INTERNATIONAL JOURNAL OF RESEARCHES IN BIOSCIENCES, AGRICULTURE & TECHNOLOGY
© VISHWASHANTI MULTIPURPOSE SOCIETY (Global Peace Multipurpose Society) R. No. MH-659/13(N)
www.vmsindia.org

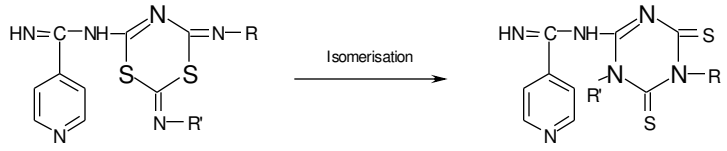
A Novel Synthesis of 1-Substitutedimino-3-Substi-Tuted-Imino-2,4-Dithio-6-(4-Pyridineimino)Amino-1,3,5-Triazines

D.T.Tayade and M.S.Lunge
Department of Chemistry, G.V.I.S.H., Amravati.
Department of Pharmaceutical Chemistry, S.R.R.L.Science College, Morshi.
Email ID: mslunge23@gmail.com, skdtayade@gmail.com.

Abstract
2-Substitutedimino-4-substitutedimino-6-(4-pyridine-imino)amino-1,3,5-dithiazines (VIIIa-o) were successfully isomerised by refluxing with 10% aqueous ethanolic sodium bicarbonate medium into 1-substitutedimino-3-substitutedimino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5- triazines (IXa-o). The structure of all the synthesized compounds were justified on the basis of chemical characteristics, elemental analysis and spectral analysis.
Keywords:2-Substitutedimino-4-substitutedimino-6-(4-pyridineimino)amino-1,3,5-dithiazines, sodium bicarbonate, ethanol, etc.

Introduction

The literature survey reveals that 1,3,5-triazine nucleus containing compounds have varieties of applications and significances in medicinal, pharmaceutical, agricultural and industrial fields[1-5]. These 1,3,5-triazines nucleus containing compounds created their own identity and importance in medicinal, pharmaceutical, industrial and agricultural sciences. Several S-triazines possesses antidiabetic[6-7], anti-tumor[8-9], anti-inflammatory[10], anti-depresent[11], hypoglycaemic[12] properties. They are also used as herbicidal[13-14], fungicidal[15-18], insecticidal[19], anti-corrosive[20], antimicrobial[21], anti-convulsant[22], anti-oxidant[23-28] and anti-cancer[29-31] properties. Hence it was thought interesting to synthesize 1-substitutedimino-3-substitutedimino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazines **(IXa-o)** by the isomerisation of 2-Substitutedimino-4-substitutedimino-6-(4-pyridineimino) amino-1,3,5-dithiazines **(VIIIa-o)** in 10% ethanolic sodium bicarbonate solution. The tentative reaction for the formation of product is depicted below,



(VIIIa-o)
2-Substitutedimino-4-substitutedimino
-6-(4-pyridineimino)amino-1,3,5-dithiazines

(IXa-o)
1-Substitutedimino-3-substitutedimino-2,4-
dithio-6-(4-pyridineimino)amino-1,3,5-triazines

Where, R= -methyl, -ethyl, -t-butyl, -phenyl, -p-chlorophenyl, -o-tolyl, -m-tolyl, -p-tolyl.
R'= -ethyl, -phenyl.

Scheme-I

Experimental

The melting point of all the compounds was recorded in using hot paraffin oil bath. The carbon and hydrogen analysis were carried out on Carlo-Ebra 1106 analyzer. Nitrogen estimation was carried out on Colman-N-analyzer-29. IR spectra were recorded on Perkin Elmerm Spectrometer in range 4000-400 cm-1 in KBr pellets. PMR spectra were recorded on Brucker Ac 300 F Spectrometer with TMS as internal standard using CDCl3 and DMSO–d6 as solvent. The purity of compound was checked on silica Gel-G Pellets by TLC with layer thickness of 0.3 mm. All chemicals used were of AR-grade.

