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Reactions of *N*,*N*-Disubstituted 5-Arylmethylidene-2-amino-thiazol-4(5*H*)-ones with CH Acids

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Summary. *N*,*N*-Disubstituted 5-arylmethylidene-2-aminothiazol-4(5*H*)-ones reacted with diethyl malonate, ethyl benzoylacetate, acetylacetone, or cyclopentadiene in refluxing toluene and in presence of powdered sodium to give the respective 5-arylmethylidene-2′-amino-2,5′-bithiazolylidene-4,4′-dione derivatives in moderate yields. 5-Benzylidene-2-morpholin-4-yl-2-thiazol-4(5*H*)-one reacted with malononitrile in toluene and in presence of powdered sodium under mild conditions to afford the 1:1 adduct, benzylmalononitrile, and 2-morpholin-4-yl-2-thiazol-4(5*H*)-one. However, similar treatment of 5-(4-methoxyphenylmethylidene)-2-morpholin-4-yl-2-thiazol-4(5*H*)-one with malononitrile yielded the 2,5′-bithiazolylidene-4,4′-dione derivative together with 4-methoxyphenylmethylidene malononitrile. Treatment of 5-benzylidene- and 5-(4-methoxyphenylmethylidene)-2-morpholin-4-yl-2-thiazol-4(5*H*)-ones with 3-phenyl-4-oxo-2-thioxo-1,3-thiazolidine in refluxing toluene and in presence of powdered sodium produced 5-arylmethylidene-3-phenyl-4-oxo-2-thioxo-1,3-thiazolidines in good yields. The structures of all products were deduced from microanalytical and spectroscopic data, mechanistic details are discussed.

Keywords. CH Acids; Powdered sodium; 2-Thiazol-4(5*H*)-ones; 1,3-Thiazolidin-4-ones.

Introduction

The electrophilicity of the C-2 atom in 2-thiazolines is well illustrated by the addition of allylic *Grignard* reagents [1, 2], acetyl chloride [3, 4], α-phenoxyacetyl chloride [3, 5], and dichloroacetyl chloride [4] in the presence of triethylamine to give the respective 2-(2-alkenyl)-thiazolidines and bicyclic β-lactams. Moreover, substitution of the alkylthio group in 2-alkylthio-2-thiazolines has been observed upon treatment with primary amines [6] and anthranilic acid [7], yielding the respective 2-alkylaminothiazolidines and thiazoloquinazolinones. In continuation of our studies on the action of nucleophiles such as sodium methoxide [8], primary amines [6, 9], secondary amines [9], ammonium carbonate [9], alcoholic potassium hydroxide [10], and *Grignard* reagents [11, 12] on *N*,*N*-disubstituted 5-arylmethylidene-2-aminothiazol-4(5*H*)-ones **1** we now report the reaction of these compounds with a variety of CH acids.

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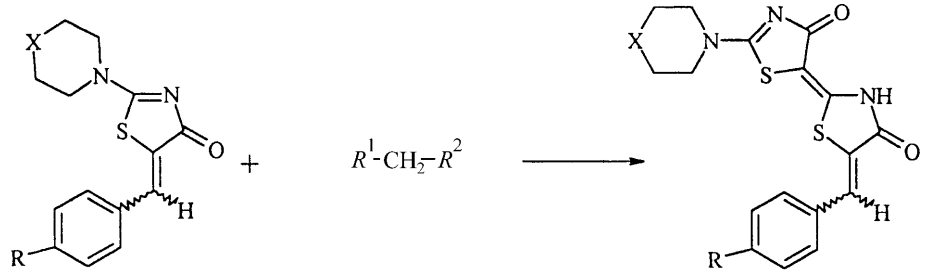
Results and Discussion

