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TRANSFORMATIONS OF DIMETHYL (2*E*,3*E*)-2-[(DIMETHYLAMINO)METHYLENE]-3-(1-METHYL-2,5-DIOXOIMIDAZOLIDIN-4-YLIDENE)SUCCINATE WITH *C*-NUCLEOPHILES

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Dedicated to Professor Dr. Albert Eschenmoser on the occasion of his 85th birthday

Abstract — (2*E*,3*E*)-2-[(Dimethylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**1**) was transformed with 1,3-dicarbonyl compounds **2a,b** *via* substituted dimethyl (2*H*-imidazol-4-yl)-2-butenedioates **3a,b** and dimethyl (2,5-dioxo-4-imidazolidinylidene)succinates **4a,b** into 2*H*-pyrano[2,3-*d*]pyrimidines **5a,b**. Compound **1** was cyclized by heating sin glacial acetic acid into dimethyl 1*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (**8**).

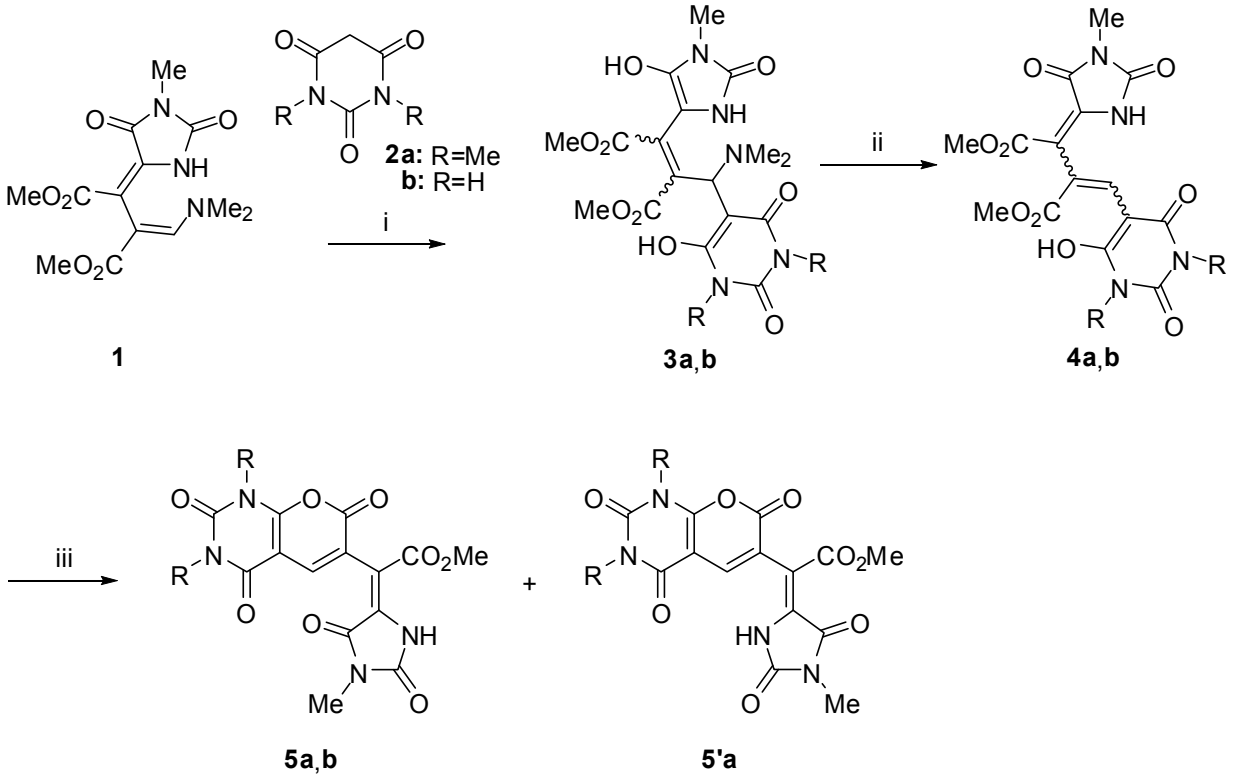
INTRODUCTION

Enaminones, masked α-formyl carbonyl compounds, are versatile intermediates extensively utilized in organic synthesis.[1] The 3-(dimethylamino)propenoates and related compounds have been demonstrated to be versatile building blocks in the synthesis of many heterocyclic systems,[2] including some natural products, especially indole alkaloids and their analogs.[3] Recently, a thermal [4+2] cycloaddition of enaminones to dimethyl acetylenedicarboxylate followed by 1,3-H shift[4] and microwave assisted regiospecific [2+2] cycloadditions of electron-poor acetylenes to 2-(acylamino)-3-(dimethylamino)-prop-2-enoates[5] and some transformations of the cycloadducts[6] including the formation of a new triazafulvalene system[7] have been reported. In this paper we describe some transformations of (2*E*,3*E*)-2-[(dimethylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**1**), prepared by [2+2] cycloaddition of (5*Z*)-5-[(dimethylamino)methylene]-3-methylimidazolidine-2,4-dione and dimethyl acetylenedicarboxylate,[5c] and *N*-methylated compound **7** with 1,3-dicarbonyl compounds, such as

