Synthesis of novel thiazolidin-4-ones by reaction of malonthioamide derivatives with dimethyl acetylenedicarboxylate

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Novel 2,5-dimethylenethiazolidin-4-one derivatives have been prepared by reaction of malonthioamide derivatives with dimethyl acetylenedicarboxylate. These compounds exist as separate (*E*,*Z*)- and (*Z*,*Z*)-isomers or as a mixture. The (*E*,*Z*)-isomer is formed as the initial product which transforms to the (*Z*,*Z*)-isomer under mild conditions. The structures of the obtained compounds have been confirmed by IR and NMR spectroscopy.

Introduction

Reactions of acetylene derivatives with compounds containing a thiocarbamoyl group are known to follow various routes to form thiazole,[1–7] thiazine[6–9] and pyridine[10] rings, as well as vinylmercapto heterocycles.[7] The outcome of the reaction has been shown to depend on both the structure of the thioamide and the nature of the acetylene component.[4,6,7,9] Despite the fact that the condensation of thioureas with dimethyl acetylenedicarboxylate (DMAD) is known to be a convenient method to prepare 2-imino-5-methoxycarbonylthiazolidin-4-ones,[1–3,5,11,12] the malonthioamide derivatives, which are the carbon analogs of thioureas, have not been subjected to this reaction yet.

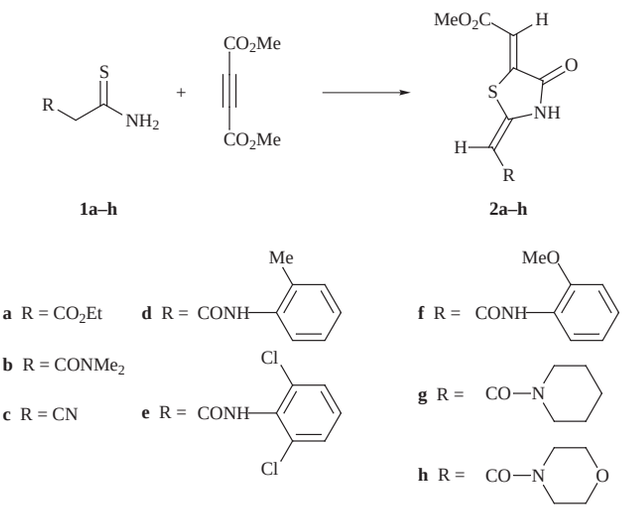
Thus, as a means to prepare novel 2,5-dimethylenethiazolidin-4-one derivatives, we have studied the cyclizations of malonthioamide derivatives with DMAD.

Results and discussion

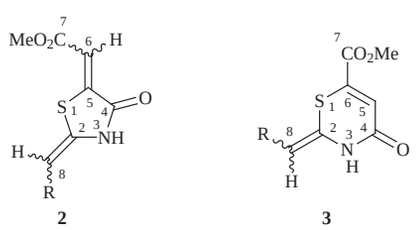
Both the acetylene and thioamide compounds possess a number of possible electrophilic and nucleophilic centers and one could expect the potential formation of at least six five-membered and six six-membered heterocycles along with a number of macrocycles and polymers.

The reaction of 2-(ethoxycarbonyl)thioacetamide **1a** with dimethyl acetylenedicarboxylate affords only one product (Scheme 1), which was identified by IR, ^{1}H and ^{13}C NMR spectroscopy as the thiazolidine **2a**.

On the basis of the ^{1}H and ^{13}C NMR data, shown in Tables 1 and 2, the correct structure could be assigned to compounds **2**. Structures having an exocyclic sulfur can be excluded because of the absence of signals in the ^{13}C NMR spectrum at 170–190 ppm which are typical for the thiocarbonyl and thiolactone carbon. The thiazinone structure **3** could be rejected on the basis of the $^2J_{C–H}$ and $^3J_{C–H}$ coupling constants. This method was successfully employed to determine the structures of compounds obtained in the reaction of thioureas with acetylene derivatives.[11] The signal for C7 in the spectra of **2a** appears as a doublet of quartets and exhibits a $^3J_{C–H}$ coupling of 4.2 Hz with the protons of the methyl ester group and a small C–H coupling of 1.1 Hz. The magnitude of the latter corresponds to a $^2J_{C7–H6}$ coupling constant (over two bonds) and is in agreement with the presence of an exocyclic double bond, which corresponds to the thiazolidine structure **2a**.



