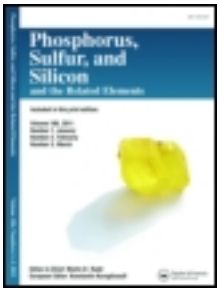

Phosphorus, Sulfur, and Silicon and the Related Elements

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REACTIONS OF 5-SUBSTITUTED-2-THIOXO-4-OXO-1,3-THIAZOLIDINES WITH 4-METHOXYPHENYLAZIDE

Mohamed T. Omar [a], Ahmed S.A. Youssef [a] & Kamal A. Kandeel [a]

[a] Chemistry Department, Faculty of Science, Ain Shams University, Abbassia, Cairo Egypt

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REACTIONS OF 5-SUBSTITUTED –2-THIOXO-4-OXO-1,3-THIAZOLIDINES WITH 4-METHOXYPHENYLAZIDE

MOHAMED T. OMAR*, AHMED S.A. YOUSSEF and KAMAL A. KANDEEL

Chemistry Department, Faculty of Science, Ain Shams University, Abbassia, Cairo Egypt

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4-Methoxyphenylazide cycloadds to the thiono function and undergoes nucleophilic attack at other electrophilic centers of 5-benzoylmethyl- (**1a**) and E,Z-5-(4-bromobenzoylmethylene)- (E,Z-**2b**) –2-thioxo-4-oxo-1,3-thiazolidines in non site selective reactions to afford variety of products. With **1a**, the attack at the thiono as well as the hetero-ring carbonyl functions leads to the 5-benzoylmethylene-2-(4-methoxyphenylimino)- derivative (**3**) and the ring fission product Z-**4**. Similar treatment of E,Z-**2b** gives a mixture of the respective E,Z-2-(4-methoxyphenylimino)-derivative (E,Z-**5**) containing 80% of the Z-configurated isomer (Z-**5**) and the ring enlarged thiazinonethione derivative (**6**), due to the attack at the thiono and exocyclic double bond functions, respectively. Rationalizations for the above mentioned conversions are given. Structures of all products are evidenced by microanalytical and spectral data.

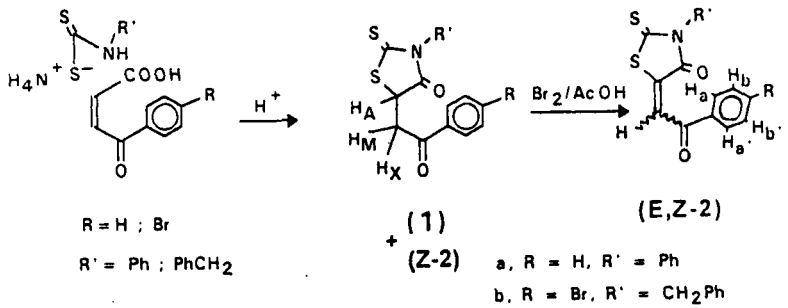
The chemistry of 4-thiazolidinones has been a subject of a series of publications[1–6] from this laboratory. Reactions of 2-thioxo-4-thiazolidinones with dipolar species in the literature are rather limited and treat the problem of alkylation of the 3-unsubstituted derivatives with diazomethane[7,8], and cycloaddition of nitrilimines to the thiono function of 5-aroylmethylene-3-phenyl-2-thioxo-4-oxo-1,3-thiazolidine[9]. The present work aimed to study the reactivity of different functions in 5-alkyl-

* Corresponding Author.

and 5-alkylidene substituted thiazolidones namely 3-phenyl-5-(2-phenyl-2-oxoethyl)-(**1a**) and E,Z-3-benzyl-5-(4-bromophenylmethylene)-(E,Z-**2b**)-4-oxo-2-thioxo-1,3-thiazolidines towards reaction with 4-methoxyphenylazide.

RESULTS AND DISCUSSION

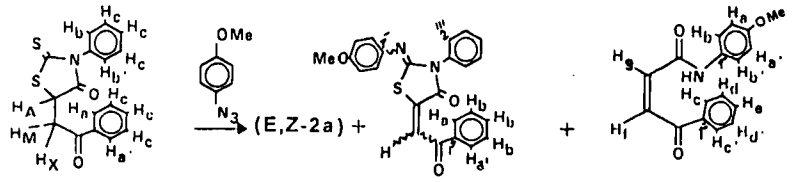
In addition to compounds **1a,b** which were synthesized following the method of Nagase[10] by treating the respective aroylpropenoic acids with ammonium phenyldithiocarbamate and ammonium benzyldithiocarbamate, respectively, few crystals of Z-**2a** and Z-**2b** were obtained by allowing mother liquors to stand at room temperature overnight. Compound **2b**, which was obtained by treating **1b** with bromine in acetic acid (**Scheme 1**), is undoubtedly a mixture of E- and Z- isomers, as Omar et.al[2] who studied the stereochemistry of the above mentioned reaction, reported the formation of the E,Z-isomers. However, the poor solubility of **2b** in most deuterated solvents don't allow for accurate estimation of the E/Z ratio. The Z- configuration has been assigned to Z-**2b** based on compairing its ^{1}H NMR spectrum with that of E,Z-**2b**. The Z-configurated isomers are relatively deshielded as compaired with the E- counterparts[1].



