



Research Article

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Design, synthesis and characterization of novel series of 1,2,4-dithiazole based chalcones

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ABSTRACT

Single step synthesis of (2E)-1-[4-(3-substitutedimino-1,2,4-dithiazolo)aminophenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**II-e**) was carried out by oxidative cyclisation of (2E)-1-[4-(5-substituted-2,4-dithiobiureto)phenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**Ia-e**) using liquid bromine in chloroform medium as an oxidizing agent. The products were isolated, characterized and justified on the basis of conventional elemental analysis, chemical characteristics and spectral studies.

INTRODUCTION

Organic compounds containing thiaziazole as the heterocycles in their structure are identified for their biological activities, pharmaceutical activities, industrial applications, agricultural purposes and in medicinal sciences. Basically structure of thiaziazole is five membered nitrogen and sulphur containing heterocyclic compound. Presence of sulphur and nitrogen in its structure enhances the biological potential of the thiaziazole. Recently reported some newer thiaziazole along with pyridine for the anti-bacterial activities² and effect of germination pattern of jowar, Bhagwatkar³ synthesized and reported the thiaziazole based triazine for the antibacterial activities and some different substituent's attached thiaziazole directly or indirectly shows effect directly in their biological, pharmaceutical and agricultural applications. The chalcone based heterocycles are five membered heterocycles containing sulphur and nitrogen as a heteroatoms were created its own background in the synthetic organic chemistry. The biological as well as industrial applications of chalcones get enhanced due the presence of the thiaziazole nucleus in their structure. Trusting the literature ideas in mind it is decided to design such organic moiety should contain thiaziazole along with the chalcones, to synthesize such series of chalcone based five member heterocycle containing sulphur and nitrogen as a heteroatom.

As a part of research work presently it has been planned to design and synthesize novel series of (2E)-1-[4-(3-substitutedimino-1,2,4-dithiazolo)aminophenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**IIa-e**) in this laboratory with the easiest and cheaper method by oxidative cyclisation of (2E)-1-[4-(5-substituted-2,4-dithiobiureto)phenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**Ia-e**) with liquid bromine in chloroform medium. The present method utilized somewhat suitable, convenient, cheaper, more practical utility and only a single step direct method for the synthesis of (**IIa-e**).

EXPERIMENTAL SECTION

Materials:

All chemicals used were of Mercks Millipore (Indian made). (2E)-1-[4-(5-substituted-2,4-dithiobiureto)phenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**Ia-e**) were prepared by known literature method³.

Method:

Method employed in the present experiments for the synthesis of series 1,2,4-dithiazole based chalcones is conventional refluxing under water bath for different hours for different experiments.

The melting points of synthesized compounds were recorded using hot paraffin bath. The carbon and hydrogen analysis was carried out on Carlo-Ebra-1106 analyzer while Nitrogen estimation was carried out on Colman-N-analyzer-29. IR spectra were recorded on Perkin Elmer spectrometer in the range 4000-400 cm⁻¹ in KBr pellets. PMR spectra were recorded on BRUKER AIIANCE II 400 NMR spectrometer with TMS as an internal standard using CDCl₃ and DMSO-d₆ as a solvent. The purity of the compounds was checked on silica gel – G plates by TLC with layer thickness of 3mm.

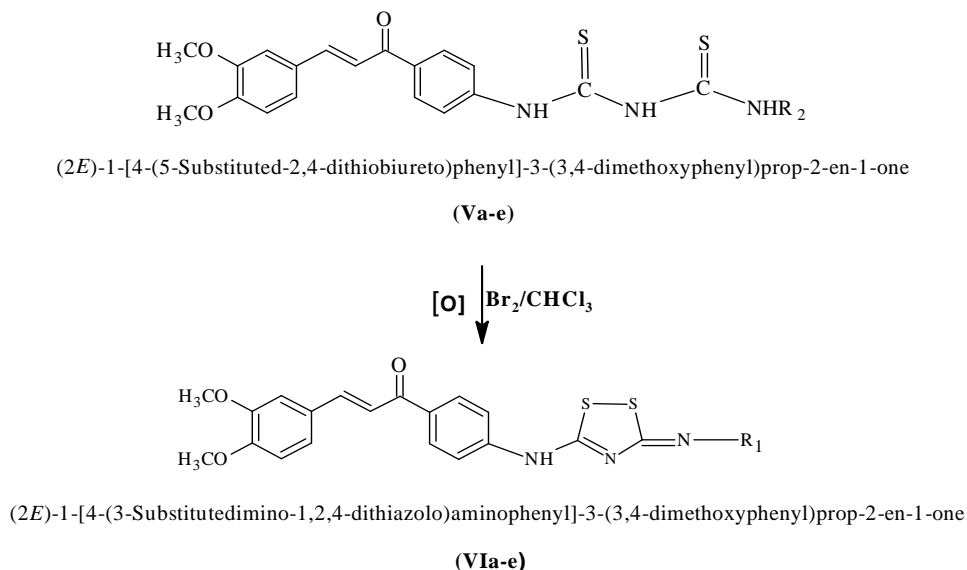
General Procedure:**Experiment No. 1****Synthesis of (2E)-1-[4-[3-(prop-2-en-1-imino)-3H-1,2,4-dithiazol-5-yl]aminophenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**IIa**):**