A series of compounds **1a–f** [9, 10, 13–15] was reacted with diethyl malonate (**2a**), ethyl benzoylacetate (**2b**), acetylacetone (**2c**), cyclopentadiene (**2d**), malononitrile (**2e**), and 3-phenyl-4-oxo-2-thioxo-1,3-thiazolidine (**8**) in presence of powdered sodium in boiling anhydrous toluene. Thus, refluxing of the piperidino derivative **1b** with **2a** in toluene in presence of powdered sodium for 7 h yielded a moderate yield of a yellow crystalline product **3b**. Similar treatment of the morpholino derivative **1a** with **2a** produced a different yellow product **3a** as evidenced from its EI-MS and ^{1}H NMR. Comparing the mass spectra as well as the ^{1}H NMR spectra of the two yellow products **3a** and **3b** inferred that they had the same structure. Furthermore, treatment of **1a** and **1b** either with **2b**, **2c**, or **2d** under the same conditions produced moderate yields of the same yellow products **3a** and **3b**. Similar treatment of 2-thiazol-4(5*H*)-one derivatives **1c**,**d** with **2c** or **2d** gave the 2,5′-bithiazolylidine-4,4′-dione derivatives **3c** and **3d**, whereas reaction of **1e**,**f** with **2a** or **2b** afforded **3e** and **3f**.



1a: R = H, X = O
1b: R = H, X = CH_2
1c: R = Cl, X = O
1d: R = Cl, X = CH_2
1e: R = OMe, X = O
1f: R = OMe, X = CH_2

2a: $R^1 = R^2 = CO_2Et$
2b: R^1 = PhCO, $R^2 = CO_2ET$
2c: $R^1 = R^2 = CH_3CO$
2d: R^1R^2 = -CH=CH-CH=CH-
2e: $R^1 = R^2$ = CN

3a: R = H, X = O
3b: R = H, X = CH_2
3c: R = Cl, X = O
3d: R = Cl, X = CH_2
3e: R = OMe, X = O
3f: R = OMe, X = CH_2

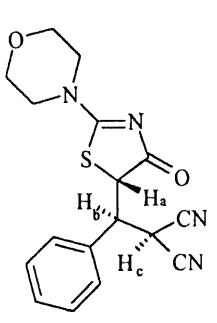
The structures of **3a–f** were deduced from microanalytical and spectroscopic data. The ^{1}H NMR spectrum of **3b** in deuterated trifluoroacetic acid revealed the (*E*, *Z*)-geometry of this compound. The configurational assignment is based on a comparison of the observed δ-values of the olefinic proton with literature data [16]. The protons of (*Z*)-configured isomers absorbs at lower field than those of (*E*)-configured ones. An accepted rule in the configuration elucidation of arylidene derivatives of azalactones [17a], indolones [17b], and pyrazolin-5-ones [17c] could be also applied (the olefinic protons of the (*Z*)-configured isomers are more deshielded by the 4-oxo group than their (*E*)-counterparts).

To test if the CH acids play a role in the formation of **3** or not, **1a** and **1b** were treated with powdered sodium under similar conditions but in absence of CH acids. The starting materials were recovered unchanged in 93% yield. Formation of **3a–f** upon treatment of **1a–f** with different carbanions inferred that the latter are involved in the primary stages of the reaction, but are then expelled. Therefore, we performed some reactions under mild conditions, hoping to be able to isolate intermediates containing the carbanion moieties participating in the reaction. The

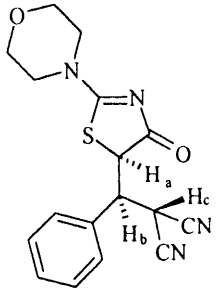
results are quite interesting and illustrate the reaction steps and the route of formation of compounds **3**.

Treatment of **1a** with **2e** in presence of powdered sodium in toluene at 70°C for 3 days provided the 1:1 adduct **4**, benzylmalononitrile (**5**), and 2-morpholin-4-yl-2-thiazol-4(5*H*)-one (**6**) which were separated by chromatography. Similarly, **1e** and **2e** afforded **3e** together with 4-methoxyphenylmethylidenemalononitrile (**7b**). The structures of **4**, **5**, **6**, and **7b** were substantiated from their spectroscopic data. Moreover, the structures of compounds **5**, **6**, and **7b** were rigidly confirmed by comparison of their melting points with those reported in the literature [18–20].

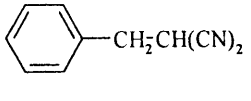
Assignment of **4a** and **4b** as the *ul* and *l* diastereomers is based on the observed coupling constants between H_a, H_b, and H_c. It was shown that H_a and H_b are transoid in **4a**, whereas they are cisoid in **4b**. The relation of H_b and H_c (cisoid in **4a**, transoid in **4b**) is due to different conformational states.



