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ORIGINAL PAPER

Triphenylphosphine-mediated chemoselective synthesis of functionalized thiazol-2(5*H*)-ones

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Abstract Stabilized phosphoranes, obtained from three-component reaction between dialkyl acetylenedicarboxylates and thiazolidine-2,4-dione in the presence of triphenylphosphine, undergo a smooth intramolecular Wittig reaction in boiling toluene to produce functionalized thiazol-2(5*H*)-ones in good yields. When alkyl propiolates were employed in these reactions, only the (*E*)-isomer of alkyl 3-(2,4-dioxothiazolidin-3-yl)acrylates were isolated. A dynamic effect was observed in the ^{1}H nuclear magnetic resonance (NMR) spectrum of ethyl (*E*)-3-(2,4-dioxothiazolidin-3-yl)-3-phenylacrylate as a result of restricted rotation ($\Delta G^{\neq} = 77$ kJ/mol) around the N–C bond between the thiazolidine moiety and the vinyl group.

Keywords Thiazol-2(5*H*)-one · Thiazolidin-2,4-dione · Hindered rotation · Intramolecular Wittig reaction · Triphenylphosphine

Introduction

Thiazole and its derivatives play a prominent role in nature, as they are found in numerous bioactive compounds. The thiazolium core present in vitamin B_1 and its coenzyme complex plays an important role in the decarboxylation of α-keto acids. A large number of thiazole derivatives obtained from microbial and marine origins exhibit important biological effects such as antitumor, antifungal, antibiotic, and antiviral activities [1]. Synthetic thiazoles have also been shown to exhibit a wide variety of bioactivity [2], while others have found application as liquid crystals [3] and cosmetic sunscreens [4]. Several methods for synthesis of thiazole derivatives have been developed [5–8], the most widely used method being Hantzsch synthesis [9].

As part of our current studies on synthesis of sulfur-containing organic compounds [10–12], herein we report an efficient procedure for chemoselective synthesis of functionalized thiazol-2(5*H*)-ones from reaction between thiazolidine-2,4-diones and acetylenic esters in the presence of triphenylphosphine (Ph_3P).

Results and discussion

The reaction of dialkyl acetylenedicarboxylates **1** with thiazolidine-2,4-dione (**2**) in the presence of Ph_3P at r.t. in ethyl acetate was completed within a few hours, and phosphoranes **3** were produced in good yields [13–16]. The ^{1}H NMR spectra of the reaction mixtures clearly showed the formation of the phosphorane **3**, and no other products could be detected. These ylides were subjected to intramolecular Wittig reaction in boiling toluene, without further purification, to produce dialkyl 2-(2,5-dihydro-2-oxothiazol-4-yl)fumarates **4** in good yields (Scheme 1). To establish the structure of the phosphoranes **3**, the ylide **3a** was isolated and characterized by infrared (IR), ^{1}H NMR, and ^{13}C NMR spectral data (see "Experimental").

Although these phosphorus ylides are stable at ambient temperature, they undergo a smooth reaction in boiling toluene to produce dialkyl 2-(2,5-dihydro-2-oxothiazol-4-yl)fumarates **4** in good yields (Scheme 1). Using 5-arylidenethiazolidine-2,4-diones **5** as the NH-acidic component in this reaction afforded dialkyl (5*Z*)-2-(5-benzylidene-2,5-dihydro-2-oxothiazol-4-yl)fumarates **7**. Structures **4** and **7**