Scheme 1



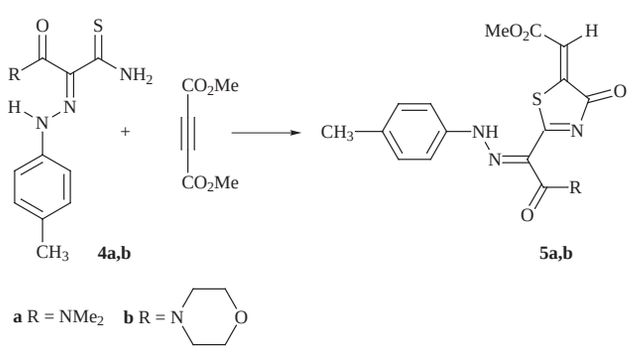
2 **3**

To determine which of the signals could be associated either with H6 or H8 we prepared the model compounds **5a**,**b** *via* the reaction of DMAD with hydrazono acyl thioacetamides **4a**,**b** (Scheme 2) and examined their ^{1}H NMR spectra. In the thiazolidines **5a**,**b**, the methylene group at C2 is absent, allowing us to assign the methylene proton at C6 more easily.

The hydrazones **4** were obtained by a diazo coupling reaction of the corresponding thioacetamides with a 4-methylphenyldiazonium salt. The treatment of thioamides **4a**,**b** with DMAD in absolute alcohol then afforded thiazolidines **5a**,**b**. The ^{1}H NMR spectra of these compounds contain a singlet corresponding to the H6 methine proton at 6.73 ppm. This allows us, by analogy, to assign the signal at 5.7 ppm in the spectra of compound **2a** to H8.

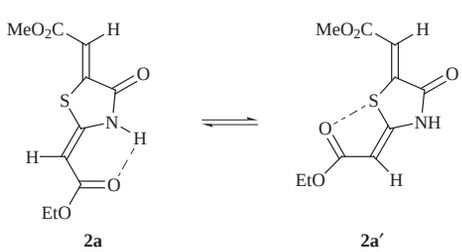
Table 1 ^{1}H NMR Chemical shifts (δ/ppm) of **2a**–**h** and **2a′**–**h′**

