Tetrahedron Letters 51 (2010) 3392–3397

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

[2+2] Cycloaddition of electron-poor acetylenes to (*E*)-3-dimethylamino-1-heteroaryl-prop-2-en-1-ones: synthesis of highly functionalized 1-heteroaroyl-1,3-butadienes

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ARTICLE INFO

Article history:
Received 4 March 2010
Revised 2 April 2010
Accepted 23 April 2010
Available online 28 April 2010

Keywords:
[2+2] Cycloaddition
(*E*)-3-Dimethylamino-1-heteroaryl-prop-2-en-1-ones
1-Heteroaroyl-1,3-butadienes

ABSTRACT

Microwave-assisted [2+2] cycloaddition of (*E*)-3-dimethylamino-1-heteroaryl-prop-2-en-1-ones to dimethyl acetylenedicarboxylates gives (2*E*,3*E*)-dimethyl-2-[(dimethylamino)methylene]-3-(substituted)succinates in 8–91% yield. In the case of a 4,5-dihydrothiazoline derivative, cycloaddition also took place at the endocyclic C=N double bond.

1. Introduction

The [2+2] cycloaddition of an alkene to an alkyne represents an important strategy for the synthesis of cyclobutene derivatives. It can be achieved by photochemical methods, thermal reactions via biradical intermediates[1] and by the use of Lewis acid catalysts.[2a–c] Recently, the formal [2+2] cycloaddition of strong electron-acceptors to electron-rich alkynes followed by retro-electrocyclization has been studied in detail.[3a–c] On the other hand, the wide applicability of 3-(dimethylamino)propenoates and related enaminones as versatile reagents in heterocyclic synthesis,[4a–d] including natural products and their analogues, for example, the aplysinopsins,[5a,b] meridianines,[6a,b] dipodazines[7a–c] and triprostatines,[8] has been demonstrated. This encouraged us to study their reactions with electron-poor acetylenes. Recently, we reported regiospecific microwave-assisted [2+2] cycloadditions of substituted 2-amino-3-(dimethylamino)propenoates with acetylenedicarboxylates which gave highly functionalized 1-amino-4-(dimethylamino)buta-1,3-dienes[9] and their transformations into highly substituted pyridines, pyrroles and pyrido[3,4-*c*]pyridazine derivatives.[10] These cycloadditions have been extended to (5*Z*)-5-[(dimethylamino)methylene]-3-methyl-imidazolidine-2,5-diones, resulting in the formation of (1*E*,3*E*)-1-(acylamino)-4-(dimethylamino)buta-1,3-dienes.[11] In this Letter, we report the preparation of highly functionalized 1-heteroaroylbuta-1,3-dienes via [2+2] cycloaddition of dimethyl acetylenedicarboxylate (DMAD) to (*E*)-3-dimethylamino-1-heteroaryl-prop-2-en-1-ones.

2. Results and discussion

When (*E*)-3-(dimethylamino)-1-heteroaryl-prop-2-en-1-ones **2a–f** and **12a** prepared from acetyl heterocycles **1a–f** and **12b** and *N*,*N*-dimethylformamide dimethylacetal (DMFDMA) or *tert*-butoxy bis(dimethylamino)methane (TBDMAM) were reacted under microwave irradiation at elevated temperatures with DMAD (**3**), as an electron-poor acetylene, the corresponding dimethyl (2*E*,3*E*)-2-[(dimethylamino)methylene]-3-(substituted)succinates **4a–f** and **14** were isolated as the only isomers in 8–91% yield (Schemes 1 and 3).

The structures of the products were determined by spectroscopic methods (IR, ^{1}H and ^{13}C NMR, MS) and by elemental analyses. Additionally, the structures of compounds **2f**, **4d** and **13a**,**b** were confirmed by X-ray diffraction analysis (Figs. 1, 2, 4 and 5).