SCHEME 1

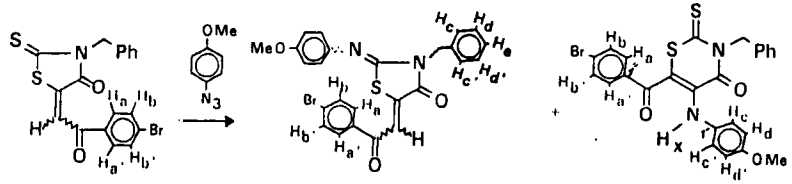
4-Methoxyphenylazide reacts with 3-phenyl- 5-(2-phenyl-2-oxoethyl)-4-oxo-2-thioxo-1,3-thiazolidine (**1a**) to afford E,Z-5-benzoylmethylene-3-phenyl-4-oxo-2-thioxo-1,3-thiazolidine (E,Z-**2a**, 28.5%) containing

85% of the Z-isomer, 5-benzoylmethylene-2-(4-methoxyphenylimino)-3-phenyl-4-oxo-1,3-thiazolidine (**3**, 50%) and Z-1-(4-methoxyphenylamino)-4-phenyl-1,4-dioxo-but-2-ene (Z-**4**, 21.5%) in an overall yield of 70%.



(1a) (E,Z-2a) + (3) + (Z-4)

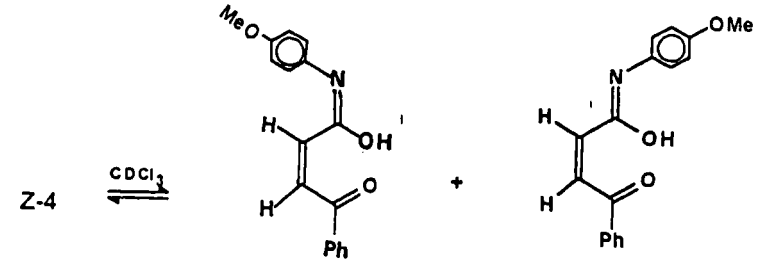
Similar treatment of E,Z-3-benzyl-5-(4-bromobenzoylmethylene)-4-oxo-2-thioxo-1,3-thiazolidine (E,Z-**2b**) with 4-methoxyphenylazide yielded E,Z-3-benzyl-5-(4-bromobenzoylmethylene)-2-(4-methoxyphenylimino)-4-oxo-1,3-thiazolidine (E,Z-**5**, 36%), (Z-**5**, 12%) and 3-benzyl-6-(4-bromobenzoyl)-5-(4-methoxphenylamino)-2,3-dihydro-4-oxo-2-thioxo-4H-1,3-thiazine (**6**, 17%) in addition to recovered E,Z-**2b** (35%), in an overall yield of 85%.



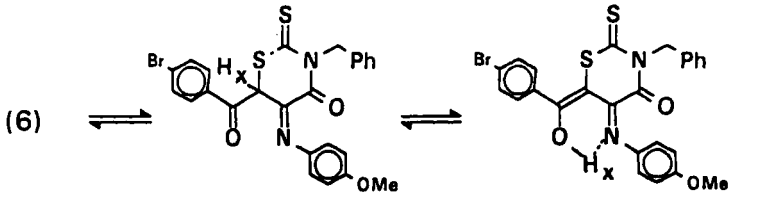
(E,Z-2b) (E,Z-5) ,(Z-5) (6)