4a



4b



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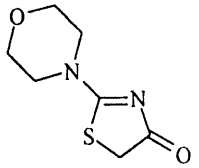

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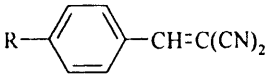
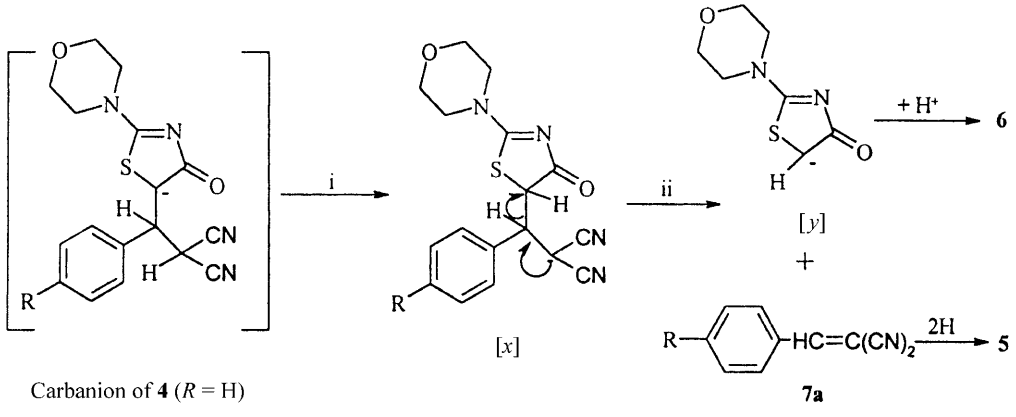


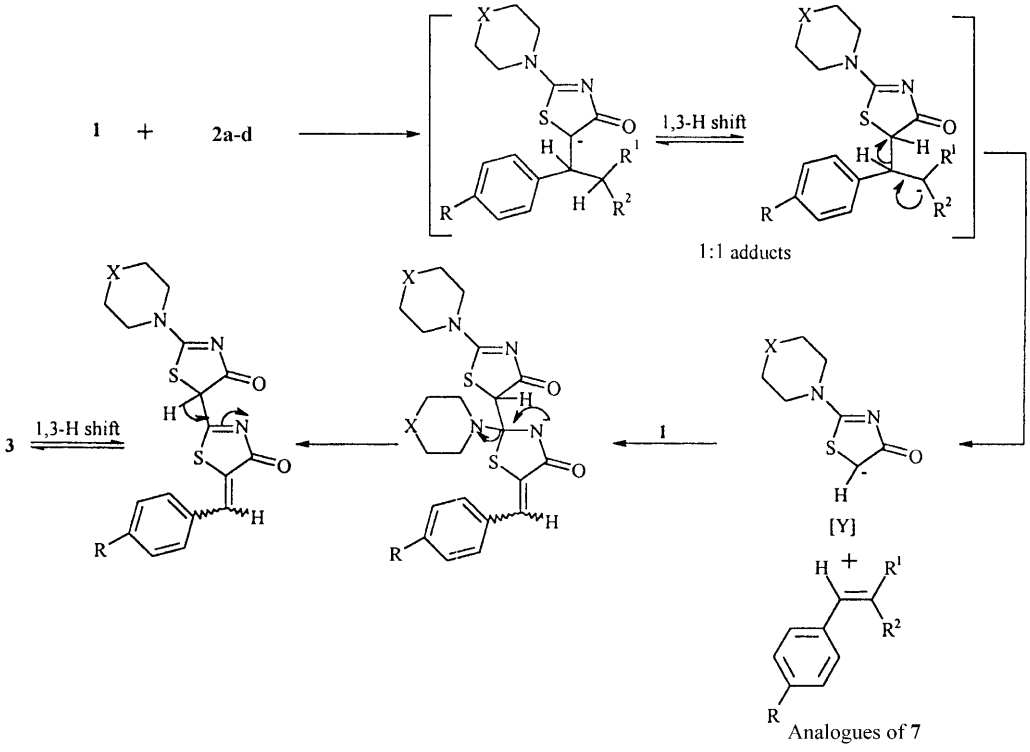
7a: *R* = H
7b: *R* = OMe

The formation and isolation of the 1:1 adduct **4** is in accordance with the possibility of addition of a malononitrile carbanion at the β-terminus of the C=C–C=O system. However, formation of compounds **5** and **6** could be explained in terms of a cleavage of the C–C bond joining C-5 of the hetero ring with the neighbouring carbon atom carrying the phenyl group in the carbanion of compound **4** first formed as represented in Scheme 1. Step (*i*) involves a 1,3-proton shift to