The pest of (2E)-1-[4-[5-phenyl-2,4-dithiobiureto]phenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**Id**) was prepared in chloroform in a clean china dish and liquid bromine in chloroform was added with constant stirring at room temperature. During the addition of bromine in chloroform solution to the pest of (**Ia**), firstly the colour of bromine disappear, further addition of bromine in chloroform colour of bromine appears and persists. Such solution of bromine in chloroform and (**Ia**) kept for 4 hours at room temperature. Basification of the reaction mixture with dilute ammonium hydroxide solution gives the formation bright cream yellow coloured product (**IIa**). Recrystallization of the product was done using ethanol.

Yield 89% M. P. 172^oC.

Similarly, (2E)-1-[4-[3-(prop-2-en-1-imino)-3H-1,2,4-dithiazol-5-yl]aminophenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**IIa**), (2E)-1-[4-[3-ethylimino-3H-1,2,4-dithiazol-5-yl]aminophenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**IIb**), (2E)-1-[4-[3-(2-methylprop-2-imino)-3H-1,2,4-dithiazol-5-yl]aminophenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**IIc**), (2E)-1-[4-(3-phenylimino-3H-1,2,4-dithiazol-5-yl)aminophenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**Id**) and (2E)-1-[4-[3-(4-chlorophenylimino)-3H-1,2,4-dithiazol-5-yl]aminophenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**IIf**) were synthesized from the oxidative cyclisation of (2E)-1-[4-[5-(prop-2-en-1-yl)-2,4-dithiobiureto]phenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**Ia**), (2E)-1-[4-(5-ethyl-2,4-dithiobiureto)phenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**Ib**), (2E)-1-[4-[5-(2-methylprop-2-yl)-2,4-dithiobiureto]phenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**Ic**), (2E)-1-[4-[5-phenyl-2,4-dithiobiureto]phenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**Id**) and (2E)-1-[4-[5-(4-chlorophenyl)-2,4-dithiobiureto]phenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (**Ie**) with liquid bromine in chloroform medium respectively by the above mentioned method in **Experiment No. 1 to 5** and the data obtained by the characterization of synthesized compound in a series (**IIa-e**) is given result section.

Reaction Scheme:



Where R₁ = -allyl, ethyl, -t-butyl, -phenyl, -p-cl-phenyl

Scheme

RESULTS AND DISCUSSION

Spectral data obtained from the present research support the formation of designed or target products. Spectral characterizations of all the synthesized compounds are also given below:

Data Analysis:

(2E)-1-[4-[3-(prop-2-en-1-imino)-3H-1,2,4-dithiazol-5-yl]aminophenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (IIa):

Cream Yellow solid, C₂₂H₂₁N₃O₃S₂, Yield-89%, M.P. 172, % Composition-found(calculated) C-59.67(60.11), H-5.42(4.82), N-9.56(9.56), S-14.1(14.59), **FTIR (KBr) v cm**-3085.89-3004.89 (Ar C-H stretching), 574.75(S-S stretching), 1587.31 (S-C=N stretching), 794.62-761.83 (C-S stretching), 1685.67 (C=O Stretch amido), 1027.99 (C-O-CH₃Stretching); **¹H NMR (400 MHz CDCl₃ δ ppm)**, singlet of 6H of -OCH₃ at δ 3.83-3.74ppm, doublet of 2H of -CH=CH- at δ 3.59, 3.15ppm, singlet of 1H of NH at δ 8.72ppm, pentate of 1H, doublet 2H and doublet of 2H of allyl at δ 2.17, 1.32 and 2.07respectively and multiplet of 7H of Ph at δ 6.37-7.79ppm; Mol. Wt.:439.