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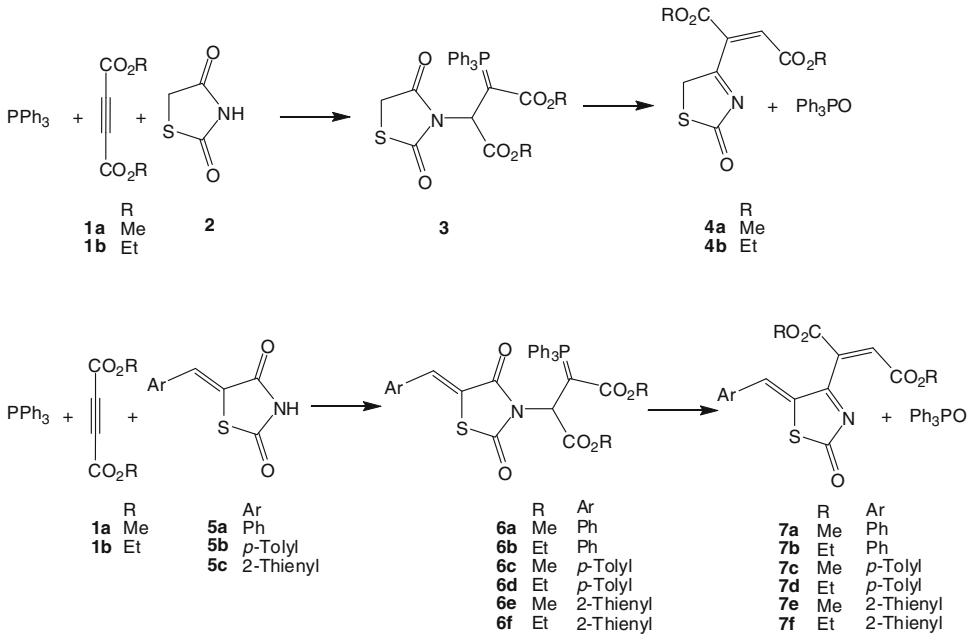
Scheme 1



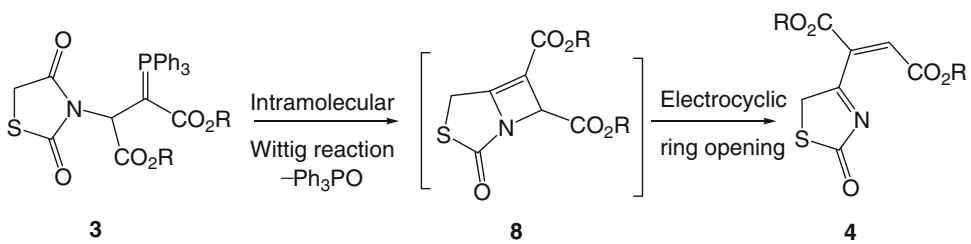
were assigned to the isolated products on the basis of their IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data. Thus, the ^{1}H NMR spectrum of each of the isolated products exhibited a C=CH proton signal at about 7.0–7.2 ppm, which is in agreement with the (*E*) configuration [17] for the vinylic moieties in compounds **4** and **7**.

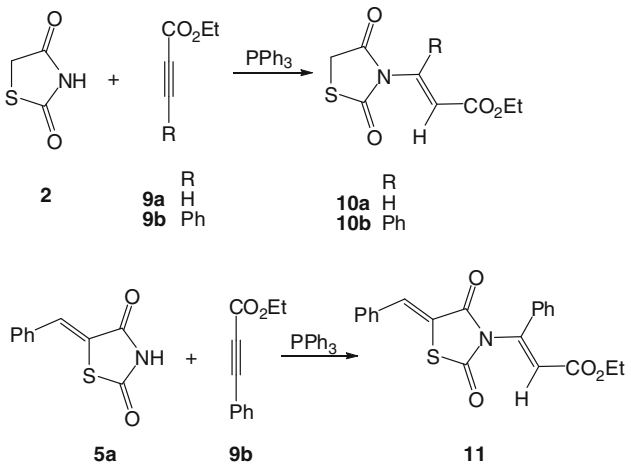
Although we have not yet established the mechanism of formation of **4** and **7** in an experimental manner, a plausible explanation is proposed in Scheme 2. Ylides **3** undergo intramolecular Wittig reaction to produce the fused bicyclic intermediates **8**, which apparently isomerize under the reaction conditions employed to produce **4** in good yields. Compound **3** has two carbonyl groups, namely the NCO and NCOS, available for intramolecular Wittig reaction. However, only the NCO carbonyl group participates in the intramolecular Wittig reaction. This chemoselectivity arises from higher electrophilic reactivity of the NCO carbonyl group toward the ylenic carbon compared with the carbonyl group of the NCOS moiety.