Two pathways for this cycloaddition can be envisioned, concerted and stepwise. In the case of a concerted cycloaddition, the reaction should proceed as a [2_s+2_a] cycloaddition resulting in cyclobutene intermediate **9**, which would undergo a conrotatory retro-electrocyclization (ring-opening) to afford (2*E*,3*E*)-**10** and/or (2*Z*,3*Z*)-**11**. In the case of a two-step mechanism, the initially formed intermediate **5** can be transformed into **5′** by rotation

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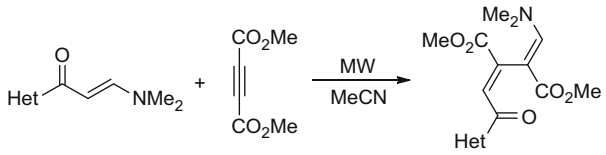
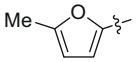
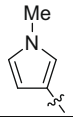
0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.04.106



2a-f **3** **4a-f**

Product	Het	Yield [%]	Time	Temp. [°C]
4a		70	20 min	100
4b		89	10 min	100
4c		87	20 min	100
4d		70	20 min	100
4e		91	24 h	r.t.
4f		16	15 min	100

Scheme 1. Microwave-assisted [2+2] cycloaddition.

around the single bond. Cyclization of **5** leads to trans-cyclobutene intermediate **9**, whereas cyclization of **5′** would give sterically unfavoured *cis*-cyclobutene intermediate **6**, which upon a conrotatory retro-electrocyclization would produce isomers (2*Z*,3*E*)-**7** and/or (2*E*,3*Z*)-**8** (Scheme 2).

The single crystal X-ray structure of product **4d** (Fig. 2) clearly demonstrates the (2*E*,3*E*) configuration at the C=C double bonds. On the other hand, the configurations at the C=C double bonds in products **4c** and **4f** were determined by NMR on the basis of long-range coupling constants, $^{3}J_{C-H}$, between the corresponding methine protons and the carbonyl carbon atoms, measured from the antiphase splitting of cross peaks in the HMBC spectrum. Generally, the magnitude of the coupling constants, $^{3}J_{C-H}$, for nuclei with a cis-configuration at the C=C double bond is smaller (2–6 Hz) than that of trans-oriented nuclei (8–12 Hz).[12] The magnitude of the coupling constants, $^{3}J_{C(1)-H(2')} = 4.5$ Hz and $^{3}J_{C(1)-H(2')} = 4.8$ Hz, for compounds **4c** and **4f**, respectively, indicates a (2*E*)-configuration. Similarly, the (3*E*)-configuration was established for both compounds **4c** and **4f** ($^{3}J_{C(3)-H(3')} = 6.9$ Hz) (Fig. 3). Finally, selected ^{1}H NMR data of cycloadducts **4a**–**f** and **14** correlate well, implying their uniform (2*E*,3*E*) configuration. This in turn indicates that the cycloaddition reactions could proceed either by a concerted mechanism or by a two-step mechanism in which rotation around the single bond is restricted due to the formation of sterically less favored *cis*-cyclobutene derivative **6**.