barbituric acid derivatives **2a,b** and 5,5-dimethyl-1,3-cyclohexanedione (**9**), into pyrano[2,3-*d*]pyrimidine and benzopyran derivatives, respectively.

RESULTS AND DISCUSSION

In the reaction of succinate **1** with 1,3-dimethylbarbituric acid (**2a**) and barbituric acid (**2b**) at room temperature addition reaction took place to give the corresponding dimethyl 2-butenedioates **3a,b**. Elimination of dimethylamine from **3a,b** was achieved by addition of hydrochloric acid to the water suspension of **3a,b** at room temperature to afford the precipitates of dimethyl succinates **4a,b**. These compounds, when heated in acetic acid, cyclized into pyrano[2,3-*d*]pyrimidine derivatives **5a,b**. The (*Z*)-isomer **5a** is the major, while the (*E*)-isomer **5´a** is the minor isomer (Scheme 1, Table 1).



Scheme 1. Reagent and conditions: (i) barbituric acid **2a**,**b**, anhydrous AcOH, rt; (ii) 37% HCl, H_2O, rt; (iii) anhydrous AcOH, reflux

Table 1. Synthesis of compounds **3-5** according to Scheme 1

	R	**3**, yield (%)	**4**, yield (%)	**5** and **5'**, yield (%)	**5** : **5'**
a	Me	60	91	28	95 : 5
b	H	88	75	70	100 : 0

5a and **5´a** can be distinguished on the basis of chemical shifts for N*H* protons in ^{1}H NMR spectrum. The N*H* signal in **5a** appears at lower field at δ = 9.51 ppm due to the hydrogen bond formation, while in **5´a** the N*H* signal appears at higher field at δ = 8.26 ppm (Figure 1).

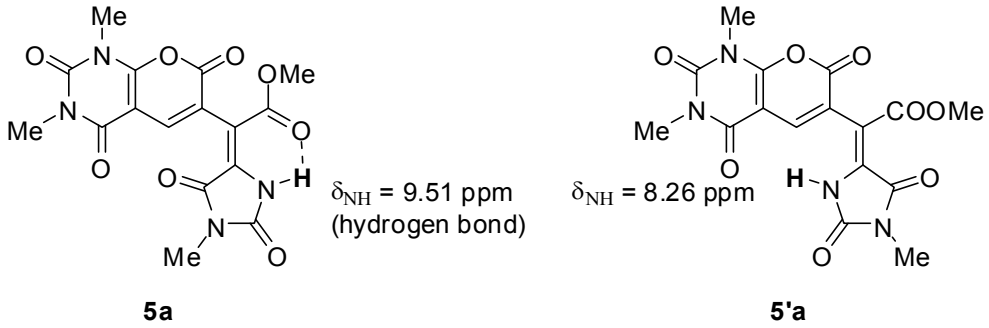


Figure 1. Structure determination of isomers **5a** and **5´a** with ^{1}H NMR spectroscopy

By cyclisation of **4b** two products can be formed, either fused 2*H*-pyranone derivative **5b** or oxepino[2,3-*d*]pyrimidine derivative **6b**. Between these two possibilities one can differentiate on the basis of the HMBC spectrum. Since there is no heterocoupling between the proton and the ^{13}C of the carbonyl group attached to the double bond, it means that pyrano[2,3-*d*]pyrimidine derivative **5b** is formed by cyclisation of **4b** and not a fused oxepine derivative **6b** (Figures 2 and 3).

