2-[(2-thio-3-methyl-6-substitutedamino)-1,3,5-thidiazino]imino-11-(piprazine-1-yl)dibenzo[b,f][1,4]oxazepines

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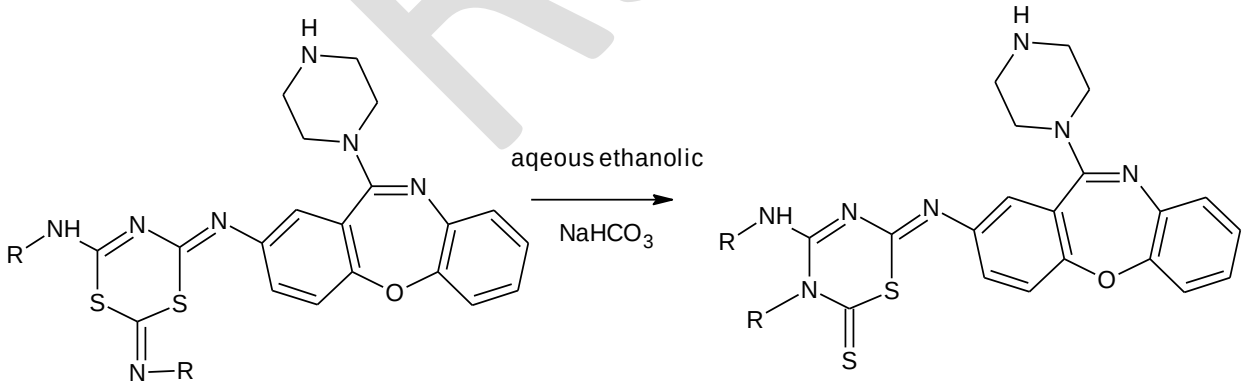
***Abstract*:- Series of 2-[(2-thio-3-methyl-6-substitutedamino)-1,3,5-thidiazino]imino11-(pipr- azine-1-yl)dibenzo[b,f][1,4] oxazepines [IXB(a-h)] was successfully synthesized by the isomerisation of 2-[(2-methylimino-6-substitutedamino)-1,3,5-dithiozino]imino-11-(pipr azine-1-yl) dibenzo [b,f][1,4] oxazepines [VIII(a-h)] by 5% aqueous sodium bicarbonate in ethanol medium. The structures of all synthesized compounds were determined on the basis of chemical characteristics, elemental analysis and spectral studies.**

***Key words*:- 2-[(2-methylimino-6-substitutedamino)-1,3,5-dithiozino]imino11-(piprazine-1-yl)dibenzo[b,f][1,4] oxazepines and 5% aqueous sodium bicarbonate in ethanol.**

I. INTRODUCTION

Oxazepine nucleus containing molecules showed biological, medicinal and pharmacological applications and significances[1] such as enzyme inhibitors[2], analgesic[3], anti-depressant[4] and psychoactive drugs[5]. Oxazepine nucleus is used for treatment of depression, anxiety and agitation[6-7]. Recently new series of 1,2,4-thiadiazoles, 1,3,5-thiadiazines and 1,3,5-dithiazines were synthesized by exploring the synthetic applications of -thiocarbamido, -amino, -halo, -cyano, etc. and their antimicrobial, antifungal, antibacterial, analgesic physiochemical parameters[8-11] were studied. [1,4] Oxazepine **(IB)** and their derivatives showed agricultural, medicinal, biological, pharmaceutical, industrial significances and applications. Hence, a novel series of 2-[(2-methylimino-6-substitutedamino)-1,3,5-dithiazino]imino-11-(piprazine-1-yl) dibenzo [b,f] [1,4] oxazepines [**VIIIB(a-f)]** was synthesised by the isomerisation of 2-[(2-methylimino-6-substitutedamino)-1,3,5-dithiozino]- imino-11-(piprazine-1-yl) dibenzo [b,f][1,4] oxazepines **[VIII(a-h)]** by 5% aqueous sodium bicarbonate in ethanol, **Scheme-1.**



[VIIIB(a-f)]

2-[(2-substitutedimino-6-substitutedamino) -1,3,5-dithiozino] imino 11-(piprazine-1-yl) dibenzo [b,f][1,4] oxazepines

[IXB(a-f)]

2-[(2-thio-3-substituted-6-substitutedamino) -1,3,5-thidiazino]imino11-(piprazine-1-yl) dibenzo[b,f][1,4]oxazepines

Where, R= -methyl, -ethyl,-t-butyl, -phenyl, p-chlorophenyl, -p-tolyl.

Scheme-1

II. SYNTHESIS OF 2-[(2-THIO-3-METHYL-6-ETHYLAMINO)-1,3,5-THIDIAZINO]IMINO-11-(PIPRAZINE-1-YL) DIBENZO[B,F][1,4]OXAZEPINE

Synthesis of 2-[(2-thio-3-methyl-6-ethylamino)-1,3,5-thidiazino] imino 11-(piprazine-1-yl)dibenzo[b,f][1,4] oxazepine **[IXB(a)]** was carried out by isomersing 2-[(2-methylimino-6-substitutedamino)-1,3,5-dithiozino]imino-11-(piprazine-1-yl) dibenzo [b,f][1,4] oxazepine **[VIIIB(a)]** in 5% aqueous sodium bicarbonate solution in ethanol. After distillation of excess solvent yellow crystals were separated out. Recrystalised from glacial acetic acid, yield 92 %, m.p. 148^0C.