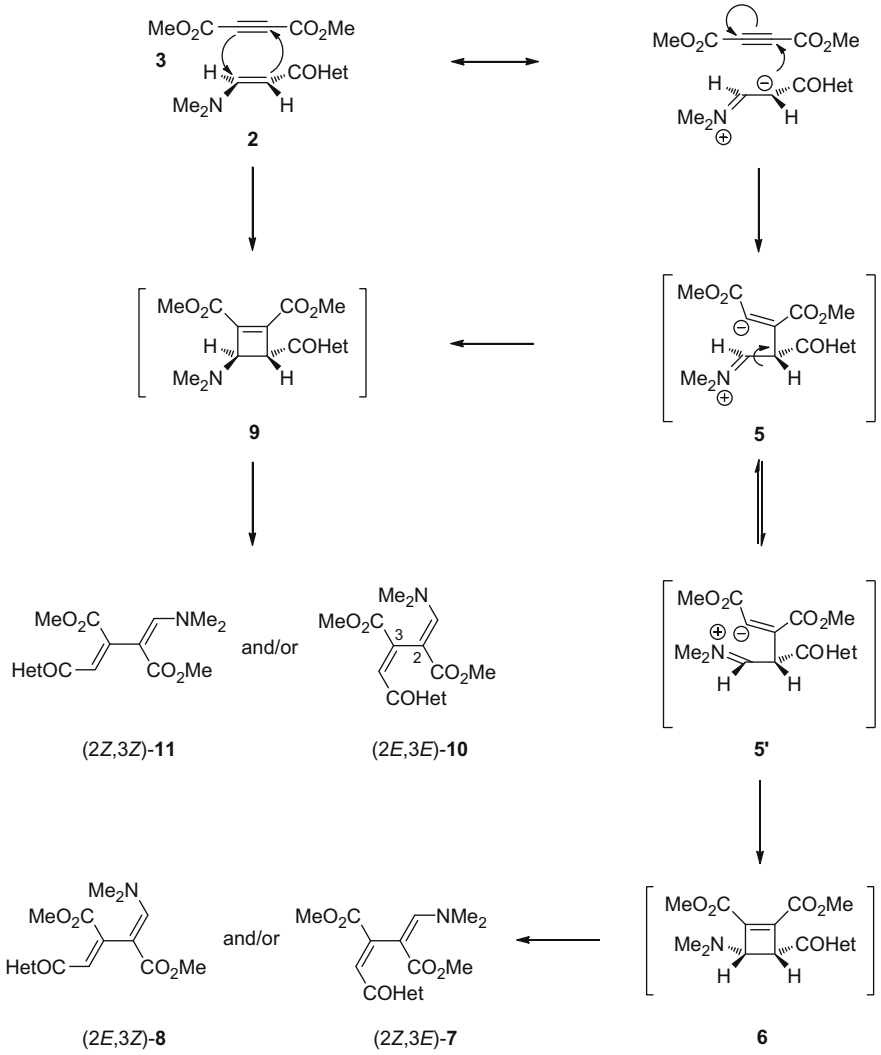
The cycloaddition of (*E*)-1-(4,5-dihydrothiazol-2-yl)-3-(dimethylamino)prop-2-en-1-one (**12a**), prepared from 1-(4,5-dihydrothiazol-2-yl)ethanone (**12b**) and DMFDMA, with DMAD (**3**), under microwave irradiation, afforded a mixture of the corresponding [2+2] cycloadduct **14** in 8% yield and (*E*)-dimethyl 6-[2-(dimethylamino)vinyl]-5-oxo-2,3,5,7a-tetrahydropyrrolo[2,1-*b*]thiazole-7,7a-dicarboxylate (**13a**) in 32% yield (Scheme 3).

The elemental analysis and HRMS spectrum for the minor product **14** gave a molecular formula of $C_{14}H_{18}N_2O_5S$, corresponding to 1:1 adduct. The ^{1}H NMR spectrum exhibited a singlet at 2.84 ppm integrating for 6 protons (N*Me*$_2$ group), two triplets at 3.32 and 4.55 ppm, each integrating for two protons, ($J = 8.7$ Hz, –CH_2CH_2– group), two singlets at 3.64 and 3.81 ppm, each integrating for three protons (two ester *Me* groups) and two singlets, each integrating for one proton at 7.70 and 7.89 ppm for C2′-H and C3′-H. On the basis of these data and their close ^{1}H NMR correlation with analogous cycloadducts **4a**–**f** (see Table 1), one can conclude that the cycloaddition of DMAD took place at the exocyclic C=C double bond of **12a**, thus forming product **14**.

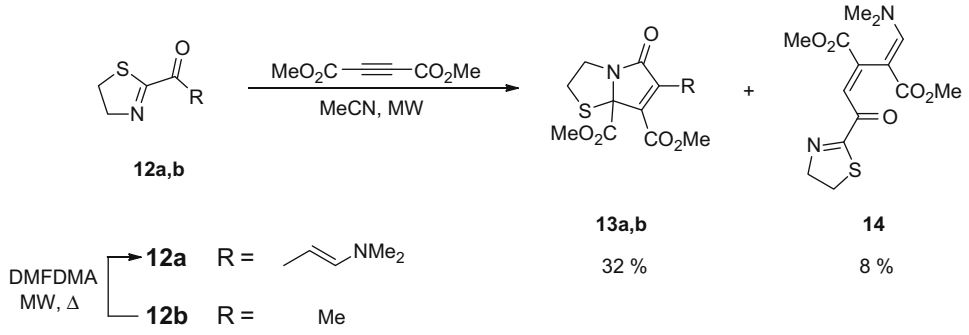
The elemental analysis and HRMS for the major product **13a** gave a molecular formula of $C_{14}H_{18}N_2O_5S$, also corresponding to 1:1 adduct. The ^{1}H NMR spectrum exhibited a singlet at 3.00 ppm (6H, N*Me*$_2$ group), two multiplets at ~3.41 ppm (3H) and ~4.29 ppm (1H) for the –CH_2CH_2– group, two singlets at 3.72 (3H) and 3.80 ppm (3H) for the two ester *Me* groups and two doublets at 5.98 (1H) and 8.49 ppm (1H) ($J = 13.2$ Hz) for the –CH=CH– (trans) structural element. On the basis of these data, we assumed that the cycloaddition of DMAD to **12a** must have taken place at the C=N double bond of the thiazolidine ring. The single crystal X-ray structure confirmed the structure of compound **13a** (Fig. 4).