The reaction of thiazolidine-2,4-dione (**2**) or 5-benzylidene-thiazolidine-2,4-dione (**5a**) with alkyl propiolates **9** in the presence of Ph_3P proceeded spontaneously at r.t. in toluene and was finished within 1–4 h. ^{1}H and ^{13}C NMR spectra of the reaction mixtures clearly indicated the presence of products **10a**, **10b**, and **11** (Scheme 3). These products were separated by column chromatography and identified by their IR, ^{1}H NMR, and ^{13}C NMR spectral data. The mass spectra of these compounds displayed molecular ion peaks at appropriate *m*/*z* values. The ^{1}H NMR spectrum of **10a** exhibited an AX system for the *trans*-olefinic protons with $^{3}J_{HH} = 14.0$ Hz. On the basis of the chemistry of trivalent phosphorus nucleophiles [14–16], it is reasonable to assume that compound **10a** results from initial addition of Ph_3P to ethyl propiolate **9a** and subsequent protonation of the 1:1 adduct by the NH-acidic **2**. Then, the positively charged ion **13** is attacked by the nitrogen atom of the conjugate base **14** to produce the zwitterionic intermediate **15**, which is converted to **10a** by elimination of Ph_3P (Scheme 4) [14, 16].

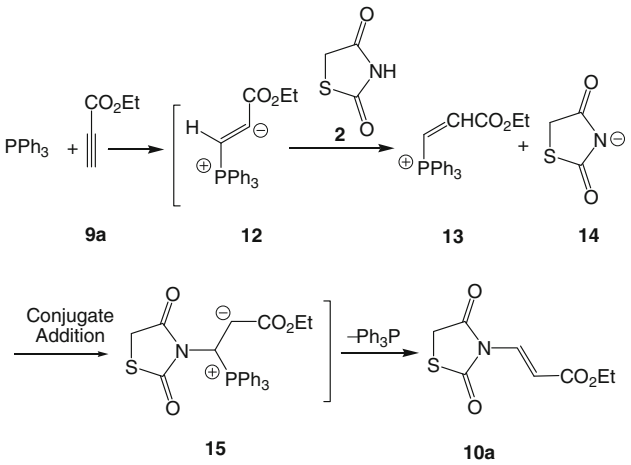
The ^{1}H NMR spectrum of **10b** exhibits a characteristic AB quartet for the diastereotopic methylene protons in $CDCl_3$ at 25 °C. The ^{1}H NMR of **10b** in 1,2-dichlorobenzene at 25 °C is similar to that measured in $CDCl_3$. Increasing the temperature results in coalescence of the CH_2 resonances. At 110 °C, a relatively broad singlet was observed for the CH_2 group. This dynamic effect is interpreted in terms of restricted rotation around the N–C bond linking the vinyl group to thiazolidine ring. Although

Scheme 2





Scheme 3



Scheme 4

extensive line-shape analysis in relation to the dynamic NMR effect observed for **10b** was not undertaken in the present work, the variable temperature spectra are sufficient to calculate the free energy of activation for the restricted N–C bond rotation. From the coalescence of the methylene protons and using the expression $k = \sqrt{\Delta v^2 + 6J_{AB}^2}$, the rate constant ($k$) was calculated to be 116 s^{-1} at 365 K. Application of the absolute rate theory with a transmission coefficient of 1 gives a free energy of activation ($\Delta G^{\neq}$) of 77 ± 2 kJ/mol for **10b**, where all known sources of errors are estimated and included [18].

In conclusion, the present method features the advantages that the reaction can be performed under neutral conditions and that the starting materials and reagents can be mixed without any modifications. The procedure described herein provides an acceptable method for preparation of highly functionalized thiazol-2(5*H*)-ones and (5*Z*)-5-arylidenethiazol-2(5*H*)-ones.