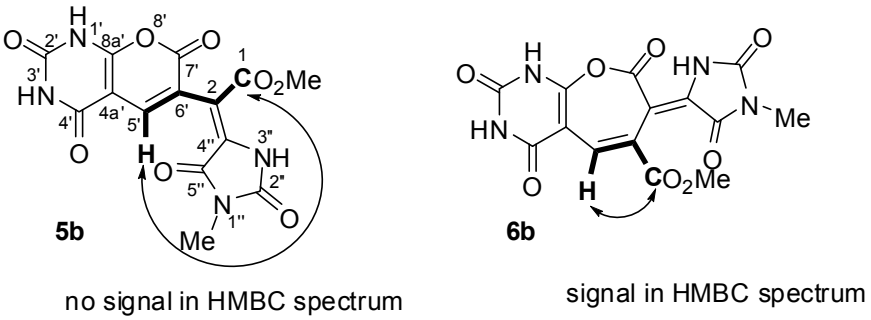
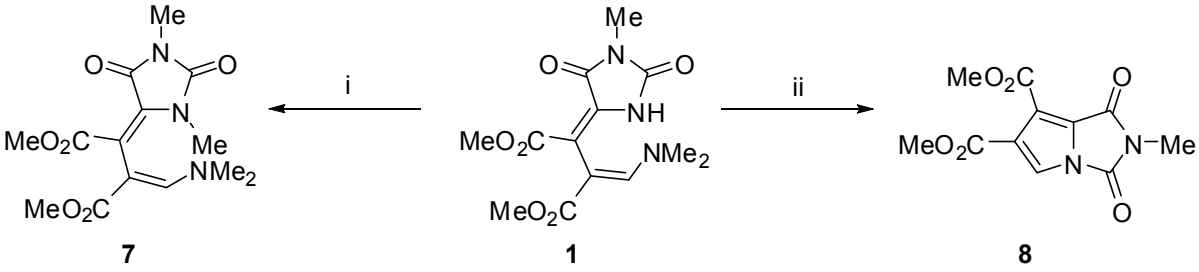


Figure 2. Structure determination of compound **5b** by HMBC

Methylation of **1** with methyl iodide in DMF at room temperature afforded the *N*-methylated product **7** in 88% yield. On the other hand, by heating **1** in glacial acetic acid cyclisation occurred to give derivative of 1*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate **8** in 99% yield (Scheme 2).

By heating compound **7** with 5,5-dimethyl-1,3-cyclohexanedione (**9**) in acetic acid *N,N*-dimethylamino group was exchanged with a C-nucleophile followed by cyclisation with the ester group to give a mixture of two isomeric 7,7-dimethyl-2,5-dioxo-5,6,7,8-tetrahydro-2*H*-chromenes **10** and **10´** (Scheme 3, Table 2).



Scheme 2. Reagents and conditions: (i) MeI, DMF, K_2CO_3, rt; (ii) anhydrous AcOH, 100 °C

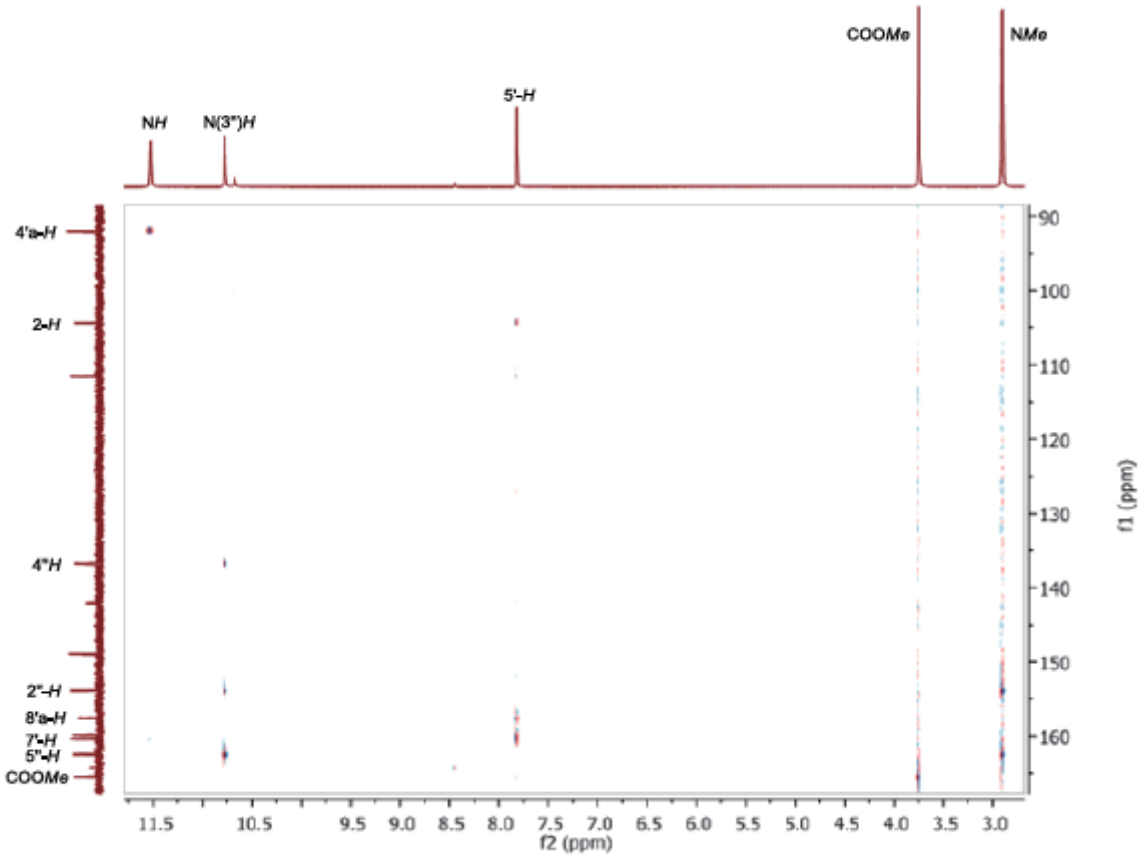
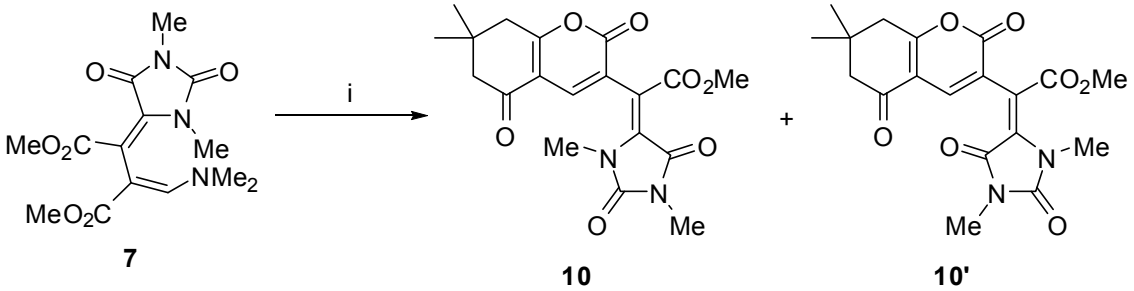