Structures of compounds **2–6** are deduced from microanalytical and spectral data. The infrared spectra of compounds **2,3,5** and **6** show two νC=O absorptions consistent with the hetero-ring and aroyl carbonyl functions. The spectra of **2** and **6** exhibit νC=S, whereas those of **3, 5** and **5′** are devoid of it, but show strong νC=N absorptions. The infrared spectrum (KBr) of **4** exhibits νNH and νC=O absorptions. The ^{1}H NMR spectra of **2a** and **3**, don't show the characteristic AMX pattern of the $CH{\cdot}CH_2COAr$ moiety, but exhibit, instead, vinyl proton singlets, which is consistent with a 5-benzoylmethylene- rather than a 5-benzoylethyl- system. Moreover, the spectra of **3** and **5** show the expected resonances of the 4-methoxyphe-

nyl moiety The structure of **3** gets a further support by ^{13}C NMR spectroscopy as its spectrum showed the resonances consistent with the given structure. In chloroform solution, the ^{1}H NMR spectrum of **4** reveals the existence of two hydroxyimino isomers namely 1-Z-,3-Z- and 1-E,3-Z-azabut-1,3-dienes, in the ratio of 3:7, respectively, based on the integration of methoxyl protons singlets. Configurational assignment around the C=N function of the hydroxyimino derivatives is based on the expected higher shielding effect exerted by a trans-rather than by a cis hydroxyl group on the neighbouring 4-methoxyphenyl- group, a phenomenon manifested in the ^{1}H NMR and ^{13}C NMR spectra of these compounds. A similar observation has been observed in the ^{1}H NMR spectra of E- and Z- oximes[12]. Compound **6** exists in chloroform solution as a mixture of tautomers **6, 6a** and **6b** involving the acidic proton (H_x) and the neighbouring C=N and C=O groups, in the ratio of 70:15:15%, respectively. Location of H_x of **6a** as two closely spaced singlets infers the existence of axial and equatorial conformations. Moreover, the ^{13}C NMR spectrum ($CDCl_3$) shows the resonances consistent with **6**, beside a resonance at 47.2 ppm consistent with the ring sp3 carbon atom of **6a**.



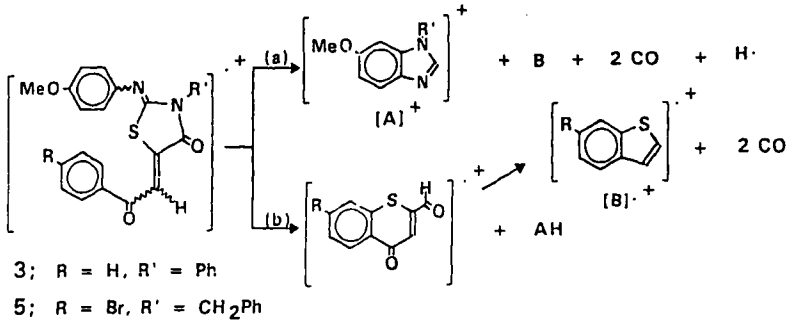
1-E,3-Z- (4) 1-Z,3-Z- (4)



(6a) (6b)

The structure of **2a** is confirmed by comparison (m.p., IR and ^{1}H NMR) with an authentic sample prepared by treating **1a** with bromine in acetic acid

The El mass spectra of **3** and **6** show correct molecular ion peaks whereas those of **4** and **5** show the [M.$^+$-2] and [M.$^+$-15]fragments respectively. The base peaks are the aroyl fragments in **3**, **4** and **6** and the tropylium cation in **5**. The common fragments of **3** and **5** are produced via the pathway presented in **Scheme 2**. It is evident that the cleavage shown will lead to fragments [A$^+$] and [B.$^+$] depending on whether the positive charge is rested on the hetero ring nitrogen (route a) or sulfur (route b) atoms, respectively.



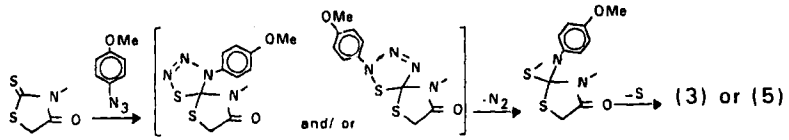
SCHEME 2

Configurational assignments to E,Z-**2a**, Z-**2a** and E,Z-**5** are based on the assumption that the vinylic proton of the Z-configurated isomers are more deshielded by the 4-oxo- group as compared with the E- counterparts. This relationship is an accepted assumption in the elucidation of the configuration of arylidene derivatives of azalactones[11a], indolones[11b] and pyazolin-5-ones[11c]. The Z- configurated isomers constitute 85% of E,Z-**2a** and 80% of-E,Z-**5**.

The Z-configuration has been conferred to compound **4** on the basis of the observed coupling constant of the doublets of the olefinic hydrogens.