Compound	Solvent	^{1}H Chemical shifts
2a	$CDCl_3$	10.8 (1H, s, NH), 6.89 (1H, s, H6), 5.35 (1H, s, H8), 4.22 (2H, q, OCH_2), 3.86 (3H, s, OMe), 1.30 (3H, t, CH_3)
2a′	$CDCl_3$	9.2 (1H, br s, NH), 6.82 (1H, s, H6), 5.75 (1H, s, H8), 4.25 (2H, q, OCH_2), 3.86 (3H, s, OMe), 1.31 (3H, t, CH_3)
2b	$CDCl_3$	11.92 (1H, s, NH), 6.85 (1H, s, H6), 5.61 (1H, s, H8), 3.85 (3H, s, OMe), 3.09 (3H, s, NCH_3), 3.02 (3H, s, NCH_3)
2b′	[$^2H_6$]DMSO	12.2 (1H, br s, NH), 6.52 (1H, s, H6), 6.18 (1H, s, H8), 3.77 (3H, s, OMe), 3.01 (3H, s, CH_3), 2.90 (3H, s, NCH_3)
2c	[$^2H_6$]DMSO	13.8–11.2 (1H, br s, NH), 6.66 (1H, s, H6), 5.43 (1H, s, H8), 3.78 (3H, s, OMe)
2c′	[$^2H_6$]DMSO	13.8–11.2 (1H, br s, NH), 6.72 (1H, s, H6), 5.38 (1H, s, H8), 3.80 (3H, s, OMe)
2d	[$^2H_6$]DMSO	12.39 (1H, s, NH), 9.47 (1H, s, NH), 8.0–8.2 (1H, m, ArH), 8.0–7.2 (3H, m, 3 ArH), 6.56 (1H, s, H6), 6.20 (1H, s, H8), 3.77 (3H, s, OCH_3), 2.22 (3H, s, $ArCH_3$)
2e	[$^2H_6$]DMSO	11.63 (1H, s, NH), 10.10 (1H, s, NH), 7.56 (2H, d, ArH), 7.37 (1H, t, ArH), 6.71 (1H, s, H6), 5.83 (1H, s, H8), 3.79 (3H, s, OCH_3)
2e′	[$^2H_6$]DMSO	12.41 (1H, s, NH), 10.06 (1H, s, NH), 7.55 (2H, d, ArH), 7.35 (1H, t, ArH), 6.55 (1H, s, H6), 6.14 (1H, s, H8), 3.76 (3H, s, OCH_3)
2f	[$^2H_6$]DMSO	11.73 (1H, s, NH), 9.41 (1H, s, NH), 7.12–6.89 (4H, m, ArH), 6.91 (1H, s, H6), 6.08 (1H, s, H8), 3.84 (3H, s, OCH_3), 3.77 (3H, s, OCH_3)
2f′	[$^2H_6$]DMSO	12.42 (1H, s, NH), 9.52 (1H, s, NH), 8.01 (1H, d, ArH), 7.08–7.03 (3H, m, ArH), 6.93–6.89 (1H, m, ArH), 6.54 (1H, s, C_6H), 6.38 (1H, s, H8), 3.84 (3H, s, OCH_3), 3.77 (3H, s, OCH_3)
2g	$CDCl_3$	11.9 (1H, s, NH), 6.85 (1H, s, H6), 5.65 (1H, s, H8), 3.85 (3H, s, OMe), 3.60 (3H, br s, NCH_3), 3.49 (3H, br s, NCH_3), 1.4–1.7 (6H, m, 3 CH_2)
2g′	$CDCl_3$	9.83 (1H, br s, NH), 6.74 (1H, s, H6), 5.18 (1H, s, H8), 3.83 (3H, s, OMe), 3.60 (3H, br s, NCH_3), 3.49 (3H, br s, NCH_3), 1.4–1.7 (6H, m, 3 CH_2)
2h	[$^2H_6$]DMSO	11.92 (1H, s, NH), 6.68 (1H, s, H6), 6.22 (1H, s, H8), 3.78 (3H, s, OCH_3), 3.4–3.6 (8H, m, 4 CH_2)
2h′	[$^2H_6$]DMSO	12.2 (1H, s, NH), 6.53 (1H, s, H6), 6.18 (1H, s, H8), 3.77 (3H, s, OCH_3), 3.3–3.7 (8H, m, 4 CH_2)
5a	[$^2H_6$]DMSO	7.92 (1H, d, NH), 7.31 and 7.52 (4H, AB, J 8.4, C_6H_4), 6.73 (1H, s, H6), 3.81 (3H, s, OCH_3), 2.88 (3H, s, CH_3), 2.35 (3H, s, CH_3)
5b	[$^2H_6$]DMSO	7.90 (1H, d, NH), 7.33 and 7.55 (4H, AB, J 8.4, C_6H_4), 6.73 (1H, s, H6), 3.81 (3H, s, OCH_3), 3.1–3.6 (8H, m, 4 CH_2), 2.37 (3H, s, CH_3)



Scheme 2

The presence of two exocyclic double bonds in the structure of **2a** allows for several geometric configurations. Indeed the heating of thiazolidine **2a** in ethanol or DMSO leads to the formation of the isomeric product **2a′** (Scheme 3). This process



Scheme 3

proceeded in 20% conversion after 7 days when chloroform was used as a solvent. A number of thioamides **1b**–**h** were reacted analogously with DMAD to afford the thiazolidine products **2b**–**h** (Scheme 1). The *N*,*N*-dimethylcarbamoyl derivative **1b** gave a mixture, from which both **2b** and an isomeric compound **2b′** were isolated. Cyanothioacetamide **1c** gave an inseparable mixture of thiazolidines **2c**,**c′**, whereas the other thioamides **1d**–**h** only yielded the isomer **2d**–**h**. The formation of the second isomers for the products **2d**–**h** were monitored by TLC and NMR spectroscopy; these isomers were not isolated. The geometric configuration of **2a**–**h** and **2a′**–**h′** was studied in detail with ^{1}H and ^{13}C NMR spectroscopy. The ^{13}C NMR chemical shifts and coupling constants ($^2J_{C7–H6} \sim 1$ Hz; $^3J_{C4–H6} \sim 5$ Hz) of **2a**–**h** and **2a′**–**h′** indicate that for both isomers **2a**–**h** and **2a′**–**h′** the C5=C6 double bond exists in the (*Z*)-configuration and therefore the formation of the second isomer of **2a**–**h** can be associated only with rotation about the C2=C8 bond (Table 2). The configuration of the C2=C8 bond was determined by 1D NOE experiments. In the case of the (*Z*,*Z*)-isomer we expected that saturation of the NH-proton would give an NOE enhancement of the H8-proton but instead we performed an excitation on the H_2O-signal because the N-H signal was broad and in some cases even not observed. Because of chemical exchange between the labile N-H proton with H_2O the transfer of saturation from H_2O to the N-H proton leads to an NOE enhancement of the H8-proton. These experiments have proved that the compounds **2a′**–**h′** can be assigned the (*Z*,*Z*)-isomeric form. The proton chemical shifts of the compounds **2a**–**h** and **2a′**–**h′** are shown in Table 1.