Figure 3. HMBC spectrum of compound **5**



Scheme 3. Reagents and conditions: (i) 5,5-dimethyl-1,3-cyclohexanedione (**9**), anhydrous AcOH, 100 °C

Table 2. Synthesis of compound **10** according to Scheme 3

10, yield (%)	**10'**, yield (%)	**10** : **10'**
42	31	58 : 42

The structures of isomeric compounds **10** and **10′** were determined by NOESY experiments. The (*E*)-isomer **10** shows the n.O.e. with the N(3″)-Me group by irradiation of the proton H(4′) and *vice versa* the irradiation of the N(3″)-Me shows the n.O.e. with the H(4′) proton, indicating the proximity of the H(4′) and N(3″)-Me groups in space, confirming thus the (*E*)-orientation around the double bond (Figure 4). The observed n.O.e. in (*E*)-isomer **10** confirms also that in cyclisation the adjacent ester group is involved to give the corresponding 2*H*-pyranone system.

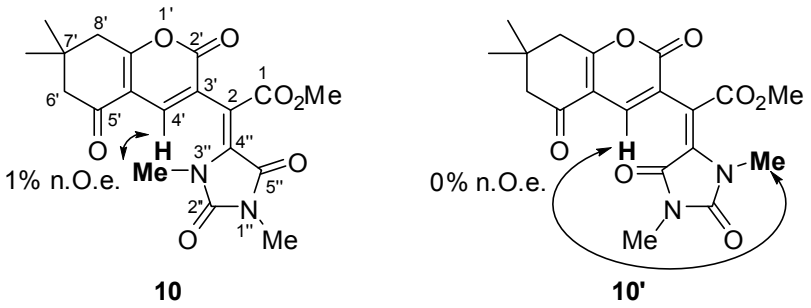
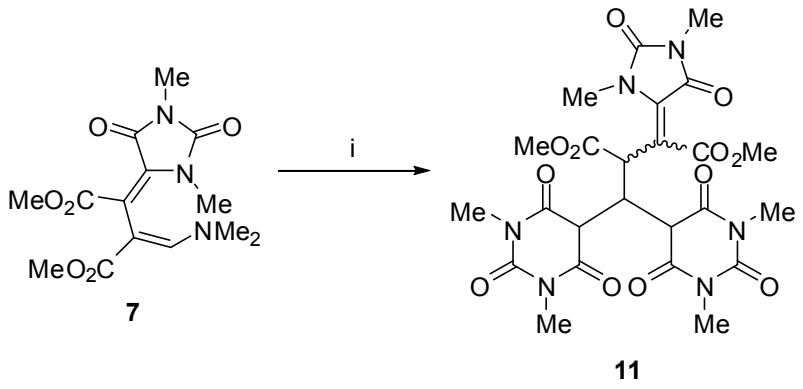


Figure 4. Determination of the configuration

When compound **7** reacted with 1,3-dimethylbarbituric acid (**2a**) at room temperature the first addition of 1,3-dimethylbarbituric acid followed by elimination of dimethylamine, is followed by the Michael addition of the second molecule of 1,3-dimethylbarbituric acid to give **11** in 25% yield (Scheme 4).