Result and Discussion

Synthesis of 1-ethylimino-3-phenylimino-2,4-dithio-6-(4-pyridineimino) amino-1,3,5-triazine (IXd)

2-Ethylimino-4-phenylimino-6-(4-pyridineimino)amino-1,3,5-dithiazine **(VIIId)** was suspended in 10% ethanolic sodium bicarbonate solution and refluxed for half an hour on water bath. During heating the reactant went into the solvent. After distillation of excess solvent yellow crystals were isolated. It was recrystallised from glacial acetic acid to obtain 1-ethylimino-3-phenylimino-2,4-dithio-6-(4-

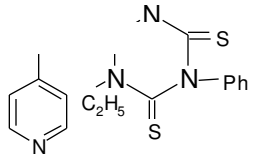
pyridineimino)amino-1,3,5-triazine **(IXd)**, yield 76%, m.p. 135^{0}C.

Properties of (IXd): It was yellow crystalline solid having m.p.135^{0}C. It gave positive test for nitrogen and sulphur. It was desulphurized when boiled with alkaline plumbite solution. It was soluble in benzene, acetic acid, DMF, dioxane and DMSO. It gave positive test for imino group.

Elemental analysis: The result of elemental analysis are Carbon (found 54.64), (Calculated 55.43), Hydrogen (found 3.50), (Calculated 4.34), Nitrogen (found 22.82), (Calculated 22.82) and Sulphur (found 17.05), (Calculated 17.39). From the analytical data the molecular formula was found to be $C_{17}H_{16}N_6S_2$.

IR Spectrum of compound[32-36]**:** IR spectrum of compound was carried out in KBr pellets and reproduce on **IR Plate No. MSL-21**, the important absorptions are correlated -NH stretching at 3389.6 cm^{-1}, Ar-H stretching at 3197.11cm^{-1}, C=NH stretching ring at 1635.6cm^{-1}, C-N stretching at 1254.24 cm^{-1}, C=S stretching at 1090.26 cm^{-1} and Monosubstituted benzene at 729.31 cm^{-1}.

PMR-Spectrum: The PMR spectrum[37, 34, 38] of compound was carried out in $CDCl_3$ and DMSO-d_6 and reproduced on **PMR Plate No. MSL-21.** This spectrum distinctly displayed the signals due to pyridino / Ar-protons at δ 6.6098-8.4552 ppm, -NH protons at δ 3.4693-3.4861 ppm, -CH_2 proton at δ 2.5412-2.5499 ppm and –CH_3 / =NH protons at δ 1.2433-1.3867 ppm. From the above properties and spectral analysis of the compound **(IXd)** was assigned the structure as 1-ethylimino-3-phenylimino-2,4-dithio-6-(4-pyridineimino) amino-1,3,5-triazine **(IXd).**



(IX d)

1-Ethylimino-3-phenylimino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine

Synthesis of 1-phenylimino-3-phenylimino-2,4-dithio-6-(4-pyridine-imino)amino-1,3,5-triazine (IX l)

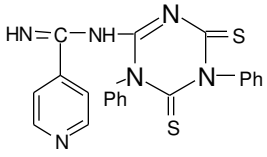
2-Phenylimino-4-phenylimino-6-(4-pyridineimino)amino-1,3,5-dithiazine **(VIII l)** was suspended in 10% ethanolic sodium bicarbonate solution and refluxed for half an hour on water bath. During heating the reactant went into the solvent. After distillation of excess solvent yellow colour crystals were isolated. It was recrystallised from glacial acetic acid to obtain 1-phenylimino-3-phenylimino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IX l)**, yield 65%, m.p. 148^{0}C.