Experimental

Chemicals were purchased from Merck and used without further purification. Compounds **5** were prepared from **2** by a known method [19]. Melting points were measured on an Electrothermal 9100 apparatus. ^{1}H and ^{13}C NMR spectra ($CDCl_3$) were measured with a Bruker Avance DRX-300 spectrometer at 300 and 75 MHz, respectively. IR spectra were measured on a Shimadzu IR-460 spectrometer. Mass spectra were recorded on a FINNIGAN-MAT 8430 spectrometer operating at ionization potential of 70 eV. Chromatography columns were prepared from Merck silica gel 70–230 mesh.

*General procedure for the preparation of compounds **3** and **6***

To a stirred solution of the thiazolidine-2,4-dione **2** or **5** (1 mmol) and dialkyl acetylenedicarboxylate **1** (1 mmol) in 5 cm^3 EtOAc was added dropwise a solution of 0.26 g Ph_3P (1 mmol) in 2 cm^3 EtOAc at 25 °C over 10 min. After 3 h stirring at r.t., the product was filtered and washed with cold EtOAc. Although products were usually pure enough and could be directly used for the preparation of compounds **4** (and **7**), **3a** was purified and spectroscopic data are given below as an example.

Dimethyl 2-(2,4-dioxo-3-thiazolidinyl)-3-(triphenylphosphoranylidene)butanedioate (**3a**, $C_{27}H_{24}NO_6PS$)

Pink powder; m.p.: 137–139 °C; yield 0.42 g (80%); IR (KBr): $\bar{\nu}$ = 1,619 (C=O), 1,691 (C=O), 1,745 (C=O), 1,434 (C=C) cm^{-1}; EI-MS: m/z = 521 (M^+, 2), 275 (12), 262 (100), 200 (10), 184 (75), 140 (18), 115 (16), 59 (8).

Major isomer (*Z*)-**3a** (55%): ^{1}H NMR ($CDCl_3$): δ = 3.12 (3H, s, MeO), 3.74 (3H, s, MeO), 3.82 (2H, s, CH_2S), 4.76 (1H, d, $^3J_{PC}$ = 15.5 Hz, CH), 7.45–7.74 (15H, m, $3C_6H_5$) ppm; ^{13}C NMR ($CDCl_3$): δ = 33.3 (CH_2S), 37.5 (d, $^1J_{PC}$ = 130.0 Hz, P–C), 49.4 (MeO), 50.9 (MeO), 59.1 (d, $^2J_{PC}$ = 17.1 Hz, CH), 126.5 (d, $^1J_{PC}$ = 91.0 Hz, P–C_{ipso}), 129.2 (d, $^3J_{PC}$ = 12.0 Hz, C_{meta}), 132.4 (d, $^4J_{PC}$ = 2.0 Hz, C_{para}), 134.0 (d, $^2J_{PC}$ = 11.1 Hz, C_{ortho}), 166.7 (C=O), 167.2 (C=O), 170.5 (d, $^2J_{PC}$ = 14.0 Hz, PC=C), 171.0 (C=O) ppm.

Minor isomer (*E*)-**3a** (45%): ^{1}H NMR ($CDCl_3$): δ = 3.60 (3H, s, MeO), 3.73 (3H, s, MeO), 3.99 (2H, s, CH_2S), 4,80 (1H, d, $^3J_{PC}$ = 17.5 Hz, CH), 7.45–7.74 (15H, m, $3C_6H_5$) ppm; ^{13}C NMR ($CDCl_3$): δ = 35.9 (CH_2S), 41.5 (d, $^1J_{PC}$ = 140.0 Hz, P–C), 52.7 (MeO), 53.3 (MeO), 58.8 (d, $^2J_{PC}$ = 17.1 Hz, CH), 127.0 (d, $^1J_{PC}$ = 93.2 Hz, P–C_{ipso}), 128.9 (d, $^3J_{PC}$ = 12.0 Hz, C_{meta}), 132.3 (d, $^4J_{PC}$ = 2.0 Hz, C_{para}), 133.8 (d, $^2J_{PC}$ = 11.2 Hz,

C_{ortho}), 163.1 (C=O), 164.2 (C=O), 168.8 (d, $^2J_{PC} = 14.2$ Hz, PC=C), 172.2 (C=O) ppm.