Carbanion of **4** (*R* = H)

Scheme 1

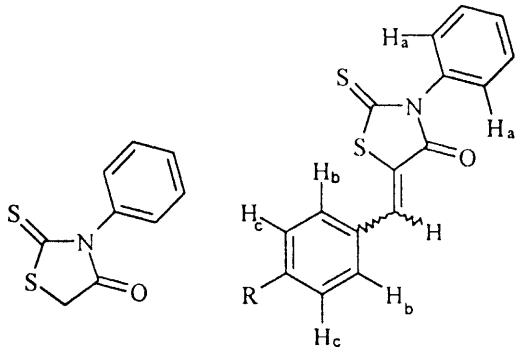


Scheme 2

give the anion [*X*] which stablizes *via* elimination of the anion [*Y*] and formation of **7a** (step (*ii*)). It is evident that protonation of [*Y*] will produce **6**, and reduction of **7a**, most likely *via* the nascent hydrogen produced upon decomposition of the reaction mixture, gives **5**.

Further evidence for the formation of 1:1 adducts and subsequent decomposition into the arylidene derivative of the CH acids was gained from the results obtained by treatment of **1a** and **1e** with 3-phenyl-2-thioxo-4-oxo-1,3-thiazolidine **8** in refluxing toluene in presence of powdered sodium. 5-arylmethylidene-3-phenyl-2-thioxo-4-oxo-1,3-thiazolidines **9a**,**b** were isolated in high yields. The structures of compounds **9a**,**b** were deduced from microanalytical and spectroscopic data and by comparison of their melting points with those of authentic samples.

Taking all results into consideration, it is possible to present a mechanism for the conversion of **1** into **3** upon reacting with CH acids **2a**–**d**. The addition of the CH-carbanions at the β-terminus of the C=C–C=O system of **1** primarily gives 1:1 adducts (Scheme 2) which are cleaved to produce arylidene derivatives of the CH acids (analogues of **7**) along with the thiazolinone carbanion [*Y*]. The attack of the thiazolinone carbanion [*Y*] to another molecule of **1** at the positively polarized carbon atom of the hetero ring azomethine with expulsion of the disubstituted amino moiety gives the 2,5′-bithiazolylidine-4,4′-dione derivatives **3**. The above results inferred that addition at the β-carbon of the α,β-unsaturated carbonyl moiety as well as at the β-terminal of the azomethine system occurred.



8 **9a**: R = H
9b: R = OMe

Experimental

Melting points are not corrected. IR spectra were measured on a Unicam SP1200 spectrometer as KBr discs. ^{1}H NMR spectra were measured in *DMSO*-d_6 or $CDCl_3$ on a Varian Gemini instrument at 200 MHz, ^{13}C NMR spectra in *DMSO*-d_6 on a Varian Gemini spectrometer at 125 MHz using the APT technique; in both cases, chemical shifts are given in ppm downfield from internal *TMS*. Mass spectra were recorded on a Shimadzu GC-MS Qp 1000 EX instrument operating at 70 eV. Column chromatography was carried out with Riedel-de Haen Silica gel S 0.063–0.1 mm. TLC was performed on Merck Kieselgel 60 F_{254} aluminum backed plates. Elemental analyses agreed favourably with the calculated values. *N,N*-Disubstituted 5-arylmethylidene-2-aminothiazol-4(5*H*)-ones **1a–f** were synthesized according to reported methods [14, 15].

Reaction of **1a–f** *with* **2a–d**

The methylene derivative (13.0 mmol) was added to 0.3 g freshly prepared powdered sodium (13 mmol) in 40 cm^3 dry toluene, and the mixture was refluxed for 2 h excluding H_2O. Then, 6.5 mmol of **1a–f** were added, and refluxing was continued for further 7 h. The dark-brown reaction mixture was concentrated, left to stand overnight at room temperature, and the residual dark-orange solid was treated with ice-cold H_2O and acidified with dilute HCl. The precipitated solid was filtered off and recrystallized from the solvent stated to give the corresponding products **3a–f**. In the case of reaction of **1a**, **1b**, **1e**, and **1f** with **2a**, compounds **3a**, **3b**, **3e**, and **3f** were obtained.