Properties of (IX l) : It was brown crystalline solid having m.p.148^{0}C. It gave positive test for nitrogen and sulphur. It was desulphurized when boiled with alkaline plumbite solution. It was soluble in benzene, acetic acid, dioxane, DMF and DMSO.

Elemental analysis: The result of elemental analysis are Carbon (found 59.70, Calculated 60.57), Hydrogen (found 2.98, Calculated 3.84), Nitrogen (found 20.19, Calculated 20.19) and Sulphur (found 14.51, Calculated 15.38). From the analytical data the molecular formula was found to be $C_{21}H_{16}N_6S_2$.

IR Spectrum of compound[32-36]**:** IR spectrum of compound was carried out in KBr pellets and reproduce on **IR Plate No. MSL-22**, the important absorptions are correlated -NH stretching at 3389.8 cm^{-1}, Ar-H stretching at 3200.12 cm^{-1}, C=NH stretching ring at 1553.12cm^{-1}, C-N stretching at 1254.2cm^{-1}, C=S stretching at 1091.8cm^{-1} and Monosubstituted benzene at 728.32cm^{-1}.

PMR-Spectrum: The PMR spectrum[37, 34, 38] of compound was carried out in $CDCl_3$ and DMSO-d_6 and reproduced on **PMR Plate No. MSL-22.** This spectrum distinctly displayed the signals due to Ar-protons at δ 6.1380-7.9602 ppm, NH proton at δ 5.5986 ppm, =NH proton at δ 3.6594 ppm and -CH proton at δ 2.3946-2.5937 ppm. From the above properties and spectral analysis of the compound **(IX l)** was assigned the structure as 1-phenylimino-3-phenylimino-2,4-dithio-6-(4-pyridineimino) amino-1,3,5-triazine **(IX l)**.



(IX l)

1-Phenylimino-3-phenylimino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine

Similarly, other substituted dithiazines were isomerized by 10% aqueous ethanolic solution by above mentioned method to isolate other substituted triazines respectively and described in **Experiment No. 3-15** and enlisted in **Table No.-I-5**

Table No. I-5

Expt. No.	2-**Substituted**imino-4-**substituted**imino-6-(4-pyridineimino)amino-1,3,5-dithiazines **(VIIIa-o)**	1-**Substituted**imino-3-**substituted**imino-2,4-dithio-6-(4-pyridineimino) amino-1,3,5-triazines **(IXa-o)**	**Yield (%)**	**m.p. (°C)**
3	2-**Ethyl**imino-4-**methyl**-imino-6-(4-pyridineimino) amino-1,3,5-dithiazine **(VIIIa)**	1-**Ethyl**imino-3-**methyl**-imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXa)**	70	211
4	2-**Ethyl**imino-4-**ethyl**-imino-6-(4-pyridineimino) amino-1,3,5-dithiazine **(VIIIb)**	1-**Ethyl**imino-3-**ethyl**-imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXb)**	71	250
5	2-**Ethyl**imino-4-**t-butyl**-imino-6-(4-pyridine-imino)amino-1,3,5-dithiazine **(VIIIc)**	1-**Ethyl**imino-3-**t-butyl**-imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXc)**	69	210
6	2-**Ethyl**imino-4-**p-chloro-phenyl**imino-6-(4-pyridineimino)amino-1,3,5-dithiazine **(VIIIe)**	1-**Ethyl**imino-3-**p-Cl-phenyl**imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXe)**	68	190
7	2-**Ethyl**imino-4-**o-tolyl**-imino-6-(4-pyridineimino) amino-1,3,5-dithiazine **(VIIIf)**	1-**Ethyl**imino-3-**o-tolyl**-imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXf)**	72	166
8	2-**Ethyl**imino-4-**m-tolyl**-imino-6-(4-pyridine imino) amino-1,3,5-dithiazine **(VIIIg)**	1-**Ethyl**imino-3-**m-tolyl**-imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXg)**	66	197
9	2-**Ethyl**imino-4-**p-tolyl**-imino-6-(4-pyridineimino) amino-1,3,5-dithiazine **(VIIIh)**	1-**Ethyl**imino-3-**p-tolyl**-imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXh)**	65	193
10	2-**Phenyl**imino-4-**methyl**-imino-6-(4-pyridineimino) amino-1,3,5-dithiazine **(VIIIi)**	1-**Phenyl**imino-3-**methyl**-imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXi)**	76	189
11	2-**Phenyl**imino-4-**t-butyl**-imino-6-(4-pyridineimino) amino-1,3,5-dithiazine **(VIIIj)**	1-**Phenyl**imino-3-**t-butyl**-imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXj)**	78	195
12	2-**Phenyl**imino-4-**p-chlorophenyl**imino-6-(4-pyridineimino)amino-1,3,5-dithiazine **(VIIIk)**	1-**Phenyl**imino-3-**p-Cl-phenyl**imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXk)**	70	207
13	2-**Phenyl**imino-4-**o-tolyl**-imino-6-(4-pyridineimino) amino-1,3,5-dithiazine **(VIIIm)**	1-**Phenyl**imino-3-**o-tolyl**-imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXm)**	72	229