Similarly, the cycloaddition of DMAD to 1-(4,5-dihydrothiazol-2-yl)ethanone (**12b**) produced a compound with the molecular formula $C_{11}H_{13}NO_5S$, corresponding again to a 1:1 cycloadduct. The ^{1}H NMR spectrum showed a singlet at 2.19 ppm (3H) for the *Me* group, three multiplets at ~3.36 ppm (1H), ~3.53 ppm (2H) and ~4.30 ppm (1H) for the –CH_2CH_2– structural element and two singlets at 3.77 ppm (3H) and 3.88 ppm (3H) for the two ester *Me* groups. The structure of this cycloadduct is similar to the structure of compound **13a** and was confirmed by single crystal X-ray analysis (Fig. 5).

We rationalize the formation of compound **13b** by initial [2+2] cycloaddition of DMAD to the endocyclic C=N double bond of **12b** to form the intermediate cycloadduct **15**, followed by a series of 1,3-sigmatropic shifts **15**→**16**→**17**→**18** to finally arrive at **13b** (Scheme 4).



Scheme 2. Proposed mechanisms for the cycloaddition–retro-electrocyclization.



Scheme 3. [2+2] Cycloaddition of **12a** with DMAD.

3. Experimental

3.1. General procedure for the synthesis of (*E*)-3-(dimethylamino) -1-substituted-prop-2-en-1-ones 2a–f and 12a[13]

To compound **1a**–**f**, **12b** (1 equiv) was added DMFDMA or TBDMAM (1.2 equiv) and the resulting mixture was stirred in a closed vessel under microwave irradiation (300 W) at an automatically controlled constant temperature (CEM Corporation discover microwave unit). After cooling to room temperature, the volatile components were evaporated in vacuo and the residue was purified by column chromatography (products **2a**,**e**, **12a**) or crystallization (products **2b**,**c**,**d**,**f**).

3.2. General procedure for the synthesis of (2*E*,3*E*)-dimethyl 2-[(dimethylamino)methylene]-3-(2-substituted)succinates 4a–f

To a solution of (*E*)-3-(dimethylamino)-1-substituted-prop-2-en-1-one **2a**–**f** (1 equiv) in MeCN (1–3 mL) was added DMAD (**3**) (2.0–2.5 equiv) and the mixture was stirred in a closed vessel

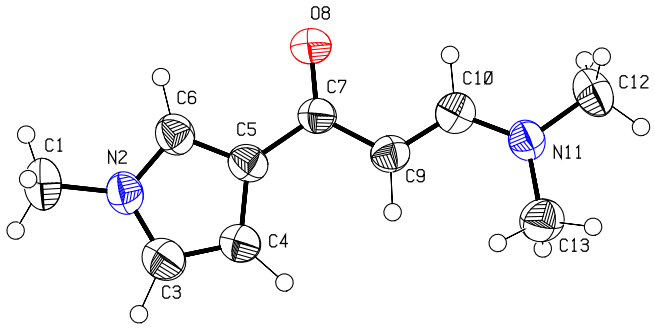


Figure 1. ORTEP view of compound **2f**.