5-Benzylidene-2′-morpholin-4-yl-2,5′-bithiazolylidene-4,4′-dione (**3a**; $C_{17}H_{15}N_3O_3S_2$)

Yellow-orange crystals; 0.72 g (30%); m.p.: 298–300°C (MeOH); IR: $\bar{\nu}$ = 3120 (NH), 3020 (=CH), 2980–2890, 2850 (CH), 1720, 1700 (CO), 750, 700 (5H) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): δ = 3.50 (br s, NCH_2), 3.72 (br s, CH_2OCH_2), 3.82 (br s, NCH_2), 7.43–7.70 (m, 5ArH + =CH), 12.38 (br s, NH, exchangeable) ppm; ^{13}C NMR (*DMSO*-d_6): δ = 179.0 (C-4′), 172.7 (C-4′), 153.5 (C-2′), 151.6 (C-2), 139.1 (C-5), 134.6 (=CH), 131.6, 131.4, 129.7, 128.7 (benzene ring), 100.4 (C-5′), 49.6, 65.9 (morpholine) ppm; MS: m/z (%) = 375 ($M^{+\cdot}$ + 2, 8), 373 ($M^{+\cdot}$, 39), 263 (7), 261 (11), 235 (12), 233 (100), 136 (7), 134 (27), 102 (10), 89 (6), 69 (10), 55 (16).

5-Benzylidene-2′-piperidin-1-yl-2,5′-bithiazolylidene-4,4′-dione (**3b**; $C_{18}H_{17}N_3O_2S_2$)

Orange crystals; 0.68 g (28%); m.p.: 272–273°C (MeOH); IR: $\bar{\nu}$ = 3200 (NH), 3020 (=CH), 2960–2930, 2750 (CH), 1720, 1700 (CO), 750, 700 (5H) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): δ = 1.66 (br s,

$(CH_2)_3$), 3.44 (br s, NCH_2), 3.82 (br s, NCH_2), 7.40–7.70 (m, 5ArH + =CH), 12.50 (br s, NH, exchangeable) ppm; ^{1}H NMR (CF_3COOD): $\delta = 2.01$ (br s, 3 CH_2-piperidyl), 3.84 (br s, NCH_2), 4.01 (br s, NCH_2), 7.58–7.80 (m, 5ArH), 8.16 and 8.24 (s, =CH, for (*E*)- and (*Z*)-isomers) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 179.0$ (C-4′), 172.7 (C-4), 156.0 (C-2′), 151.2 (C-2), 139.1 (C-5), 134.6 (=CH), 134.1, 131.4, 129.7, 128.7 (benzene ring), 100.8 (C-5′), 51.9, 26.1, 24.7 (piperidine) ppm; MS: m/z (%) = 373 ($M^{+\cdot}$ + 2, 6), 371 ($M^{+\cdot}$, 30), 263 (1), 261 (6), 235 (13), 233 (100), 136 (5), 134 (48), 104 (2), 102 (15), 89 (14), 69 (15), 55 (25).

5-(4-Methoxyphenylmethylidene)-2′-morpholin-4-yl-2,5′-bithiazolylidene-4,4′-dione
(**3e**; $C_{18}H_{17}N_3O_4S_2$)

Yellow-orange crystals; 0.63 g (24%); m.p.: 280–282°C (EtOH); IR: $\bar{\nu} = 3140$ (NH), 3060 (=CH), 2970–2920, 2840 (CH), 1710, 1695 (CO), 820 (2H) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 3.45$–3.58 (br s, NCH_2), 3.60–3.75 (br s, CH_2OCH_2), 3.75–3.80 (br s, NCH_2), 3.85 (s, OMe), 7.16 (d, $J = 8.6$ Hz, 2ArH), 7.54 (s, =CH), 7.62 (d, $J = 8.6$ Hz, 2ArH), 12.45 (br s, NH, exchangeable) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 184.3$ (C-4′), 172.7 (C-4), 160.0 (COMe), 153.5 (C-2′), 151.6 (C-2), 139.1 (C-5), 134.6 (=CH), 132.2, 124.9, 115.1 (benzene ring), 100.4 (C-5′), 65.9, 49.6 (morpholine), 55.2 (OMe) ppm; MS: m/z (%) = 405 ($M^{+\cdot}$ + 2, 14), 403 ($M^{+\cdot}$, 39), 291 (11), 265(5), 263 (100), 166 (5), 164 (37), 132 (4), 89 (13), 69 (5), 55 (9).