We have also studied the conversion of **2a**–**h** [the (*E*,*Z*)-isomer] to **2a′**–**h′** [the (*Z*,*Z*)-isomer] in [$^2H_6$]DMSO by ^{1}H NMR spectroscopy at 298 K. The compounds **2b**,**e**,**f** convert in 100% yield to their (*Z*,*Z*)-isomer, compound **2c** in 82% and compound **2h** in 80%. In $CDCl_3$, **2a** only converts in 10% yield to **2a′**. Clearly, the (*E*,*Z*)-isomers **2** are stabilized in non-polar solvents by the formation of an intramolecular hydrogen bond. In a polar solvent, such as [$^2H_6$]DMSO, intermolecular hydrogen bonding with the solvent allows the formation of the (*Z*,*Z*)-isomers, which now may be stabilized by a close S···O contact.[13] This also explains the formation of the two isomers in the case of **2c**–**c′**, where the cyano function will not interact either with the sulfur or the NH-group of the thiazolidine ring.

Conclusions

Thus, reaction of malonthioamide derivatives with dimethyl acetylenedicarboxylate leads to new thiazole derivatives, and to the previously unknown 2,5-dimethylenethiazolidin-4-one system. It is worth noting that compounds **1**, in contrast to thiocarbamoylazomethine ylide[7] and enamino thioamides,[6] do not enter into the reaction with methyl propiolate, which reveals their relatively low nucleophilicity.

Table 2 ^{13}C NMR Chemical shifts (δ/ppm) and coupling constants for **2a**–**h** and **2a′**–**h′** [a]

		^{13}C Chemical shifts δ											
	Solvent	C2	C4	C5	C6	C7	C8	C=O (R^1)	$^3J_{C4–H6}$	$^2J_{C7–H6}$	$^2J_{C5–H6}$	$^1J_{C8–H8}$	$^1J_{C6–H6}$
2a	$CDCl_3$	150.5 (dd)	164.6 (dd)	140.6 (dd)	115.8 (d)	166.6 (dq)	92.8 (d)	167.0 (t)	5.1	1.1	1.8	170.2	173.0
2a′	$CDCl_3$	150.1 (dd)	165.9 (dd)	142.4 (dd)	116.4 (d)	166.1 (dq)	94.9 (d)	166.5 (t)	5.4	1.4	1.2	166.2	173.0
2b	$CDCl_3$	148.4 (dd)	164.6 (d)	141.2 (br d)	114.7 (d)	166.8 (dq)	91.4 (d)	165.7 (qqd)	5.1	1.1		163.5	172.6
2b′	[$^2H_6$]DMSO	148.4 (s)	165.0 (d)	145.5 (br s)	113.0 (d)	166.0 (dq)	93.0 (d)	165.6 (qqd)	5.5	1.4		161.8	171.0
2c	[$^2H_6$]DMSO	153.6	165.8 (d)	142.7 (d)	114.5 (d)	166.1	70.0 (d)				1.8	181.0	173.0
2c′	[$^2H_6$]DMSO	154.9 (d)	165.3 (d)	141.8 (dd)	114.5 (d)	166.0 (dq)	72.1 (d)		5.0	1.0	1.0	180.6	180.6
2e′	[$^2H_6$]DMSO	148.4 (s)	164.4 (d)	144.9 (br s)	113.5 (d)	166.1 (dq)	95.7 (d)	165.3 (qqd)					
2f′	[$^2H_6$]DMSO	147.2 (br s)	164.5 (d)	145.2	112.9	166.0 (dq)	97.6	165.2					
2h	[$^2H_6$]DMSO	147.1 (br s)	164.2 (d)	141.6	113.2	166.2 (dq)	92.2	164.4	5.0				
2h′	[$^2H_6$]DMSO	149.6 (br s)	165.0 (d)	145.3	113.2	166.0 (dq)	92.2	164.6	5.0	1.8			
2g	$CDCl_3$	148.4 (br s)	164.6 (dd)	141.4 (dd)	114.6 (d)	166.9 (dq)	91.3 (d)	164.7 (m)	5.8	1.1	2.1	163.0	173.0
2g′	$CDCl_3$	148.9 (s)	166.1 (br d)	143.3 (s)	115.6 (d)	165.9 (dq)	93.3 (d)	165.9 (m)	5.8	1.4		159.9	172.0