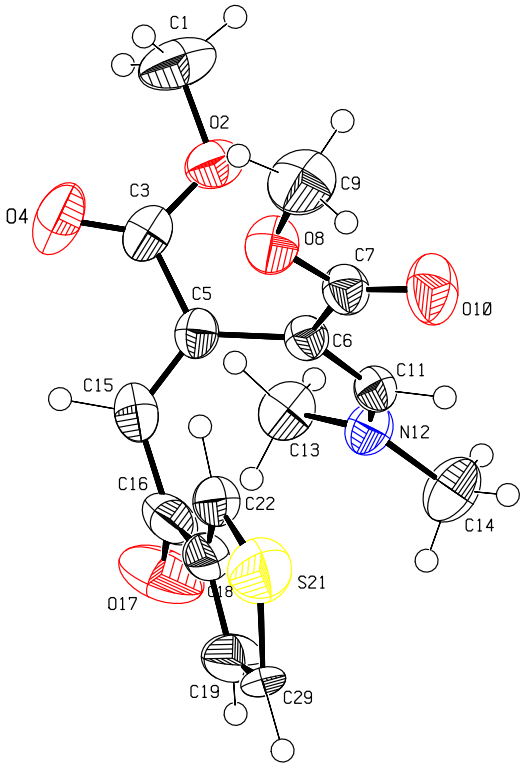
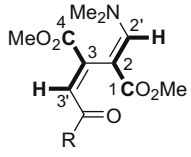


Figure 2. ORTEP view of compound **4d**.



4c: R = 2-thienyl
$^3J_{C(1)\text{-}H(2')}$ = 4.5 Hz (*cis*)
$^3J_{C(4)\text{-}H(3')}$ = 6.9 Hz (*cis*)

4f: R = 1-methyl-1*H*-pyrrol-3-yl
$^3J_{C(1)\text{-}H(2')}$ = 4.8 Hz (*cis*)
$^3J_{C(4)\text{-}H(3')}$ = 6.9 Hz (*cis*)

Figure 3. Determination of the configuration by HMBC spectroscopy.

under microwave irradiation (300 W) at automatically controlled elevated constant temperature (CEM Corporation discover microwave unit) or at room temperature. After cooling to room temperature, volatile compounds were evaporated in vacuo and the residue was purified by column chromatography (products **4a**,**b**,**c**,**e**,**f**) or crystallization (product **4d**).

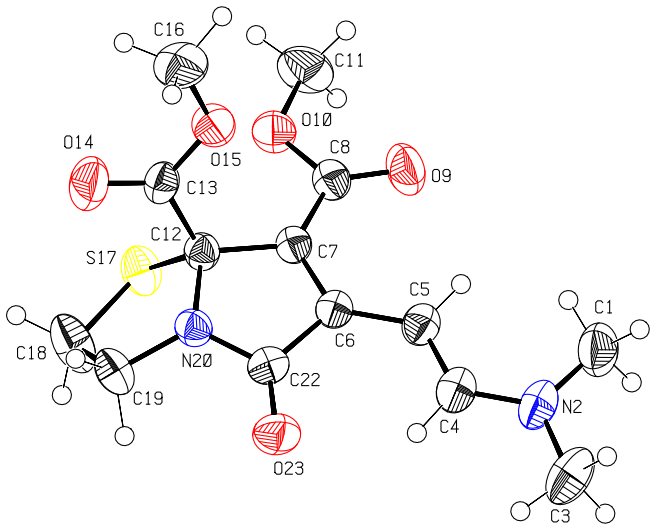


Figure 4. ORTEP view of compound **13a**.