Conversion of the 2-thiono compounds **1a** and **2b** to the respective 2-(4-methoxyphenylimino)- derivatives **3** and **5** involved the 1,3-cycloadduct spiro-1,2,3,4-thiatriazoles **7** and/or **8** as intermediates[13] which undergo elimination of nitrogen and sulfur, most likely via spiro cyclic thi-

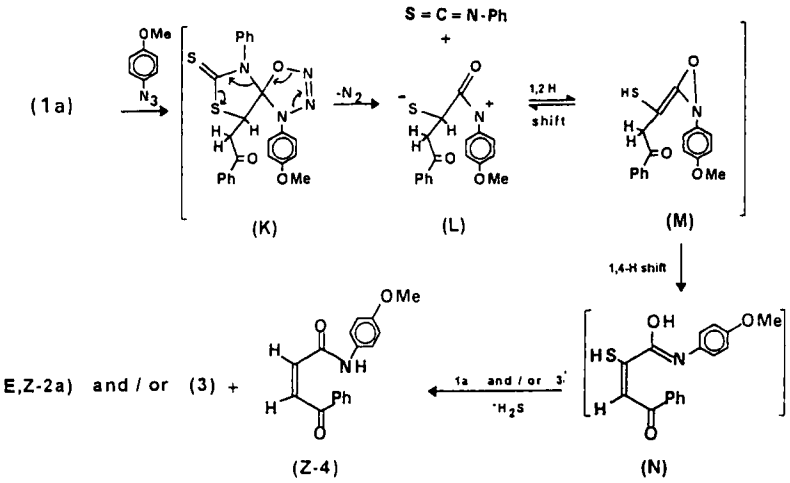
aziridene (**9**).[14,15] Elimination of sulfur in a similar sequence was observed in several reactions.[13,16] Conversion of thiocarbonyl compounds to imines by reaction with organoazides is documented.[13,17,18] Huisgen et.al[19] reported that the preference for dipolar species to react with thiono rather than oxo groups was attributed to the polarisability of the sulfur function. Formation of the 5-benzoylmethylene derivative (**3**) rather than the expected 5-(2-phenyl-2-oxoethyl)- derivative (**3'**) is rationalized in terms of the ease air oxidation of similar systems.



(7) (8) (9)

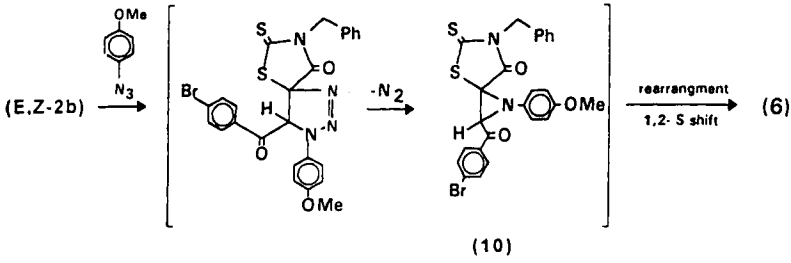
Conversion of **1a** into **2a, 3** and Z-**4** upon treating **1a** with 4-methoxyphenylazide could be explained by the route mentioned in Scheme 3. The cycloadduct (K) obtained by attack of the azide molecule at the 4-oxo-group of the heteroring of **1a** eliminates phenylisothiocyanate and nitrogen to give the dipolar species (L). Successive 1,2-proton shift and cyclization of L affords the oxazeridine (M) which in turn undergoes ring opening via a 1,4-poton shift to give N. A hydrogen transfer reaction of N with **1a** and/or 2-(4-methoxyphenylimino)-3-phenyl-5-(2-phenyl-2-oxoethyl)-4-oxo-1,3-thiazolidine (**3'**) to give Z-**4** in addition to **2a** and/or **3**, respectively. The last step has occurred, momst likely, via addition of hydrogen to the enethiol bond of N followed by elimination of hydrogen sulphide gas. Isolation of phenylisothiocyanate from the reaction mixture via chromatography supports the assumed route. Participation of compounds **1** as hydrogen donors gets a support from the ease conversion of **1** into **2** (cf. exp), which is believed to occur via air oxidation.

Formation of **6** is interpreted in **Scheme 4** where initial [3+2] cyclo-addition of azide molecule to the exocyclic double bond of **2b** leads to the unstable spiro dihydrotriazole ring system. The zwitterion formed after spiro ring opening eliminates nitrogen and the aziridine intermediate **10** obtained undergoes ring expansion to the thiazine (**6**). Ring expansion occurs by a 1,2-shift of the more soft sulfur atom of the thiazolidinone ring rather than by the nitrogen atom of the aziridine ring. This route is supported by the observation of Quast et.al[20,21] who reported the formation of



SCHEME 3

5-imino-1,4,5,6-tetrahydro-1,2,3,4-tetrazines upon treating 5-alkylidene tetrazoles with electrophilic azides via a ring enlargement process. Although few aziridines are isolated upon treating sulphonium ylides[22] and olefines[23] with azides, this is not our case as the ^{1}H NMR spectrum of **6** don't show the aziridine ring proton.