[a] *J* Values are given in Hz.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker AMX 400 with $SiMe_4$ as internal reference in either [$^2H_6$]DMSO or $CDCl_3$ solutions. IR Spectra were obtained on a Specord IR spectrometer as KBr pellets. Products were analyzed by TLC on DC-Plastikfolen Kieselgel 60 F 254 plates. The melting points are uncorrected. The monothioamides (**1a**–**h**) were prepared by the reaction of the corresponding nitriles with hydrogen sulfide, as reported.[14]

(*E*)-2-(Ethoxycarbonylmethylene)-(*Z*)-5-(methoxycarbonylmethylene)thiazolidin-4-one 2a

DMAD (0.002 mol) Was added to a solution of thioacetamide **1a** (0.002 mol) in chloroform. The mixture was stirred at room temperature for 2 h. Filtration gave compound **2a** as yellow crystals, mp 175–178 °C (from ethanol). Yield 64% (Found: C, 46.36; H, 3.98; N, 5.80; S, 12.9. Calc. for $C_{10}H_{11}NO_5S$: C, 46.70; H, 4.28; N, 5.40; S, 12.45%); ν_{max}/cm^{-1} 3190, 3050, 1730, 1690.

2-(*N*,*N*-Dimethylcarbamoylmethylene)-5-(methoxycarbonylmethylene)thiazolidin-4-one 2b

DMAD (0.002 mol) Was added to a stirred solution of **1b** (0.002 mol) in chloroform. After 30 min a precipitate of (*Z*)-2-(*N*,*N*-dimethylcarbamoylmethylene)-(*Z*)-5-(methoxycarbonylmethylene)thiazolidin-4-one **2b′** was collected as yellow crystals, mp 224–227 °C (from ethanol). Yield 17% (Found: C, 47.26; H, 4.87; N, 10.93; S, 12.88. Calc. for $C_{10}H_{12}N_2O_4S$: C, 46.87; H, 4.72; N, 10.93; S, 12.51%); ν_{max}/cm^{-1} 3050, 1730, 1630.

Evaporation of the filtrate gave yellow needles of (*E*)-2-(*N*,*N*-dimethylcarbamoylmethylene)-(*Z*)-5-(methoxycarbonylmethylene)thiazolidin-4-one **2b**, mp 178–180 °C (from ethanol). Yield 66% (Found: C, 47.12; H, 5.12; N, 11.10; S, 13.0. Calc. for $C_{10}H_{12}N_2O_4S$: C, 46.87; H, 4.72; N, 10.93; S, 12.51%); ν_{max}/cm^{-1} 3160, 3040, 1730, 1680.

(*E*,*Z*)-2-Cyanomethylene-(*Z*)-5-(methoxycarbonylmethylene)-thiazolidin-4-one 2c

Following the method for the preparation of **2a**, compound **2c** was obtained as a mixture of yellow needles, yield 46%, mp 231–233 °C (from ethanol) (Found: N, 13.33; S, 15.28. Calc. for $C_8H_6N_2O_3S$: N, 13.45; S, 15.27%).

(*E*)-2-[*N*-(2-Methylphenyl)carbamoylmethylene]-(*Z*)-5-(methoxycarbonylmethylene)thiazolidin-4-one 2d

Following the method for the preparation of **2a**, compound **2d** was obtained as yellow needles, yield 66%, mp 222–225 °C (from ethanol) (Found: N, 9.1; S, 10.5. Calc. for $C_{15}H_{14}N_2O_4S$: N, 8.8; S, 10.1%).