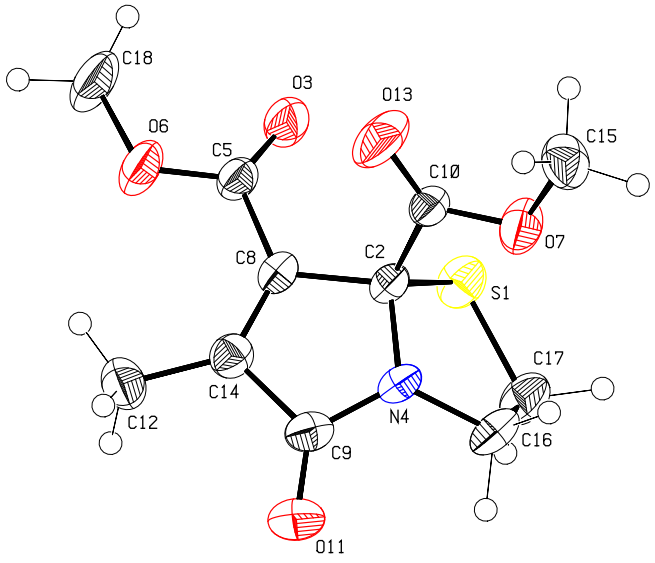
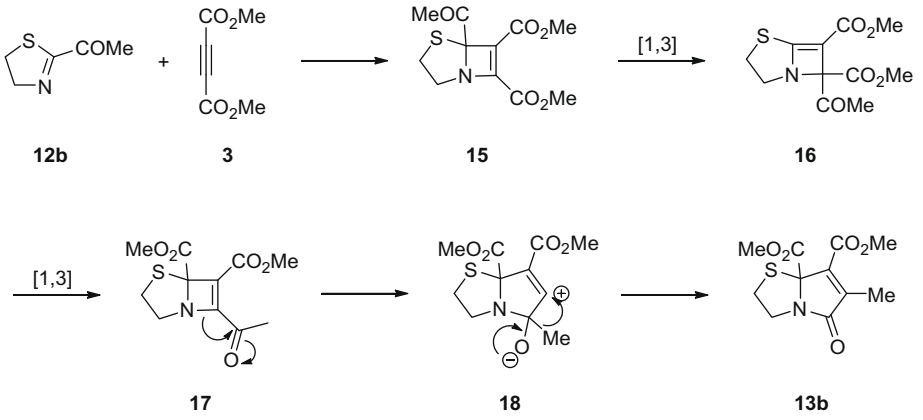


Figure 5. ORTEP view of compound **13b**.

Table 1
Selected ^{1}H NMR data of cycloadducts **4a–f** and **14**

Product	δ NMe_2 (ppm)	δ COOMe (ppm)	δ $H^{3'}$ (ppm)	δ $H^{2'}$ (ppm)
4a	2.89	3.62 3.83	7.53	7.77
4b	2.89	3.62 3.82	7.47	7.72
4c	2.89	3.60 3.83	7.52	7.67
4d	2.89	3.60 3.83	7.48	7.56
4e	2.90	3.82 3.90	7.53	7.56
4f	2.90	3.65 3.81	7.39	7.55
14	2.84	3.64 3.81	7.70	7.89



Scheme 4. The proposed mechanism for the formation of **13b**.

3.3. (*E*)-Dimethyl 6-[2-(dimethylamino)vinyl]-5-oxo-2,3,5,7*a*-tetrahydropyrrolo[2,1-*b*]thiazole-7,7a-dicarboxylate (13a) and (2*E*,3*E*)-dimethyl 2-[2-(4,5-dihydrothiazol-2-yl)-2-oxoethylidene]-3-[(dimethylamino)methylene]succinate (14)

Prepared from (*E*)-1-(4,5-dihydrothiazol-2-yl)-3-(dimethylamino)prop-2-en-1-one (**12a**) (276 mg, 1.5 mmol) and DMAD (**3**) (366 μL, 3.0 mmol) in MeCN (1.5 mL), 60 °C, 10 min. The two products were separated by column chromatography (EtOAc/petroleum ether = 1:2). Fractions containing the products were combined and evaporated in vacuo.

3.4. Major product 13a

Elutes first, recrystallized from EtOAc/petroleum ether. Yield: 156 mg (32%); yellow solid; mp 103–115 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.00 (6H, s, N*Me*$_2$); 3.31–3.53 (3H, m, 3H of thiazolidine); 3.72 (3H, s, COO*Me*); 3.80 (3H, s, COO*Me*); 4.29–4.36 (1H, m, 1H of thiazolidine); 5.98 (1H, d, J = 13.2 Hz, C*H*); 8.49 (1H, d, J = 13.2 Hz, C*H*). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 36.0, 43.9, 51.4, 53.5, 79.0, 90.1, 120.4, 140.4, 150.9, 164.4, 169.6, 172.3. ($C_{14}H_{18}N_2O_5S$ requires: C, 51.52; H, 5.56; N, 8.58; found C, 51.30; H, 5.56; N, 8.42); EI-HRMS: m/z = 327.1012 (MH^+); $C_{14}H_{19}N_2O_5S$ requires: m/z = 327.1015 (MH^+); ν_{max} (KBr) 2948, 1755, 1735, 1697, 1611, 1565, 1431, 1406, 1341, 1251, 1191, 1162, 1109, 1040, 1011, 974, 861 cm^{-1}.