SCHEME 4

EXPERIMENTAL

All melting points are not corrected. IR Spectra were measured on a Unicam SP1200 Spectrometer as KBr discs. Unless otherwise stated the ^{1}H

NMR spectra were measured in $CDCl_3$ solutions on Varian Gemini 200 MHz or Brucker ES200 MHz Instruments with chemical shifts (δ) expressed in ppm downfield from Me_4Si. ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on Jeol, 75 MHz instrument. Mass spectra were recorded on Shimadzu GC-MS-Qp 1000EX or Finnigan GCQ Instruments operating at 70ev. Column chromatography and TLC were runned on Silica Gel Voeim, activity III/30mm according to Brockmann & Schodder and TLC aluminium sheets Silica Gel 60 F_{254} (Merck).

Reactions of 3-Aroyl-2-propenoic acids with Ammonium dithiocarbamates

Ammonium phenyldithiocarbamate (2.0 g, 10.75 mmol) or ammonium benzyldithiocarbamate (2.1 g, 10.75 mmol) is added portionwise to a stirred solution of 3-benzoyl-2-propenoic acid[24] (1.75 g, 10 mmol) or 3-(4-bromobenzoyl)-2-propenoic acid[24] (2.54 g, 10 mmol) in ethanol (10 ml) and the whole mixture is stirred for 30 min. at room temperature. The solid precipitated after addition of conc. hydrochloric acid (3 ml) is filtered off to give **1a** or **1b** and the mother liquor is left to stand at room temperature to afford Z-**2a** or Z-**2b**.

3-Phenyl-5-(2-Phenyl-2-oxoethyl)-4-oxo-2-thioxo-1,3-thiazolidine (1a)

2.9 g (88%), colourless crystals (benzene-ethanol), m.p. 138–139 C; IR: ν= 3040 (aryl-H), 2910 (alkyl-H), 1735,1670 (C=O), 1060 (C=S), 735, 685 cm^{-1}; ^1H NMR: δ = 3.76 (dd. H_X, J_{AX} = 9.2 Hz, J_{MX} = 18.6 Hz), 4.10 (dd, H_M, J_{AM}= 3.2 Hz), 4.73 (dd, H_A), 7.29 (dd,H_b,$H_{b'}$ J_o = 8.0Hz, J_{m-} = 1.4Hz), 7.45–7.67 (m, 6H_c), 7.96(d, H_a,$H_{a'}$, J = 8.0 Hz). Anal. Calcd for $C_{17}H_{13}NO_2S_2$: C, 62.36; H, 4.00; N, 4.28. Found: C, 62.45; H, 4.10; N, 4.15%.

Z-5-Benzoylmethylene-3-phenyl-4-oxo-2-thioxo-1,3-thiazolidine (Z-2a)

0.1 g (3%), lemon yellow crystals (benzene), m.p. 216–218 C. IR: ν= 3060 (aryl-H), 1725, 1635 (C=O), 1040 (C=S), 735, 690 cm^{-1}; ^1H NMR: δ = 7.32 (d, 2 ortho hydroges N-Ph), 7.57 – 7.76 (m, 6H, rest of aromatic H), 8.06 (s, = H), 8.16 (d, H_a, $H_{a'}$, J = 7.6 Hz). Anal. Calcd for

$C_{17}H_{11}NO_2S_2$: C, 62.75; H, 3.40: N, 4.30; Found: C, 62.63; H, 3.55: N, 4.20%

3-Benzyl-5-(2-(4-bromophenyl)-2-oxoethyl)-4-oxo-2-thioxo-1,3-thiazolidine (1b)

3.6 g (85%), colourless crystals (benzene), m.p. 128–130 C, Lit.[25], m.p. 128–129 C.

Z-3-Benzyl-5-(4-bromobenzoylmetylene)-4-oxo-2-thioxo-1,3-thiazolidine (Z-2b)

0.1 g (2.4%), golden yellow crystals (glacial acetic acid) m.p. 254–256 C. IR: ν = 1725, 1650 (C=O), 1050 (C=S), 830, 750, 690. ^{1}H NMR; δ = 5.27 (s, $\underline{CH_2}$-Ph), 7.34 (br s, $5H_{phenyl}$), 7.83 (d, H_b, $H_{b'}$, J = 8.6 Hz), 8.14 (s, = H), 8.16 (d, H_a, $H_{a'}$, J = 8.6 Hz). Anal. Calcd for C_{18} H_{12} $BrNO_2S_2$: C, 51.68; H, 2.89; N, 3.35 Found: C, 51.63; H, 2.88; N, 3.55%.