14	2-**Phenyl**imino-4-**m-tolyl**-imino-6-(4-pyridineimino) amino-1,3,5-dithiazine **(VIIIn)**	1-**Phenyl**imino-3-**m-tolyl**-imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXn)**	68	180
15	2-**Phenyl**imino-4-**p-tolyl**-imino-6-(4-pyridineimino) amino-1,3,5-dithiazine **(VIIIo)**	1-**Phenyl**imino-3-**p-tolyl**-imino-2,4-dithio-6-(4-pyridineimino)amino-1,3,5-triazine **(IXo)**	68	178

ACKNOWLEDGEMENT

Author is very much thankful to S.A.I.F. Punjab University, Chandigarh for valuable help during this work.

References:

Hamady N.A., Abdel-Aziz H.A., Farog A.M.and Fakhr Issa.M.A., *Monatshefte fur chemie*., 138, **2007**,1001-1010.

Patel B.V., Patel H.S. and Patel K.C., *Ind.J.Chem*., -B, 47B (06), **2008**, 0376-4699.

Ali T. El-sayad and Ibrahim M.A. *J.Braz. Chem.Soc.*, 446(2117), **2010**, 1445-1468.

Chan-Thaw C.E., Villa A., Katekonon P., Sus D., Thomas A. and Prate L., *NanoLett.*, 10(2), **2010**, 537-541.

Kurumurthy C., Veeraswamy B. Rao P. S., Kumar G.S., Reddy V.L., Rao J.V. and Narsaiah B., *Bioorganic and Medicinal Chemistry Lett*., 24(3),**2014**, 746-749.

Sztanke K., Pasternak K., Rajtar B., Sztakne M., Majek M. and Polz-Dacewicz M., *J.Bioorganic and Med.Chem.*,15, **2007**, 5480-5486.

Simanek E.E., Abdou H., Lalwani S., Lim J.J., Mintzer M., Venditto V.J. and Vittur B., *Proc. R. Soc. A*, 466(2117), **2003**, 1445-1468.

Krutz L.J., Shaner D.L.,Weaver M.A., Webb R.M.T Zablotowicz R.M., Reddy K.N. Huang Y. and Thomson S.J., *Pest Management Sci.,* 66(5), **2010**, 461-481.

Lim J., Mintzer M.A., Perez L.M. and Simanek E.E., *Org.Lett.,* 12(6)**, 2010**, 1148-1151.

Mirano K.,*Chem. Abstr.,* 79, **1973**, 137200.

Zhuo J., He C., Yao W., *United States, Patent Application Publication,* US2013/0345224 A1, **2013**.

Pittis W.J., Guo J., Dhar T.G.,Shen Z., Gu H., Watterson S.H. and Bednarz M.S., *J.Bioorg.Med.Chem.,* 12(2), **1997**.