Scheme 4. Reagents and conditions: (i) 1,3-dimethylbarbituric acid (**2a**), anhydrous AcOH, rt

In summary, the above mentioned experiments can be conveniently employed for the preparation of 2*H*-pyrano[2,3-*d*]pyrimidine derivatives and pyrrolo[1,2-*c*]imidazole-6,7-carboxylate, since the starting materials are readily available by [2+2] cycloaddition of [(dimethylamino)methylene]imidazolidine-2,4-diones to acetylenedicarboxylate.

EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. The NMR spectra were obtained on a Bruker Advance DPX 300 (300 MHz) spectrometer in DMSO-d_6 or $CDCl_3$ with TMS as the internal standard, MS spectra on a Q-Tof Premier spectrometer, IR spectra on a Perkin-Elmer 1310 infrared spectrophotometer and elemental analyses for C, H and N on a Perkin-Elmer CHN Analyser 2400.

Dimethyl 2-[(dimethylamino)(6-hydroxy-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-methyl]-3-(5-hydroxy-1-methyl-2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)but-2-enedioate (3a)

A mixture of dimethyl (2*E*,3*E*)-2-[(dimethylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-yl-idene)succinate (**1**; 0.623 g, 2 mmol) and 1,3-dimethylbarbituric acid (**2a**; 0.370 g, 2.4 mmol) in anhydrous acetic acid (5 mL) was stirred at rt for 48 h. After the reaction was completed volatile components were evaporated *in vacuo* and the residue was disolved in EtOH (4 mL). The product was left to precipitate for 5 days at 4 °C and then filtered under reduced pressure. Yield: 0.560 g (60%); mp 154–156 °C (toluene/DMF). ^{1}H NMR (DMSO-d_6): δ 2.55 (6H, s, N*Me*$_2$); 2.84 (3H, s, N*Me*); 3.01 (6H, s, 2×N*Me*); 3.49 (3H, s, COO*Me*); 3.57 (3H, s, COO*Me*); 8.10 (1H, s, C*H*); 8.14 (2H, br s, N*H* in O*H*); 9.93 (1H, br s, O*H*). Anal. Calcd for $C_{19}H_{25}N_5O_9$: C, 48.82; H, 5.39; N, 14.98. Found: C, 48.53; H, 5.65; N, 15.17. ν_{max} (KBr) 3502, 3410, 3265, 2958, 1768, 1722, 1704, 1691, 1626, 1609, 1428, 1393, 1271, 1251, 1235, 1187, 1162, 777 cm^{-1}.

Dimethyl 2-[(dimethylamino)(6-hydroxy-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)methyl]-3-(5-hydroxy-1-methyl-2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)but-2-enedioate (3b)

A mixture of dimethyl (2*E*,3*E*)-2-[(dimethylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-yl-idene)succinate (**1**; 0.623 g, 2 mmol) and barbituric acid (**2b**; 0.256 g, 2 mmol) in anhydrous acetic acid (8 mL) was stirred at rt for 72 h. After the reaction was completed the precipitated product was filtered under reduced pressure. Yield: 0.777 g (88%); mp decomposition above 172 °C. ^{1}H NMR (DMSO-d_6): δ 2.55 (6H, s, N*Me*$_2$); 2.84 (3H, s, N*Me*); 3.48 (3H, s, COO*Me*); 3.58 (3H, s, COO*Me*); 7.99 (1H, s, C*H*); 8.15 (2H, br s, N*H* and O*H*); 9.34 (2H, s, 2×N*H*); 9.80 (1H, br s, O*H*). Anal. Calcd for $C_{17}H_{21}N_5O_9$: C, 46.47; H, 4.82; N, 15.94. Found: C, 46.17; H, 4.77; N, 16.22. ν_{max} (KBr) 3433, 3178, 1771, 1726, 1688, 1645, 1591, 1452, 1434, 1403, 1339, 1243, 1156, 1064, 779, 531 cm^{-1}.

Synthesis of dimethyl 2-[(6-hydroxy-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinates. General procedure for the preparation of 4:

To a stirred suspension of dimethyl-2-[(dimethylamino)(6-hydroxy-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)methyl]-3-(5-hydroxy-1-methyl-2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)but-2-endioate **3a,b** in water (2 mL) 37% HCl (0.5 mL) was added dropwise. The suspension was stirred at room temperature. After the reaction was completed, the product was filtered under reduced pressure and washed with water.