E,Z-3-Benzyl-5-(4-bromobenzoylmethylene)-4-oxo-2-thioxo-1,3-thiazolidine (E,Z-2b)

To a solution of **1b**[25] (4.2 g, 10 mmol) in glacial acetic acid (20 ml), bromine (1.9 g, 12 mmol) is added and the whole mixture warmed on a water bath for 5 min. The cold reaction mixture is diluted with water and the precipitated product is filtered off and recrystallized from glacial acetic acid to give 5-E,Z- **2b**: 3.35 g (80%); golden yellow crystals; m.p. 54–256 C; IR: ν = 1725, 1650 (C=O), 1050 (C=S), 830, 750, 700 cm^{-1}. Anal. Calcd for $C_{18}H_{12}BrNO_2S_2$: C, 51.68; H, 2.89; N, 3.35, Found: C, 51, 45; H, 2.75; N, 3.59%.

Reaction of 1a with 4-Methoxyphenylazide

A mixture of 4-methoxyphenylazide[26] (0.9 g, 6.0 mmol) and **1a** (1.0 g, 3.0 mmol) is refluxed in anhydrous toluene (30 ml) for 20 h and the concentrated solution (10 ml) is left to stand at room temperature overnight to precipitate E,Z-**2a**. The toluene mother liquor is concentrated (3.0 ml) and chromatographed over silica gel. Successive elution with light petroleum

(b.p. 40–60) produces phenylisothiocyanate then with petroleum ether (b.p. 40–60)/ ether (2:1 V/V) gives **3** and further elution with petroleum ether (b.p. 40–60)/ether (1:1 V/V) afforded first Z-**4** then an additional amount of E,Z-**2a**. Separation was monitored by TLC. Phenylisothiocyanate: b.p. 221 C, identical (IR and ^{1}H NMR) with an authentic sample.

E,Z-5-Benzoylmethylene-3-phenyl-4-oxo-2-thioxo-1,3-thiazolidine (E,Z-2a)

0.19 g (20%); orange crystals (benzene); m.p. 216–218 C; IR: ν = 3060 (aryl-H), 1725, 1635 (C=O), 1040 (C=S), 735, 690 cm^{-1}; ^{1}H NMR: δ = 7.26–7.31 (m, $2H_{arom}$), 7.52–7.63 (m, $6H_{arom}$), **for Z-isomer**: δ = 7.67 (d, H_a, $H_{a'}$, $J_{ab} = J_{a'b'}$ = 9.0 Hz), 8.10 (s, = H); **for E-isomer**: δ= 8.11 (d, H_a, $H_{a'}$, $J_{ab} = J_{a'b'}$ = 9.0Hz), 8.02 (s, = H). Anal. Calcd for $C_{17}H_{11}NO_2S_2$: C, 62.75; H, 3.40; N, 4.30. Found: C, 62.94; H, 3.25; N, 4.10%.

5-Benzoylmethylene-3-phenyl-2-(4-methoxyphenylimino)-4-oxo-1,3-thiazolidine (3)

0.43 g (35%); red needles (benzene); m.p. 163–165 C; IR: ν = 3080 (aryl-H), 1720 (C=O), 1622 (C=N), 825, 750, 700 cm^{-1}; ^{1}H NMR: δ = 3.86 (s, OMe), 6.95 (dAB_q,$4H_{anisyl}$), 7.48–7.61 (m, $5H_{phenyl}$), 7.68 (app t, $3H_b$), 8.12 (d, H_a, $H_{a'}$, $J_{ab} = J_{a'b'}$ = 7.12Hz), 8.18 (s, = H); ^{13}C NMR: δ = 188.8(C-7), 165.4 (C-4), 157.2 (C-2), 152.8 (C-4′), 141.9 (C-1′), 140.5 (C-5), 136.7 (C-1″), 133.9 (C-1″), 129.4 (C-6), 129.3, 129.0, 128.9, 128.4, 122.2, 114.4 (aromatic methine C), 55.5 (OCH_3); MS:m/z = 399 (8.3%) [M.$^+$- Me], 252 (12%) [M.$^+$- Me – CO – PhNCC], 223 (4.0%) [A^+], 134 (2.7%) [B^+], 105 [Base]. Anal. Calcd for $C_{24}H_{18}N_2O_3S$: C, 69.55; H, 4.38; N, 6.76. Found: C, 69.63; H, 4.46; N, 6.87%.