General procedure for the preparation of compounds ***4*** *and* ***7***

To a stirred solution of the thiazolidine-2,4-dione (**2** or **5**, 2 mmol) and dialkyl acetylenedicarboxylate (**1**, 2 mmol) in 10 cm^3 toluene was added dropwise a solution of 0.52 g Ph_3P (2 mmol) in 5 cm^3 toluene at r.t. over 10 min. After 1 h stirring at r.t., the reaction mixture was refluxed. After completion of the reaction [1–4 h, thin-layer chromatography (TLC): AcOEt/hexane 2:1], the solvent was removed from reaction mixture at reduced pressure and the residue was purified by column chromatography [silica gel 230–240 mesh (Merck), hexane/AcOEt 4:1].

Dimethyl (E)-2-(2,5-dihydro-2-oxothiazol-4-yl)-butenedioate (**4a**, $C_9H_9NO_5S$)
Yellow crystals; m.p.: 107–109 °C; yield 0.34 g (67%); IR (KBr): $\bar{\nu} = 1{,}693$ (C=O), 1,741 (C=O), 1,436 (C=C) cm^{-1}; EI-MS: $m/z = 243$ (M^+, 10), 125 (14), 77 (25), 74 (10), 69 (42), 57 (33), 43 (100); ^{1}H NMR ($CDCl_3$): $\delta = 3.80$ (3H, s, MeO), 3.89 (3H, s, MeO), 4.14 (2H, s, CH_2S), 7.20 (1H, s, CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 35.9$ (CH_2S), 53.1 (MeO), 54.0 (MeO), 132.1 (C), 143.4 (CH), 161.3, 162.6, 170.1 (3C=O), 170.4 (C=N) ppm.

Diethyl (E)-2-(2,5-dihydro-2-oxothiazol-4-yl)butenedioate (**4b**, $C_{11}H_{13}NO_5S$)
Yellow crystals; m.p.: 108–111 °C; yield 0.36 g (65%); IR (KBr) $\bar{\nu} = 1{,}691$ (C=O), 1,739 (C=O), 1,435 (C=C) cm^{-1}; EI-MS: $m/z = 271$ (M^+, 8), 125 (15), 77 (27), 74 (11), 69 (45), 57 (36), 43 (100); ^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (3H, t, $^3J = 7.1$ Hz, Me), 1.35 (3H, t, $^3J = 7.1$ Hz, Me), 4.14 (2H, s, CH_2S), 4.27 (2H, q, $^3J = 7.1$ Hz, CH_2O), 4.33 (2H, q, $^3J = 7.1$ Hz, CH_2O), 7.05 (1H, s, CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.3$ (Me), 14.4 (Me), 35.9 (CH_2S), 62.2 (CH_2O), 63.4 (CH_2O), 132.0 (C), 143.3 (CH), 161.2, 162.6, 170.1, (3C=O), 170.3 (C=N) ppm.

Dimethyl (E)-2-((5Z)-5-benzylidene-2,5-dihydro-2-oxothiazol-4-yl)butenedioate (**7a**, $C_{16}H_{13}NO_5S$)
Yellow crystals; m.p.: 99–101 °C; yield 0.44 g (64%); IR (KBr): $\bar{\nu} = 1{,}628$ (C=O), 1,749 (C=O), 1,424 (C=C) cm^{-1}; EI-MS: $m/z = 331$ (M^+, 7), 267 (24), 241 (33), 227 (15), 161 (16), 134 (100), 90 (23), 84 (9), 77 (21), 69 (33), 57 (20), 43 (61); ^{1}H NMR ($CDCl_3$): $\delta = 3.80$ (3H, s, MeO), 3.91 (3H, s, MeO), 7.25 (1H, s, CH), 7.47–7.58 (5H, m, 5 CH), 7.95 (1H, s, CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 53.3$ (MeO), 54.0 (MeO), 121.4 (CH), 129.7 (CH), 130.7 (2CH), 130.9 (2CH), 131.2 (C), 133.1 (CH), 133.4 (C), 135.3 (C), 161.3, 162.7, 170.2 (3C=O), 170.6 (C=N) ppm.