Dimethyl 2-[(6-hydroxy-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-yilidene)succinate (4a)

Prepared from dimethyl 2-[(dimethylamino)(6-hydroxy-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)methyl]-3-(5-hydroxy-1-methyl-2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)but-2-endioate (**3a**; 0.206 g, 0.44 mmol) and 37% HCl (6 drops) in water (2 mL), 20 minutes. Yield: 0.169 g (91%); mp 116–118 °C (washed with H_2O). Ratio of isomers: 90:10. ESI-MS: *m*/*z* = 421.1 ($(M–H)^-$). ^{1}H NMR (DMSO-d_6): major isomer: δ 2.84 (3H, s, N*Me*); 3.02 (6H, s, 2×N*Me*); 3.49 (3H, s, COO*Me*); 3.57 (3H, s, COO*Me*); 8.07 (1H, s, C*H*); 9.95 (1H, s, N*H*); O*H* exchanged; minor isomer: δ 2.82 (3H, s, N*Me*); 3.00 (6H, s, 2×N*Me*); 3.56 (3H, s, COO*Me*); 8.16 (1H, s, C*H*); 8.69 (1H, s, N*H*). Anal. Calcd for $C_{17}H_{18}N_4O_9$: C, 48.34; H, 4.30; N, 13.27. Found: C, 48.18; H, 4.53; N, 13.07. ESI-HRMS: *m*/*z* = 421.0981 ($(M–H)^-$); $C_{17}H_{17}N_4O_9$ requires: *m*/*z* = 421.0996 ($(M–H)^-$). ν_{max} (KBr) 3353, 2955, 1780, 1732, 1703, 1689, 1637, 1606, 1458, 1440, 1395, 1283, 1257, 1246, 1216, 1156, 770, 753 cm^{-1}.

Dimethyl 2-[(6-hydroxy-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (4b)

Prepared from dimethyl 2-[(dimethylamino)(6-hydroxy-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-methyl]-3-(5-hydroxy-1-methyl-2-oxo-2,3-dihydro-1*H*-imidazol-4-yl)but-2-endioate (**3b**; 0.659 g, 1.5 mmol) and 37% HCl (1 mL) in water (3 mL), 20 minutes. Yield: 0.445 g (75%); mp decomp. above 195 °C (washed with H_2O). Ratio of isomers: 92:8. ESI-MS: *m*/*z* = 393.1 ($(M–H)^-$). ^{1}H NMR (DMSO-d_6): major isomer: δ 2.85 (3H, s, N*Me*); 3.53 (3H, s, COO*Me*); 3.60 (3H, s, COO*Me*); 7.81 (1H, s, C*H*); 9.94 (2H, br s, 2×N*H*); 10.02 (1H, s, N*H*); O*H* exchanged; minor isomer: δ 2.86 (3H, s, N*Me*); 3.56 (3H, s, COO*Me*); 8.21 (1H, s, C*H*); 9.73 (1H, s, N*H*); 9.94 (2H, br s, 2×N*H*). Anal. Calcd for $C_{15}H_{14}N_4O_9$: C, 45.69; H, 3.58; N, 14.21. Found: C, 45.42; H, 3.83; N, 13.99. ESI-HRMS: *m*/*z* = 393.0670 ($(M–H)^-$); $C_{15}H_{13}N_4O_9$ requires: *m*/*z* = 393.0683 ($(M–H)^-$). ν_{max} (KBr) 3376, 3280, 3236, 2959, 1781, 1740, 1721, 1703, 1647, 1604, 1438, 1391, 1343, 1260, 1143, 1063, 770 cm^{-1}.

(*Z*)-Methyl 2-(1,3-dimethyl-2,4,7-trioxo-2,3,4,7-tetrahydro-1*H*-pyrano[2,3-*d*]pyrimidin-6-yl)-2-(1-

methyl-2,5-dioxoimidazolidin-4-ylidene)acetate (5a) and (*E*)-isomer (5´a)