III. PROPERTIES OF [IXB(a)]

It is brown colour crystalline solid having melting point 148^0C. It gave positive test for nitrogen and sulphur. It was desulphurized by alkaline plumbite solution which clearly indicate the presence of C=S group. It was soluble in water, ethanol, DMSO-d_6 while insoluble in carbon tetrachloride, chloroform, benzene, petroleum ether. It formed picrate having melting point 209^0C.

Elemental analysis: **[**C: 57.20% (found), 57.62% (calculated)], [H: 05.06% (found), 05.21 % (calculated)], [N: 20.45% (found), 20.45 % (calculated)], [S: 13.44% (found), 13.36 % (calculated)].

IR Spectrum: The IR spectrum was carried out in KBr-pellets The important absorptions are correlated as (cm^{-1}) 3054.38 N–H stretching, 2845.63 C-H stretching, 1745.47 N=C-N stretching, 1532.53 N-C=S stretching, 1245.63 C-N stretching, 1032.64 C=S stretching.

*NMR Spectrum***:** The NMR spectrum was carried out in DMSO-d_6 and $CDCl_3$ This spectrum distinctly displayed the signals due to Ar-H protons at δ 7.5373-6.3247 ppm, -NH proton at δ 4.2673-3.2173 ppm, -CH_3 protons at δ 1.2641-1.1434 ppm.

Similarly, 2-[(2-methylimino-6-phenylamino)1,3,5-dithiazino]imino-11-(piperazine-1-yl) dibenzo [b,f] [1,4] oxazepine **[VIIIB(b)],** 2-[(2-methylimino-6-methylamino)-1,3,5-dithiazino]imino-11-(piperazine-1-yl)dibenzo [b,f] [1,4] oxazepine **[VIIIB(c)],** 2-[(2-methyl imino-6-tertbutylamino)-1,3,5-dithiazino]imino-11-(piperazine-1-yl)dibenzo [b,f] [1,4] oxaze pine **[VIIIB(d)],** 2-[(2-methylimino-6-p-chlorophenylamino)- 1,3,5-dithiazino] imino-11-(pip erazine-1-yl)dibenzo[b,f][1,4]oxazepine**[VIIIB(e)],** 2-[(2-ethylimino-6-p-tolylamino)-1,3,5-dithiazino]imino-11-(piperazine-1-yl)dibenzo[b,f][1,4]oxazepine **[VIIIB(f)]** were isomerized by 5% aqueous sodium bicarbonate solution by above mentioned method to isolate 2-[(2-thio-3-methyl-6-phenylamino)-1,3,5-thiadiazino]imino-11-(piperazine-1-yl)dibenzo[b,f] [1,4] oxazepine **[IXB(b)],** 2-[(2-thio-3-methyl-6-methylamino)-1,3,5-thiadiazino]imino-11-(piper azine-1-yl)dibenzo [b,f][1,4] oxazepine **[IXB(c)],** 2-[(2-thio-3-methyl-6-tertbutylamino)-1,3,5-thiadiazino]imino-11-(piperazine-1-yl)dibenzo[b,f][1,4]oxazepine **[IXB(d)],** 2-[(2-thio-3-methyl-6-p-chorophenylamino)-1,3,5-thiadiazino]imino-11-(piperazine-1-yl)dibenzo [b,f] [1,4] oxazepine **[IXB(e)],** 2-[(2-thio-3-methyl-6-p-tolylamino)-1,3,5-thiadiazino]imino-11-(piperazine-1-yl)dibenzo[b,f][1,4] oxazepine **[IXB(f)],** by the above mentioned method and enlisted in **Table No. I**

Table No. I

Sr. No.	**Compd. No.**	2-[(2-methylimino-6-**substituted**amino)1,3,5-dithiazino]imino-11-(piperazine-1-yl) dibenzo [b,f] [1,4]oxazepine	**Yield (%)**	**m.pt. (^{0}C)**
1	**[IXB(b)]**	2-[(2-Thio-3-methyl-6-**phenyl**amino)------- oxazepine	78	254
2	**[IXB(c)]**	2-[(2-Thio-3-methyl-6-**methyl**amino)------- oxazepine	84	127
3	**[IXB(d)]**	2-[(2-Thio-3-methyl-6-**t-butyl**amino)------ oxazepine	81	109
4	**[IXB(e)]**	2-[(2-Thio-3-methyl-6-**p-chloro**phenyl amino) ------- oxazepine	92	217
5	**[IXB(f)]**	2-[(2-Thio-3-methyl-6-**p-tolyl**amino)-----oxazepine	72	204

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