Diethyl (E)-2-((5Z)-5-benzylidene-2,5-dihydro-2-oxothiazol-4-yl)butenedioate (**7b**, $C_{18}H_{17}NO_5S$)
Yellow crystals; m.p.: 98–100 °C; yield 0.52 g (73%); IR (KBr): $\bar{\nu} = 1{,}676$ (C=O), 1,735 (C=O), 1,424 (C=C) cm^{-1}; EI-MS: $m/z = 359$ (M^+, 6), 294 (38), 269 (17), 161 (15), 134 (100), 98 (11), 90 (27), 77 (29), 69 (40), 57 (24), 43 (67); ^{1}H NMR ($CDCl_3$): $\delta = 1.28$ (3H, t, $^3J = 7.1$ Hz, Me), 1.38 (3H, t, $^3J = 7.1$ Hz, Me), 4.23 (2H, q, $^3J = 7.1$ Hz, CH_2O), 4.35 (2H, q, $^3J = 7.1$ Hz, CH_2O), 7.23 (1H, s, CH), 7.46–7.58 (5H, m, CH), 7.95 (1H, s, CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.3$ (Me), 14.4 (Me), 62.2 (CH_2O), 63.4 (CH_2O), 121.4 (CH), 121.8 (CH), 130.4 (2CH), 130.8 (2CH), 132.8 (CH), 133.5 (C), 135.3 (C), 143.5 (C), 161.3, 162.6, 170.3 (3C=O), 170.6 (C=N) ppm.

Dimethyl (E)-2-((5Z)-5-(4-methylbenzylidene)-2,5-dihydro-2-oxothiazol-4-yl)butenedioate (**7c**, $C_{17}H_{15}NO_5S$)
Colorless crystals; m.p.: 109–111 °C; yield 0.52 g (74%); IR (KBr): $\bar{\nu} = 1{,}681$ (C=O), 1,749 (C=O), 1,429 (C=C) cm^{-1}; EI-MS: $m/z = 345$ (M^+, 7), 267 (22), 241 (34), 227 (11), 176 (12), 148 (100), 104 (24), 91 (34), 84 (8), 77 (19), 69 (30), 57 (28), 43 (65); ^{1}H NMR ($CDCl_3$): $\delta = 2.38$ (3H, s, Me), 3.79 (3H, s, Me), 3.90 (3H, s, Me), 7.24 (1H, s, CH), 7.31 (2H, d, $^3J = 7.5$ Hz, 2CH), 7.44 (2H, d, $^3J = 7.5$ Hz, 2CH), 7.93 (1H, s, CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 22.0$ (Me), 53.1 (MeO), 54.0 (MeO), 121.6 (CH), 129.9 (CH), 130.8 (2CH), 130.9 (2CH), 131.5 (C), 133.3 (C), 133.5 (C), 135.3 (C), 161.3, 162.8, 170.2 (3C=O), 170.6 (C=N) ppm.

Diethyl (E)-2-((5Z)-5-(4-methylbenzylidene)-2,5-dihydro-2-oxothiazol-4-yl)butenedioate (**7d**, $C_{19}H_{19}NO_5S$)
Colorless crystals; m.p.: 110–112 °C; yield 0.54 g (72%); IR (KBr): $\bar{\nu} = 1{,}671$ (C=O), 1,737 (C=O), 1,428 (C=C) cm^{-1}; EI-MS: $m/z = 373$ (M^+, 10), 294 (26), 269 (38), 227 (13), 176 (15), 148 (100), 104 (21), 98 (10), 91 (35), 77 (18), 69 (35), 57 (31), 43 (60); ^{1}H NMR ($CDCl_3$): $\delta = 1.28$ (3H, t, $^3J = 7.1$ Hz, Me), 1.33 (3H, t, $^3J = 7.1$ Hz, Me), 2.43 (3H, s, Me), 4.23 (2H, q, $^3J = 7.1$ Hz, CH_2O), 4.33 (2H, q, $^3J = 7.1$ Hz, CH_2O), 7.23 (1H, s, CH), 7.31 (2H, d, $^3J = 7.5$ Hz, 2CH), 7.44 (2H, d, $^3J = 7.5$ Hz, 2CH), 7.93 (1H, s, CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.3$ (Me), 14.4 (Me), 22.0 (Me), 62.3 (CH_2O), 63.4 (CH_2O), 121.6 (CH), 129.9 (CH), 130.8 (2CH), 130.9 (2CH), 131.5 (C), 133.3 (C), 133.5 (C), 135.3 (C), 161.3, 162.8, 170.2 (3C=O), 170.6 (C=N) ppm.