A solution of dimethyl 2-[(6-hydroxy-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**4a**; 170 g, 0.4 mmol) in anhydrous acetic acid (3 mL) was refluxed for 8 h. Volatile components were evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetat/petroleum ether = 2/1). Fractions containing the product were combined and volatile components were evaporated in *vacuo*. Yield: 0.044 g (28%); mp 234–237 °C (EtOH). Ratio of isomers: **5a**:**5´a** = 95:5. ^{1}H NMR ($CDCl_3$): (*Z*)-isomer: δ 3.07 (3H, s, N*Me*); 3.42 (3H, s, N*Me*); 3.61 (3H, s, N*Me*); 3.81 (3H, s, COO*Me*); 7.87 (1H, s, C*H*); 9.51 (1H, br s, N*H*); (*E*)-isomer: δ 3.10 (3H, s, N*Me*); 3.43 (3H, s, N*Me*); 3.62 (3H, s N*Me*); 8.15 (1H, s, C*H*); 8.26 (1H, br s, N*H*). Anal. Calcd for $C_{16}H_{14}N_4O_8$: C, 49.24; H, 3.62; N, 14.35. Found: C, 49.17; H, 3.64; N, 14.17. ν_{max} (KBr) 3303, 2954, 1787, 1755, 1736, 1720, 1698, 1670, 1660, 1581, 1500, 1444, 1390, 1277, 1244, 1143, 771 cm^{-1}.

(*Z*)-Methyl 2-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)-2-(2,4,7-trioxo-2,3,4,7-tetrahydro-1*H*-pyrano[2,3-*d*]pyrimidin-6-yl)acetate (5b)

A solution of dimethyl 2-[(6-hydroxy-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**4b**; 0.197 g, 0.5 mmol) in anhydrous acetic acid (2 mL) was refluxed for 7 h. The precipitated product was filtered under reduced pressure. Yield: 0.127 g (70%); mp decomp. above 193°C (EtOH). ESI-MS: *m*/*z* = 361.0 ((M–H)$^-$). ^{1}H NMR (DMSO-d_6): δ 2.90 (3H, s, N*Me*); 3.74 (3H, s, COO*Me*); 7.80 (1H, s, C*H*); 10.76 (1H, s, N*H*); 11.52 (1H, s, N*H*); 12.92 (1H, br s, N*H*). ^{13}C NMR (DMSO-d_6): δ 24.4, 52.5, 92.0, 104.4, 111.6, 136.7, 142.1, 148.9, 153.9, 157.6, 159.8, 160.4, 162.4, 165.5. Anal. Calcd for $C_{14}H_{10}N_4O_8$: C, 46.42; H, 2.78; N, 15.47. Found: C, 46.65; H, 2.89; N, 15.29. ESI-HRMS: *m*/*z* = 361.0430 ((M–H)$^-$); $C_{14}H_9N_4O_8$ requires: *m*/*z* = 361.0420 ((M–H)$^-$). ν_{max} (KBr) 3282, 3217, 3053, 1784, 1756, 1727, 1708, 1681, 1645, 1584, 1535, 1458, 1436, 1394, 1360, 1336, 1229, 1144, 815, 785, 772 cm^{-1}.

(2*E*,3*E*)-Dimethyl 2-(1,3-dimethyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(dimethylamino)methylene]-succinate (7)

Iodomethane (0.124 mL, 2 mmol) was added dropwise to a stirred mixture of dimethyl (2*E*,3*E*)-2-[(dimethylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**1**; 0.311 g, 1 mmol) and K_2CO_3 (0.276 g, 2 mmol) in DMF (5 mL) at rt. The mixture was stirred for 2.5 h. After the reaction was completed water (1 mL) was added to the reaction mixture and volatile components were evaporated *in vacuo*. The residue was suspended in water (5 mL) and the product was extracted with $CHCl_3$ (2×5 mL). The organic phase was dried with anhydrous Na_2SO_4. Na_2SO_4 was removed by filtration and

chloroform was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 2/1). Fractions containing the product were combined and volatile components were evaporated *in vacuo*. Yield: 0.286 g (88%) of oily product. ESI-MS: *m*/*z* = 326.1 (MH^+). ^{1}H NMR ($CDCl_3$): δ 3.03 (6H, s, N*Me*$_2$); 3.08 (3H, s, N*Me*); 3.12 (3H, s, N*Me*); 3.69 (3H, s, COO*Me*); 3.84 (3H, s, COO*Me*); 7.63 (1H, s, C*H*). ^{13}C NMR (DMSO-d_6): δ 25.0, 28.8, 51.6, 53.0, 88.2, 115.1, 131.1, 152.4, 155.2, 161.7, 168.3, 168.4. Anal. Calcd for $C_{14}H_{19}N_3O_6 \times ½H_2O$: C, 50.33; H, 6.03; N, 12.57. Found: C, 50.56; H, 5.86; N, 12.69. ESI-HRMS: *m*/*z* = 326.1358 (MH^+); $C_{14}H_{20}N_3O_6$ requires: *m*/*z* = 326.1352 (MH^+). ν_{max} (KBr) 2995, 2951, 1771, 1719, 1686, 1603, 1455, 1430, 1392, 1286, 1218, 1123, 1095, 1043, 1009, 784, 767 cm^{-1}.