5-(4-Methoxyphenylmethylidene)-2′-piperidin-1-yl-2,5′-bithiazolylidene-4,4′-dione
(**3f**; $C_{19}H_{19}N_3O_3S_2$)

Yellow-orange crystals; 0.68 g (26%); m.p.: 262–264°C (MeOH); IR: $\bar{\nu} = 3130$ (NH), 3050 (=CH), 2960–2920, 2850 (CH), 1710, 1700 (CO), 815 (2H) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.66$ (br s, $(CH_2)_3$), 3.43 (br s, NCH_2), 3.85 (br s, NCH_2), 3.852 (s, OMe), 7.17 (d, $J = 8.8$ Hz, 2ArH), 7.53 (s, =CH), 7.62 (d, $J = 8.8$ Hz, 2ArH), 12.35 (br s, NH, exchangeable) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 184.3$ (C-4′), 172.7 (C-4), 156.1 (C–OMe), 156.0 (C-2′), 151.6 (C-2), 139.1 (C-5), 134.6 (=CH), 132.2, 124.9, 115.1 (benzene ring), 100.1 (C-5′), 55.3 (OMe), 51.9, 26.1, 24.7 (piperidine) ppm.

Reaction of **1a**, **1b**, **1e**, and **1f** with **2b** gave **3a**, **3b**, **3e**, and **3f** in 35, 30, 32, and 33% yield. They were identified by comparison with the samples obtained above. In the case of reaction of **1a–d** with **2c**, **3a–d** were obtained. **3a** and **3b** (30 and 23% yield) were identified by comparison with authentic samples.

5-(4-Chlorophenylmethylidene)-2′-morpholin-4-yl-2,5′-bithiazolylidene-4,4′-dione
(**3c**; $C_{17}H_{14}ClN_3O_3S_2$)

Orange crystals; 1.1 g (40%); m.p.: 324–326°C (acetic acid); IR: $\bar{\nu} = 3140$ (NH), 3080 (=CH), 2950–2900, 2840 (CH), 1710, 1700 (CO), 820 (2H) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 3.48$ (br s, NCH_2), 3.75 (br s, CH_2OCH_2), 3.86 (br s, NCH_2), 7.56 (s, =CH), 7.66 (br s, 4ArH), 12.45 (br s, NH, exchangeable) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 184.3$ (C-4′), 172.7 (C-4), 153.5 (C-2′), 151.6 (C-2), 139.1 (C-5), 134.6 (=CH), 134.4 (C–Cl), 132.2, 131.3, 130.1 (benzene ring), 100.4 (C-5′), 65.9, 49.6 (morpholine) ppm; MS: m/z (%) = 409 ($M^{+\cdot}$ + 2, 17), 407 ($M^{+\cdot}$, 39), 297 (5), 295 (9), 269 (40), 267 (100), 170 (11), 168 (25), 138 (5), 136 (10), 89 (13.7), 69 (15), 55 (21).

5-(4-Chlorophenylmethylidene)-2′-piperidin-1-yl-2,5′-bithiazolylidene-4,4′-dione
(**3d**; $C_{18}H_{16}ClN_3O_2S_2$)

Orange crystals; 1.13 g (43%); m.p.: 310–312°C (benzene/methanol); IR: $\bar{\nu} = 3140$ (NH), 3080 (=CH), 2950–2930, 2860 (CH), 1720, 1710 (CO), 817 (2H) cm^{-1}; ^{1}H NMR (*DMSO*-d_6): $\delta = 1.66$ (br s, $(CH_2)_3$), 3.44 (br s, NCH_2), 3.82 (br s, NCH_2), 7.54 (s, =CH), 7.66 (br s, 4ArH), 12.50 (br s, NH, exchangeable) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 184.3$ (C-4′), 172.7 (C-4), 156.0 (C-2′), 151.6 (C-2),

139.1 (C-5), 134.6 (=CH), 134.4(C–Cl), 132.2, 131.3, 130.1 (benzene ring), 100.4 (C-5′), 51.9, 26.1, 24.7 (piperidine) ppm; MS: m/z (%) = 407 ($M^{+\cdot}$ + 2, 19), 405 ($M^{+\cdot}$, 36), 297 (2), 295 (15), 269 (45), 267 (100), 170 (8), 168 (26), 138 (4), 136 (9), 89 (12), 69 (12), 55 (23).