Hajiduk P.J., Dinges J., Schkeryantz J.M., Janowick D., Kaminski M., Tufano M., Augeri., *J.Med.Chem.,* 42, **1999**, 3852-3859.

Irikura T., Abe Y., Okamura K., Higo K., Maeda A., Morinaga F., Shirai G. And Hatae S., *J.Med.Chem.,* 13, **1970,** 1081-1089.

Bossinger C.D. and Tekeshi .,*Chem.Abstr.,* 77, **1972**, 34590.

Tani M., *Japan Patent,* 71(34), **1971**, 429.

Peultner F.E., *Chem*.Abstr., 72, **1970**, 111516.

Gaigu A.G., *Siess Patent*, 393, **1965**, 344.

Toye, Kobtan Industries Ltd., *Chem*.Abstr., 64, **1966**, 35744.

Cyril V. And Milan M., *Chem*.Abstr., 86, **1977**, 190015.

Davis J., *U.S.Patent*, 4, **1980**, 186, 265.

Bitzer D., *Chem, Abstr.*, 93, **1980,** 8217.

Costeacho S.,*Chem*.Abstr., 93, **1980**, 95301.

Alfred K. And Tantaway A., *Chem. Abstr.*, 90, **1979**, 54913.

Jiang H., Deng X., Wang J., Wamg J., Peng J., Zhou T., *PLoS ONE*, 9(4):e93654,doi.1013711/ Journal Pone 0093654, **2014.**

Jhala A.J., Sandell L.D., Rana N., Kruger G.R., and Khezevic S., *Weed Technology,* 28(1), **2014,** 28-38.

Helmut B., Willi K., Walfgang K., Edger M., And Peter R., *Germ. Offen*, 2, **1978**, 630/849; *Chem. Abstr.*, 88, **1978**, 152668.

Berrer D. And Garade R.,*Chem.Abstr.*, 92, **1980**, 58833.

Wetwitayaklung P., LimmatvapiratC., Phaechamucd T., *Indian Journal of Pharmaceutical Sciene* 756, **2013,** 649-656.

Matsuno T., Kato M., Sasahara H., Watanbe S., Inaba M., Takahash M., Yaguchi S.I., Yoshioka K., Sakato M., and Kawashima S., *Chem. Pharm. Bull*, 48, **2000,** 1778-1781.

Xiong Y. Z., Chen F.E., Balzarini J., Declercq E. and Pannecouque C., *Eur, J. Med, Chem*, 43, **2008**, 1230-1236.

Colthup N.B., Daly L.H., *Introduction of IR and Raman and S.E.Wiberley Spectroscopy,* Academic Press, New York, **1964**, p. 344.

Mota J. F., Manuel J., Fernandez G., Mellet C.O. and Adril M.A.P., *Carbohy.res*, **1989,** 188, 35-44.

R.M. Sliverstein, G.C. Bassler, T.C. Morill, Spectroscopic identification of organic compounds. 5th Ed, John Wiley and Sons, Inc, NewYork, **1991,** 109, 123, 127.

Tayade D.T., *Proc.*, 83rd *Ind. Sci. Cong.*, **1996**.

Shelke M.E., *Synthesis of 1,3-diformamidinothiocarbamide hydrochlorides derivatives and their cyclisation to substituted imino/amino 1,3,5-thiadiazine hydrochlorides and 1,3,5-triazines*, Ph.D. Thesis, S.G.B.Amravati University, Amravati **2005.**

Margareta Acaram and Maleesov C.H., *Infrared Spectroscopy application in organic compounds*, 5th Ed, John Wiley and Sons, Inc, NewYork, **1970,** 293.

Willams D.H. and Fleming J., *Spectroscopic methods of organic chemistry*, 4th Tata McGraw Hill, NewDelhi, 55.

❖❖❖❖❖