Dimethyl (E)-2-((5Z)-5-(thiophen-2-ylmethylene)-2,5-dihydro-2-oxothiazol-4-yl)butenedioate (**7e**, $C_{14}H_{11}NO_5S_2$)
Yellow crystals; m.p.: 87–89 °C; yield 0.46 g (70%); IR (KBr): $\bar{\nu} = 1{,}689$ (C=O), 1,735 (C=O), 1,431 (C=C) cm^{-1}; EI-MS: $m/z = 337$ (M^+, 5), 241 (36), 219 (17), 167 (16),

140 (100), 96 (30), 84 (7), 83 (39), 77 (21), 69 (32), 57 (25), 43 (62); ^{1}H NMR ($CDCl_3$): $\delta = 3.80$ (3H, s, MeO), 3.89 (3H, s, MeO), 7.18 (1H, dd, $^3J = 4.5$ Hz, $^3J = 3.6$ Hz, CH), 7.24 (1H, s, CH), 7.44 (1H, d, $^3J = 3.6$ Hz, CH), 7.71 (1H, d, $^3J = 4.5$ Hz, CH), 8.11 (1H, s, CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 53.1$ (MeO), 54.0 (MeO), 119.0 (C), 128.0 (CH), 129.1 (CH), 130.5 (CH), 132.9 (CH), 133.3 (C), 134.3 (CH), 137.8 (C), 161.4, 162.9, 170.3 (3C=O), 170.6 (C=N) ppm.

Diethyl (E)-2-((5Z)-5-(thiophen-2-ylmethylene)-2,5-dihydro-2-oxothiazol-4-yl)butenedioate (**7f**, $C_{16}H_{15}NO_5S_2$)

Yellow crystals; m.p.: 90–92 °C; yield 0.76 g (69%); IR (KBr): $\bar{\nu} = 1{,}683$ (C=O), 1,737 (C=O), 1,426 (C=C) cm^{-1}; EI-MS: $m/z = 365$ (M^+, 7), 269 (40), 219 (18), 167 (19), 140 (100), 98 (8), 96 (29), 83 (37), 77 (23), 69 (38), 57 (26), 43 (67); ^{1}H NMR ($CDCl_3$): $\delta = 1.28$ (3H, t, $^3J = 7.1$ Hz, Me), 1.34 (3H, t, $^3J = 7.1$ Hz, Me), 4.22 (2H, q, $^3J = 7.1$ Hz, CH_2O), 4.34 (2H, q, $^3J = 7.1$ Hz, CH_2O), 7.18 (1H, dd, $^3J = 4.9$ Hz, $^3J = 3.5$ Hz, CH), 7.24 (1H, s, CH), 7.44 (1H, d, $^3J = 3.5$ Hz, CH), 7.71 (1H, d, $^3J = 4.9$ Hz, CH), 8.11 (1H, s, CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.3$ (Me), 14.4 (Me), 62.2 (CH_2O), 63.4 (CH_2O), 119.0 (C), 127.8 (CH), 129.1 (CH), 130.7 (CH), 132.8 (CH), 133.3 (C), 134.3 (CH), 137.8 (C), 161.4, 162.7, 170.5 (3C=O), 170.8 (C=N) ppm.

*General procedure for the preparation of compounds **10** and **11***

To a stirred solution of the thiazolidine-2,4-dione (**2** or **5a**, 2 mmol) and 0.52 g Ph_3P (2 mmol) in 10 cm^3 toluene was added dropwise a solution of the propiolate (2 mmol) in 5 cm^3 toluene at r.t. After completion of the reaction (1–4 h, TLC: AcOEt/hexane 2:1), the solvent was removed from the reaction mixture at reduced pressure and the residue was purified by column chromatography [silica gel 230–240 mesh (Merck), hexane/AcOEt 4:1].