Z-1-(4-Methoxyphenylamino)-4-phenyl-1,4-dioxo-but-2-ene (Z-4)

0.13 g (15%); colourless crystals (benzene); m.p. 210–212 C; IR: ν = 3300 (O-H), 3210 (N-H), 3100, 3050 (aryl-H), 1680 (C=O), 740, 690 cm^{-1}; ^{1}H NMR: **for 1-E-3-Z- tautomer**: δ = 3.86 (s, OMe), 7.10 (d, H_a, $H_{a'}$, $J_{ab} = J_{a'b'}$ = 8.88Hz), 7.39 (app t, H_d, $H_{d'}$, H_e, $J_{de} = J_{d'e'}$ = 7.26Hz), 7.51 (d,

H_b, $H_{b'}$, $J_{ab} = J_{a'b'} = 8.88$Hz), 7.63 (d, H_f, $J_{fg} = 7.78$Hz), 7.79 (d, H_g), 8.31 (d, H_c, $H_{c'}$, $J_{cd} = J_{c'd'} = 7.26$Hz), 11.76 (s, OH); ^{13}C NMR: $\delta = 190.5$ (C-5), 167.0 (C-2), 154.2 (C-4′), 137,6 (C-1″), 135.7 (C-1′), 134.6 (C-4″), 131.8 (C-4), 130.1 (C-2″), 129.4 (C-3″), 128.8 (C-3), 121.6 (C-2″), 120.7 (C-3″), 55.9 (OCH_3)). **for 1-Z-3-Z-tautomer**: $\delta = 3.93$ (s, OMe), 6.97 (d, H_a,$H_{a'}$,$J_{ab} = J_{a'b'} = 8.88$Hz), 7.20 (app t, H_d,$H_{d'}$,H_e, $J = 7.30$Hz), 7.60 (d, H_b,$H_{b'}$), 7.63 (d, H_f, $J_{fg} = 7.78$Hz), 7.73 (d,H_c,$H_{c'}$, $J_{cd} = J_{c'd'} = 7.30$Hz), 7.79 (d, H_g), 11.76 (s, OH); ^{13}C NMR: $\delta = 190.5$ (C-5), 161.1 (C-2), 154.2 (C-4′), 143.0 (C-1′), 137.6 (C-1″), 136.6 (C-4), 134.6 (C-4″), 130.1 (C-2″), 129.4 (C-3″), 127.2 (C-3), 125,4 (C-2′), 114.6 (C-3′), 55.9 (OCH_3); MS: m/z = 279 (16.6%) [M.$^+$-2H], 266 (3.3%) [M.$^+$-Me], 236 (2.8%) [M.$^+$-Me-CO-2H], 105 [Base]. Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.75; H, 5.38; N, 4.98. Found: C, 72.43; H, 5.22; N, 5.13%.

Reaction of E,Z-2b with 4-Methoxyphenylazide. E,Z-2b

(1.0 g, 2.4 mmol) and 4-methoxyphenylazide (0.7 g, 4.7 mmol) are refluxed in anhydrous toluene (30 ml) for 20 h and the solution is left to stand at room temperature overnight. The precipitated solid is recrystallized from dioxan to give orange crystals of **E,Z-2b** (0.35 g, 35%), m.p. 254–256 C (identical, m.p., IR and ^{1}H NMR with the starting material). The toluene mother liquor is concentrated (10 ml), left to stand for 12 h and the precipitated red solid is filtered off and recrystallized from benzene-methanol to give E,Z-**5** (0.37 g, 36%). The filtrate is concentrated (3.0 ml), chromatographed over silica gel, eluted successively with light petroleum (b.p. 40–60) – ether mixtures (4:1 V/V) then with ethyl acetate and the fractions are monitored by TLC. The ether containing fractions give Z-**5** (0.13 g, 12%) and the ethyl acetate fractions produce **6** (0.19 g, 17%).

E,Z-3-Benzyl-5-(4-bromobenzoylmethylene)-2-(4-methoxyphenylimino)-4-oxo-1,3-thiazolidine (E,Z-5)

Red needles (benzene-methanol), m.p. 173–175 C; IR: $\nu = 3050$ (aryl-H), 2915 (alkyl-H), 1710 (C=O), 1625 (C=N), 750, 700 cm^{-1}; ^{1}H NMR: $\delta = 6.95$ (dAB_q, $4H_{anisyl}$), 7.29–7.38 (m, H_d, $H_{d'}$, H_e). In addition to the above mentioned absorptions the following resonances characterize the specified isomer. **for Z-isomer**: $\delta = 3.84$ (s, OMe), 5.19 (s, CH_2Ph), 7.48, 7.55 (each d, H_c,$H_{c'}$,$J_{cd} = J_{c'd'} = 7.8$Hz), 7.66 (d, H_b,$H_{b'}$, $J_{ab} = J_{a'b'} =$