In the case of reaction of **1a–d** with **2d**, the derivatives **3a–d** were obtained in 45, 42, 35, and 32% yield. **3a–d** were identified by comparison with authentic samples.

Action of sodium on **1a** *and* **1b**

A mixture of 0.5 g **1a** or **1b** (18 mmol) and 40 mg freshly prepared powdered Na (1.8 mmol) in 20 cm^3 dry toluene was refluxed for 7 h. The mixture was cooled, concentrated, treated with ice-cold H_2O, and acidified with conc HCl. The precipitated solid was filtered and recrystallized from EtOH to give 0.47 g unchanged **1a** or **1b** (93%) which were identified by comparison with authentic samples.

Reaction of **1a** *and* **1e** *with* **2e**

Malononitrile (**2e**; 0.3 g, 4.5 mmol) was added to 0.104 g freshly prepared powdered Na (4.5 mmol) in 20 cm^3 dry toluene, and the mixture was stirred at 70°C for 2 h under exclusion of H_2O. **1a** or **1e** (1.0 and 1.1 g, respectively, 3.6 mmol) was added to this mixture, and stirring was continued at 70°C for 3 days. The mixture was cooled, and the precipitated solid was filtered off and washed with 10 cm^3 cold EtOH while the toluene layer was kept.

Each of the precipitated solids and the concentrated toluene layers were treated with ice cold H_2O and acidified with conc HCl to give 0.40 g unreacted **1a** and **1e** (40%) which were identified by comparison with authentic samples.

The ethanolic washings obtained above were diluted with H_2O, acidified with 1 cm^3 conc HCl, extracted with $CHCl_3$, dried ($CaCl_2$), concentrated, and chromatographed over silica gel.

In the case of **1a** and **2e**, elution with light petroleum (b.p.: 60–80°C) gave 28 mg benzylmalononitrile (**5**; Ref. [18]: m.p.: 78–79°C). Elution with ethyl acetate:ether mixture = 1:1 gave **4** followed by **6**.

2-Morpholin-4-yl-5-(1-phenyl-2,2-dicyanoethyl)-2-thiazole-4(5H)-one (**4**; $C_{17}H_{16}H_4O_2S$)

Colourless crystals; 0.22 g (18%); m.p.: 161°C (EtOH); IR: $\bar{\nu}$ = 3060 (=CH), 2920 (C–H), 2268 (C≡N), 1684 (C=O), 1555 (C=N and/or C=C), 750 and 701 (5H) cm^{-1}; ^{1}H NMR ($CDCl_3$): **4a** (67%): δ = 3.54–3.80 (m, 8 morpholino), 3.86 (dd, J = 11.2 and 4.0 Hz, H_b), 4.85 (dd, J = 4.0 and 1.2 Hz, H_c), 5.37 (dd, J = 11.2 and 1.2 Hz, H_a), 7.20–7.55 (m, 5ArH) ppm; **4b** (33%): δ = 3.54–3.80 (m, 8 morpholino), 3.96 (dd, J = 11.2 and 4.2 Hz, H_b), 4.90 (dd, J = 11.2 and 1.2 Hz, H_c), 5.83 (dd, J = 4.2 and 1.2 Hz, H_a), 7.20–7.55 (m, 5ArH) ppm.

2-Morpholin-4-yl-2-thiazole-4(5H)-one (**6**; $C_7H_{10}N_2O_2S$)

Colourless crystals; 47 mg (7%); m.p.: 172°C (Ref. [19]: m.p.: 196.5°C); IR: $\bar{\nu}$ = 2920, 2866 (C–H), 1692 (C=O), 1548 (C=N and/or C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 3.49–3.57 (m, NCH_2), 3.73–3.83 (m, CH_2OCH_2), 3.97–4.03 (m, NCH_2), 3.96 (s, CH_2); MS: m/z (%) = 186 ($M^{+\cdot}$, 54), 112 (88), 86 (33), 85 (11), 55 (100).