Ethyl (E)-3-(2,4-dioxothiazolidin-3-yl)-2-propenoate (**10a**, $C_8H_9NO_4S$)

Yellow crystals; m.p.: 88–91 °C; yield 0.32 g (75%); IR (KBr): $\bar{\nu} = 1{,}625$ (C=O), 1,696 (C=O), 1,743 (C=O), 1,428 (C=C) cm^{-1}; EI-MS: $m/z = 215$ (M^+, 11), 187 (26), 142 (68), 77 (10), 73 (24), 69 (88), 57 (99), 43 (100) ppm; ^{1}H NMR ($CDCl_3$): $\delta = 1.33$ (3H, t, $^3J = 7.1$ Hz, Me), 4.05 (2H, s, CH_2S), 4.27 (2H, q, $^3J = 7.1$ Hz, CH_2O), 6.99 (1H, d, $^3J = 14.0$ Hz, CH), 7.78 (1H, d, $^3J = 14.0$ Hz, CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.4$ (Me), 34.5 (CH_2S), 62.7 (CH_2O), 132 (CH), 145 (CH), 162.6, 170.1, 170.5 (3C=O) ppm.

Ethyl (E)-3-(2,4-dioxothiazolidin-3-yl)-3-phenyl-2-propenoate (**10b**, $C_{14}H_{13}NO_4S$)

Yellow crystals; m.p.: 97–99 °C; yield 0.46 g (78%); IR (KBr): $\bar{\nu} = 1{,}631$ (C=O), 1,695 (C=O), 1,747 (C=O), 1,430 (C=C) cm^{-1}; EI-MS: $m/z = 291$ (M^+, 14), 263 (30), 218 (79), 77 (11), 73 (27), 69 (85), 57 (98), 43 (100); ^{1}H NMR ($CDCl_3$): $\delta = 1.33$ (3H, t, $^3J = 7.1$ Hz, Me), 4.05 (2H, ABq, $J_{AB} = 17.5$ Hz, $\Delta\nu_{AB} = 30$ Hz, CH_2S), 4.27 (2H, q, $^3J = 7.1$ Hz, CH_2O), 7.35–7.47 (5H, m, CH), 8.10 (1H, s, CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.4$ (Me), 34.5 (CH_2S), 62.7 (CH_2O), 122.0 (CH), 129.2 (2CH), 129.4 (2CH), 131.3 (CH), 132.1 (C), 143.4 (C), 162.8, 170.1, 170.4 (3C=O) ppm.

Ethyl (E)-3-((Z)-5-benzylidene-2,4-dioxothiazolidin-3-yl)-3-phenyl-2-propenoate (**11**, $C_{21}H_{17}NO_4S$)

Yellow crystals; m.p.: 90–92 °C; yield 0.56 g (73%); IR (KBr): $\bar{\nu} = 1{,}637$ (C=O), 1,696 (C=O), 1,740 (C=O), 1,435 (C=C) cm^{-1}; EI-MS: $m/z = 379$ (M^+, 15), 351 (28), 315 (13), 306 (70), 289 (35), 90 (25), 77 (34), 73 (26), 69 (87), 57 (97), 43 (100); ^{1}H NMR ($CDCl_3$): $\delta = 1.35$ (3H, t, $^3J = 7.1$ Hz, Me), 4.34 (2H, q, $^3J = 7.1$ Hz, CH_2O), 7.33-7.44 (5H, m, CH), 7.46–7.63 (5H, m, CH), 7.95 (1H, s, CH), 8.12 (1H, s, CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.6$ (Me), 62.7 (CH_2O), 121.5 (CH), 121.8 (CH), 129.5 (CH), 129.6 (2CH), 129.7 (2CH), 130.8 (2CH), 131.2 (CH), 131.3 (CH), 132.2 (C), 133.4 (C), 135.3 (C), 143.4 (C), 162.6, 165.4, 166.6 (3C=O) ppm.

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