8.8Hz), 7.90 (d, H_a,$H_{a'}$), 8.00 (s, = H); **for E-isomer**: δ = 3.89 (s, OMe), 4.59, 4.61 (d, CH_2Ph, two central peaks of ABq), 7.07 (s, = H), 7.42 (d, H_c,$H_{c'}$ J_{cd}= $J_{c'd'}$ = 8.8Hz), 7.69 (d,H_b,$H_{b'}$, J_{ab} = $J_{a'b'}$ = 8.8Hz), 8.13 (d, H_a,$H_{a'}$); MS: m/z = 506 (13.5%) [M.$^+$], 238 (37.7%) [M.$^+$- CO – 4-$BrC_6H_4COCHCS$], 237 (21.7%) [A$^+$], 212 (2.1%) [B$^+$], 183 (9.0%) [4-$BrC_6H_4CO^+$], 147 (13%) [M.$^+$- CO – 4$BrC_6H_4COCHCS$ – CH_2Ph], 91 [Base]. Anal. Calcd for $C_{25}H_{19}BrN_2O_3S$: C, 59.18; H, 3.77; N, 5.52. Found: C, 59.33; H, 3.67; N, 5.78%.

***Z*-5**. Red needles(benzene-methanol), m.p. 173–175 C; IR and ^{1}H NMR are identical with the respective spectra of the Z-isomer of E,Z-**5**.

3-Benzyl-6-(4-bromobenzoyl)-5-(4-methoxyphenylamino)-2,3-dihydro-4-oxo-2-thioxo-4H-1,3-thiazine (6)

Cumin needles (benzene-methanol); m.p. 198–200 C; IR: ν = 3290 (N-H), 3060 (aryl-H), 2915 (alkyl-H), 1715, 1665 (C=O), 1080 (C=S), 840, 730, 690 cm^{-1}; ^{1}H NMR: δ = 3.93 (s, OMe), 4.62, 4.65 (CH_2Ph, two central peaks of ABq), 7.07 (d, H_d,$H_{d'}$, J_{cd} = $J_{c'd'}$ = 8.92Hz), 7.30–7.42(m, CH_2Ph), 7.46 (d, H_c,$H_{c'}$), 7.73 (d, H_b,$H_{b'}$, J_{ab} = $J_{a'b'}$ = 8.52Hz). In addition to the above mentioned absorptions the following resonances characterize the specified tautomers. for **6**: δ = 8.16 (d, H_a,$H_{a'}$,J_{ab} = $J_{a'b'}$ = 8.52Hz), 9.71 (br s, NH_x); for **6a**: δ = 4.97 (s, Hx_{ax}), 5.37 (s, Hx_{eq}), 8.16 (d, H_a,$H_{a'}$, J_{ab}= $J_{a'b'}$ = 8.52Hz) for **6b**: δ = 7.97 (d, H_a,$H_{a'}$, J_{ab}= $J_{a'b'}$ = 8.52Hz), 8.82 (br s, OH_x); ^{13}C NMR: δ = 178.1 (C-7), 160.8 (C-4), 156.4 (C-2), 142.8 (C-1′), 137.2 (C-1‴), 135.1 (C-1″), 132.7 (C-2″), 131,8 (C-2″), 129.6 (C-3″), 128.7 (C-3‴), 127.8 (C-4‴), 126.7 (C-2′), 116.8 (C-6), 114.2 (C-2′), 55.6 (OCH_3) 43.9 (CH_2Ph); MS: m/z = 538 (1.0%) [M.$^+$], 461 (53.2%) [M.$^+$- Ph], 417 (77.3%) [M.$^+$- Ph – CS], 328 (28.6%) [M.$^+$- Ph – CS – $SCONHCH_2$], 183 (93.5%) [4-$BrC_6H_4CO^+$], 149 (83.4%) [$PhCH_2NCS^+$]. All the above fragments are accompanied by the respective isotope peaks and the base peak is the isotope peak of fragment m/z 183. Anal. Calcd for $C_{25}H_{19}BrN_2O_3S_2$: C, 55.67; H, 3.55; N, 5.19. Found: C, 55.60; H, 3.65; N, 5.26%.

Reaction of 1a with Bromine

A mixture of 1a (0.2 g, 0.6 mmol), glacial acetic acid (5.0 ml) and bromine (0.1 g, 0.6 mmol) is refluxed for 15 min and left to stand overnight. The

precipitated solid (0.19 g, 95%) is crystallized from benzene/methanol to give E,Z-**2a**, m.p. 216–218 C. IR and ^{1}H NMR spectra are identical with those of the sample obtained by reacting **1a** with 4-methoxyphenylazide.

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