point 190-192ºC, 59% yield .FTIR (KBr)/cm^{-1}):1630,1684(C=C Ali), 827, 764 (CH –Ar bend, double), 2922 (Ali C-H), 3309(NH), 1599 (NH Bnd). 1520,1580 (Ar C=C str), 1632 (C-C), 784,723 (C-Cl),1028 (C-N), 674 (C-S), 3116 (Ar-H), 2922(C-H Ali), 1129, 961 (C-H)

FOR COMPOUND AII$_5$: A BROWNISH YELLOW crystal was obtained, It was purified by recrystallization in hot ethanol. Melting point 185-187ºC, 61% yield .FTIR (KBr)/cm^{-1}):1602 (C=C), 849, 771 (CH –Ar bend, double), 3432,(NHstr), 1599 (NH Bnd). 1159 (C=C Ar), 1028,1326 (C-C), 1086 (C-N), 693 (C-S), 693 (C-Br), 3060 (Ar-H).

FOR COMPOUND AII$_6$: A pale yellow crystal was obtained, It was purified by recrystallization in hot ethanol. Melting point 199-202ºC, 67% yield . FTIR (KBr)/cm^{-1}):1621 (C=C Ali), 823 (CH –Ar bend, double), 2847,2948(Ali C-H), 3384 (NHstr), 1565 (NH Bnd). 1490 (C=C Arstr), 1319 (C-C), 1069 (C-N), 741 (C-S), 741 (C-Br), 1189 (C-H Ar), 3116 (Ar- H).

V. CONCLUSION

The analytical and other informational data, available in literature so far, have rendered thiazole significantly important class of heterocyclic compounds and their applications in ever challenging dye synthesis of various classifications. All the synthesized intermediates exhibited moderate to significant properties. They were found to

possess good coupling properties as well as high degree of brightness and a colour deepening effect compared to other heterocyclic couplers obtained from aniline and anthraquinone dyes.

This particular research study, in reference, would extend great deal of help to researchers in reckoning and determining the best and most productive, economical, suggestive and conclusive access to various thiazoles of organic and synthetic importance superseding other coupling compounds of their class.

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