In the case of reaction of **1e** and malononitrile (**2e**), elution with light petroleum (b.p.: 60–80°C) gave **7b**.

4-Methoxyphenylmethylidene malononitrile (**7b**; $C_{11}H_8N_2O$)

Colourless crystals; 40 mg (6%); m.p.: 112–114°C (light petroleum, b.p.: 60–80°C) (Ref. [20]: m.p.: 114.5–115°C); IR: $\bar{\nu}$ = 3027 (=C–H), 2940, 2847 (C–H), 2221 (C≡N), 1604 (C=N and/or C=C),

833 (2H) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.92$ (s, OMe), 7.02 (dd, $J = 9.0$ and 2.0 Hz, 2ArH), 7.66 (s, =CH), 7.92 (dd, $J = 9.0$ and 2.0 Hz, 2ArH). Elution with ethyl acetate:ether = 1:1 gave **3e** (0.16 g (15%), m.p.: 280–282°, undepressed upon admixture with an authentic sample and identical IR and TLC behaviour).

Reaction of **1a** *and* **1b** *with* **8**

3-Phenyl-4-oxo-2-thioxo-1,3-thiazolidine (**8**; 0.94 g, 4.5 mmol) was added to 0.1 g freshly prepared powdered sodium (4.5 mmol) in 20 cm^3 dry toluene, and the mixture was refluxed for 1 h under exclusion of moisture. Each of the derivatives **1a** and **1e** (1.3 and 1.4 g, respectively, 4.5 mmol) was added to the mixture, and refluxing was continued for further 4 h. The mixture was cooled, and the precipitated solid was filtered; the liquid phase was treated with ice-cold H_2O and acidified with conc. HCl, then extracted with $CHCl_3$, dried ($CaCl_2$), concentrated (2 cm^3), and chromatographed over silica gel.

In the case of **1a** and **8**, elution with light petroleum (b.p.: 60–80°C):ethyl acetate = 10:1 gave **9a**.

3-Phenyl-5-phenylmethylidene-4-oxo-2-thioxo-1,3-thiazolidine (**9a**; $C_{16}H_{11}NOS_2$)

Yellow needles; 0.67 (72% based on reacted **1a**); m.p.: 182–184°C (benzene/light petroleum, b.p.: 60–80°C) (Ref. [21]: m.p.: 187–189°C); IR: $\bar{\nu} = 3007$ (=C–H), 1691 (C=O), 1202 (S–CS–N), 760 and 705 (5H) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.30$ (dd, $J = 7.4$ and 2.2 Hz, 2Ha), 7.45–7.65 (m, 8ArH), 7.83 (s, =CH) ppm; MS: m/z (%) = 297 ($M^{+\cdot}$, 21), 298 ($M^{+\cdot} + 1$, 20), 162 (5), 134 (100).

In the case of **1e** and **8**, elution with light petroleum (b.p.: 60–80°C):ethyl acetate = 10:1 afforded **9b**.

5-(4-Methoxyphenylmethylidene)-3-phenyl-4-oxo-2-thioxo-1,3-thiazolidine (**9b**; $C_{17}H_{13}NO_2S_2$)

Yellow crystals; 0.74 g (74% based on reacted **1e**); m.p.: 218–220°C (benzene/light petroleum, b.p.: 60–80°C) (Ref. [22]: m.p.: 225–227°C); IR: $\bar{\nu} = 3057$, 3020 (=C–H), 2950 (C–H), 1710 (C=O), 1229 (S–CS–N), 758, 692 (5H) and 823 (2H) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.90$ (s, OMe), 7.03 (d, $J = 9.0$ Hz, $2H_c$), 7.29 (dd, $J = 8.2$ and 2.2 Hz, $2H_a$), 7.53 (d, $J = 9.0$ Hz, $2H_b$), 7.51–7.58 (m, 3ArH), 7.77 (s, =CH) ppm; MS: m/z (%) = 327 ($M^{+\cdot}$, 16), 328 ($M^{\cdot +} + 1$, 4), 164 (100), 149 (43).

The toluene layer in each case was concentrated, treated with ice-cold H_2O, and acidified with conc. HCl to give unreacted **1a** and **1e** (0.39 g (30%) and 0.42 g (30%), respectively) which were identified by comparison with authentic samples.

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