(2E)-1-[4-[3-(ethylimino)-3H-1,2,4-dithiazol-5-yl]aminophenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (IIb):

Dark Yellow solid, C₂₁H₂₁N₃O₃S, Yield-92%, M.P. 168°C, Composition-found(calculated) C-59.52 (58.99), H-4.82 (4.95), N-9.83(9.83), S-13.82(15.00), **FTIR (KBr) v cm**-3085.89-3004.89(Ar-H Stretching), 574.75(S-S stretching), 1587.31(-C=N stretching), 794.62-761.83(C-S stretching), 1685.67(C=O stretching) and 1027.99(C-O-C stretching); **¹H NMR (400 MHz CDCl₃ δ ppm)**, singlet of 6H, OCH₃ at δ3.88, 3.89ppm, doublet of 2H of -CH=CH- at δ 3.62, 3.20ppm, multiplet of 7H, Ph at δ 6.52-8.01ppm, singlet of 1H, NH at δ 8.35ppm and quartet of 2H and triplet of 3H of ethyl at δ1.42 and δ 1.37respectively; Mol. Wt.: 427.

(2E)-1-[4-[3-(2-methylprop-2-imino)-3H-1,2,4-dithiazol-5-yl]aminophenyl]-3-(3,4-dimethoxyphenyl) prop-2-en-1-one (IIc)

Yellow solid, C₂₃H₂₅N₃O₃S₂, Yield-84%, M.P. 179°C, Composition-found(calculated) C-60.51 (60.63), H-5.56 (5.53), N-9.25 (9.22), S-14.10 (14.08), **FTIR (KBr) v cm**-3085.89-3004.89 (Ar-H Stretching), 574.75 (S-S stretching), 1587.31 (-C=N stretching), 794.62-761.83 (C-S stretching), 1685.67 (C=O stretching) and 1027.99 (C-O-C stretching); **¹H NMR (400 MHz CDCl₃ δ ppm)** singlet of 9H, CH₃ at δ 1.36ppm, singlet of 6H, OCH₃ at δ 3.88-3.89ppm, doublet of 2H of -CH=CH- at δ 3.68, 2.61ppm, multiplet of 7H, Ph at δ 7.97-6.02ppm and singlet of

¹H, NH at δ 9.26ppm; ESI-MS (m/z) base at m/z+=139.00, 74.04, 227.05 and molecular ion i.e. molecular weight is 455..

(2E)-1-[4-[3-phenylimino-3H-1,2,4-dithiazol-5-yl]aminophenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (IIc)

Yellow, C₂₅H₂₁N₃O₃S₂, Yield-88%, M.P. 174°C, Composition-found(calculated) C-63.02 (62.87), H-4.57 (4.85), N-8.70 (8.70), S-13.43 (13.48), FTIR (KBr) ν cm- 3056.96-3004.89 (Ar-H Stretching), 592.11 (S-S stretching), 1587.31 (-C=N stretching), 794.62-761.83 (C-S stretching), 1685.67 (C=O stretching) and 1027.99 (C-O-C stretching); ¹H NMR (400 MHz CDCl₃ δ ppm), singlet of 6H, -OCH₃ at δ 3.90-3.96ppm, doublet of 2H of -CH=CH- at δ 3.87, 3.22ppm, multiplet of 12H, Ph at δ 6.11-8.02ppm and singlet of 1H, -NH at δ 8.34ppm; ESI-MS (m/z) gives base at m/z+=226.98, 74.90, 359.93 and molecular ion i.e. molecular weight is 475.

(2E)-1-[4-[3-(4-chlorophenylimino)-3H-1,2,4-dithiazol-5-yl]aminophenyl]-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (IIe):

Yellow solid, C₂₂H₂₀N₃O₃S₂Cl, Yield-509.5%, M.P.-156°C Composition-found(calculated) C-59.2(58.88), H-3.56(3.95), N-8.24 (8.24), S-12.68(12.57) and Cl-6.76(6.95); FTIR (KBr) ν cm-3056.96-3004.89(ArC-H stretching), 592.11(S-S stretching), 1587.31(S-C=N stretching), 794.62-761.83 (C-S stretching), 1685.67 (C=O Strech amido) and 1027.99 (C-O-CH₃Strching); ¹H NMR (400 MHz CDCl₃ δ ppm) singlet of 6H, -OCH₃ at δ 3.86-3.93ppm, doublet of 2H of -CH=CH- at δ 3.79, 3.27ppm, multiplet of 11H, Ph at δ 6.23-7.91ppm and singlet of 1H, -NH at δ 8.31ppm; Mol. Wt.: 509.5.

In the present work is best cheaper and less time consuming method of cyclisation of organic compound. Route of mechanism of the present synthesis is due to the conjugation of amido-H with thionyl Sulphur. Among all the synthesised of compounds (IIa-IIe), percentage of yield of compound (IIb) is highest i.e. 92%.. However (IIa) and (IIc) shows comparable yield with the (IIb).

CONCLUSION

In all the synthesised compounds, maximum yield of (IIb) displays ethyl group is electrometrically donating group on nitrogen in 2,4-dithiobiurets with increases the rate of reaction by giving its electrons.

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