3.5. Minor product 14

Elutes second. Yield: 38 mg (8%); red oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.84 (6H, s, N*Me*$_2$); 3.32 (2H, t, J = 8.7 Hz, C*H*$_2$ of thiazolidine); 3.64 (3H, s, COO*Me*); 3.81 (3H, s, COO*Me*); 4.55 (2H, t, J = 8.7 Hz, C*H*$_2$ of thiazolidine); 7.70 (1H, s, C(3′)-*H*); 7.89 (1H, s, C(2′)-*H*). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 32.9, 43.9, 51.6, 53.1, 66.4, 93.3, 120.7, 142.4, 155.5, 168.7, 169.1, 172.2, 181.0. EI-HRMS: m/z = 327.1006 (MH^+); $C_{14}H_{19}N_2O_5S$ requires: m/z = 327.1015 (MH^+);$_{ax}$ (KBr) 2949, 1723, 1692, 1604, 1538, 1433, 1400, 1328, 1255, 1217, 1135, 1089, 1046, 997, 942, 923 cm^{-1}.

3.6. Dimethyl 6-methyl-5-oxo-2,3,5,7*a*-tetrahydropyrrolo[2,1-*b*]thiazole-7,7*a*-dicarboxylate (13b)

Prepared from 1-(4,5-dihydrothiazol-2-yl)ethanone (**12b**) (440 mg, 3.4 mmol) and DMAD (**3**) (830 μL, 6.8 mmol) in MeCN (3 mL), 60 °C, 15 min, column chromatography (EtOAc/petroleum ether = 1:3), recrystallized from EtOAc/petroleum ether. Yield: 171 mg (19%); white solid; mp 106–109 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.19 (3H, s, C*H*$_3$); 3.31–3.42 (1H, m, 1H of thiazolidine CH$_2$); 3.48–3.57 (2H, m, C*H*$_2$ of thiazolidine); 3.77 (3H, s, COO*Me*); 3.88 (3H, s, COO*Me*); 4.29–4.40 (1H, m, 1H of thiazolidine CH$_2$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 11.0, 36.9, 44.6, 52.5, 53.8, 78.3, 141.5, 143.0, 162.9, 168.5, 172.6. ($C_{11}H_{13}NO_5S$ requires: C, 48.70; H, 4.83; N, 5.16; found C, 48.75; H, 4.66; N, 5.07); EI-HRMS: m/z = 272.0588 (MH^+); $C_{11}H_{14}NO_5S$ requires: m/z = 272.0593 (MH^+); ν_{max} (KBr) 3008, 2959, 1734, 1706, 1464, 1438, 1347, 1326, 1278, 1217, 1161, 1071, 990, 955, 925 cm^{-1}.

3.7. X-ray structure analysis for compounds 2f, 4d, 13a and 13b

Single crystal X-ray diffraction data of compounds **2f**, **4d**, **13a** and **13b** were collected at room temperature on a Nonius Kappa CCD diffractometer using the Nonius Collect Software.[14] DENZO and SCALEPACK[15] were used for indexing and scaling of the data and the structures were solved by means of SIR97.[16] Refinement was performed using the XTAL3.4[17] program package and the crystallographic plots were prepared by ORTEP III.[18] Crystal structures were refined on F values using the full-matrix least-squares procedure. The non-hydrogen atoms were refined anisotropically in all cases, while the positions of the hydrogen atoms were geometrically calculated and their positional and isotropic atomic displacement parameters were not refined. Absorption correction was not necessary. Regina[19] weighting scheme was used in all cases.

Acknowledgements

Financial support from the Slovenian Research Agency through grants P0-0502-0103, P1-0179 and J1-6689-0103-04 is gratefully acknowledged. We also thank the Krka d.d. (Novo mesto, Slovenia) and Lek d.d., a Sandoz Company (Ljubljana, Slovenia) for financial support.

Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 768092 (**2f**), 768093 (**4d**), 768094 (**13a**) and 768095(**13b**). Copies of these data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.04.106.

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