(*E*)-2-[*N*-(2,6-Dichlorophenyl)carbamoylmethylene]-(*Z*)-5-(methoxycarbonylmethylene)thiazolidin-4-one 2e

Following the method for the preparation of **2a**, compound **2e** was obtained as yellow crystals, yield 54%, mp 237–240 °C (from ethanol) (Found: N, 7.2; S, 8.3. Calc. for $C_{14}H_{10}Cl_2N_2O_4S$: N, 7.5; S, 8.6%).

(*E*)-2-[*N*-(2-Methoxyphenyl)carbamoylmethylene]-(*Z*)-5-(methoxycarbonylmethylene)thiazolidin-4-one 2f

Following the method for the preparation of **2a**, compound **2f** was obtained as yellow crystals, yield 54%, mp 216–218 °C (from ethanol) (Found: N, 8.6; S, 9.4. Calc. for $C_{15}H_{14}N_2O_5S$: N, 8.4; S, 9.6%).

(*E*)-2-(2-Oxo-2-piperidinoethylidene)-(*Z*)-5-(methoxycarbonylmethylene)thiazolidin-4-one 2g

Following the method for the preparation of **2a**, compound **2g** was obtained as yellow needles, yield 74%, mp 143–145 °C (from ethanol) (Found: N, 9.63; S, 11.30. Calc. for $C_{13}H_{16}N_2O_4S$: N, 9.46; S, 10.81%); ν_{max}/cm^{-1} 3200, 3060, 1720, 1680.

(*E*)-2-[2-Oxo-2-(morpholin-4-yl)ethylidene]-(*Z*)-5-(methoxycarbonylmethylene)thiazolidin-4-one 2h

Following the method for the preparation of **2a**, compound **2h** was obtained as yellow needles, yield 76%, mp 168–172 °C (from ethanol) (Found: C, 48.57; H, 4.87; N, 9.14; S, 11.22. Calc. for $C_{12}H_{14}N_2O_5S$: C, 48.32; H, 4.73; N, 9.39; S, 10.75%); ν_{max}/cm^{-1} 3160, 3020, 1720, 1690.

2-(*N*,*N*-Dimethylcarbamoyl)-2-(*p*-tolylhydrazono)thioacetamide 4a

A solution of $NaNO_2$ (0.0027 mol) in water (5 ml) was added to an ice-cooled solution of *p*-toluidine (0.0027 mol) in 7% hydrochloric acid. This diazonium salt solution was added to a stirred solution of thioacetamide **1b** (0.0027 mol) in ethanol at

5–10 °C. The pH of the reaction mixture was kept at 6–7 by addition of solid sodium acetate. The reaction mixture was left overnight in the refrigerator. Filtration gave the yellow aryl hydrazone **4a**, mp 218–220 °C (from ethanol). Yield 64% (Found: N, 20.78; S, 12.53. Calc. for $C_{12}H_{16}N_4OS$: N, 21.19; S, 12.13%).

2-(Morpholin-4-ylcarbonyl)-2-(*p*-tolylhydrazono)thioacetamide 4b

Following the method for the preparation of **4a**, compound **4b** was obtained as yellow crystals, yield 60%, mp 223–225 °C (from ethanol) (Found: C, 55.27; H, 5.97; N, 18.73. Calc. for $C_{14}H_{18}N_4O_2S$: C, 54.90; H, 5.88; N, 18.30%).

2-[*p*-Tolylhydrazono(*N*,*N*-dimethylcarbamoyl)methylene]-methoxycarbonylmethylene-4,5-dihydrothiazol-4-one 5a

DMAD (0.0025 mol) Was added to a solution of hydrazone **4a** (0.002 mol) in absolute ethanol. The mixture was stirred at room temperature for 2 h. Filtration gave the compound **5a** (66%) as red crystals, mp 238–240 °C (from ethanol) (Found: N, 14.54; S, 8.56. Calc. for $C_{17}H_{18}N_4O_4S$: N, 14.96; S, 8.56%).

2-[*p*-Tolylhydrazono(morpholin-4-ylcarbonyl)methylene]-5-(methoxycarbonylmethylene)thiazolidin-4-one 5b

Following the method for the preparation of **5a**, compound **5b** was obtained (68%) as red crystals, yield 68%, mp 223–225 °C (from ethanol) (Found: N, 13.86; S, 8.12. Calc. for $C_{19}H_{20}N_4O_5S$: N, 13.45; S, 7.70%).

Acknowledgements

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