Dimethyl 2-methyl-1,3-dioxo-2,3-dihydro-1*H*-pyrrolo[1,2-*c*]imidazole-6,7-dicarboxylate (8)

A solution of dimethyl (2*E*,3*E*)-2-[(dimethylamino)methylene]-3-(1-methyl-2,5-dioxoimidazolidin-4-ylidene)succinate (**1**; 0.104 g, 0.33 mmol) in anhydrous acetic acid (1.5 mL) was heated to 100 °C for 45 minutes. Volatile components were evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/2). Fractions containing the product were combined and and volatile components were evaporated *in vacuo*. Yield: 0.088 g (99%); mp 143–144 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 3.19 (3H, s, N*Me*); 3.87 (3H, s, COO*Me*); 3.96 (3H, s, COO*Me*); 7.76 (1H, s, C*H*). Anal. Calcd for $C_{11}H_{10}N_2O_6$: C, 49.63; H, 3.79; N, 10.52. Found: C, 49.89; H, 3.81; N, 10.53. ν_{max} (KBr) 3122, 2958, 1809, 1751, 1742, 1720, 1509, 1435, 1382, 1361, 1298, 1227, 1206, 1184, 1074, 768, 744 cm^{-1}.

Preparation of compounds 10 and 10': A mixture of (2*E*,3*E*)-dimethyl 2-(1,3-dimethyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(dimethylamino)methylene]succinate (**7**; 0.325 g, 1 mmol) and 5,5-dimethylcyclohexane-1,3-dione (**9**; 0.168 g, 1.2 mmol) in anhydrous acetic acid (3 mL) was heated to 100 °C for 7 h. Volatile components were evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 2/3 and ethyl acetate). Fractions containing the product were combined and and volatile components were evaporated *in vacuo.*

(*E*)-Methyl 2-(7,7-dimethyl-2,5-dioxo-5,6,7,8-tetrahydro-2*H*-chromen-3-yl)-2-(1,3-dimethyl-2,5-dioxoimidazolidin-4-ylidene)acetate (10)

Yield: 0.163 g (42%); mp 208–210 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.18 (6H, s, C(C*H*$_3$)$_2$); 2.46 (2H, s, C*H*$_2$); 2.79 (2H, s, C*H*$_2$); 2.97 (3H, s, N(3')-*Me*); 3.12 (3H, s, N(1')-*Me*); 3.87 (3H, s, COO*Me*); 7.75 (1H, s, C*H*). Anal. Calcd for $C_{19}H_{20}N_2O_7$: C, 58.72; H, 5.19; N, 7.21. Found: C, 58.91; H, 5.02; N, 7.25. ν_{max} (KBr) 2958, 1770, 1746, 1714, 1687, 1622, 1573, 1472, 1431, 1397, 1283, 1200, 1127, 1019, 748 cm^{-1}.

(*Z*)-Methyl 2-(7,7-dimethyl-2,5-dioxo-5,6,7,8-tetrahydro-2*H*-chromen-3-yl)-2-(1,3-dimethyl-2,5-dioxoimidazoli-din-4-ylidene)acetate (10′)

Yield: 0.121 g (31 %); mp 169–172 °C (EtOH). ^{1}H NMR ($CDCl_3$): δ 1.17 (6H, s, C(C*H*$_3$)$_2$); 2.44 (2H, s, C*H*$_2$); 2.77 (2H, s, C*H*$_2$); 3.06 (3H, s, N(3')-*Me*); 3.22 (3H, s, N(1')-*Me*); 3.82 (3H, s, COO*Me*); 7.76 (1H, s, C*H*). Anal. Calcd for $C_{19}H_{20}N_2O_7$: C, 58.72; H, 5.19; N, 7.21. Found: C, 58.65; H, 5.07; N, 7.14. ν_{max} (KBr) 3054, 2962, 1785, 1739, 1716, 1677, 1621, 1562, 1461, 1443, 1395, 1276, 1208, 1111, 1062, 749 cm^{-1}.

Dimethyl 2-[bis(1,3-dimethyl-2,4,6-trioxohexahydropyrimidin-5-yl)methyl]-3-(1,3-dimethyl-2,5-dioxoimidazolidin-4-ylidene)succinate (11)

A mixture of (2*E*,3*E*)-dimethyl 2-(1,3-dimethyl-2,5-dioxoimidazolidin-4-ylidene)-3-[(dimethylamino)-methylene]succinate (**7**; 0.325 g, 1 mmol) and 1,3-dimethylbarbituric acid (**2a**; 0.187 g, 1.2 mmol) in anhydrous acetic acid (2 mL) was stirred at rt for 4 days. The precipitated product was filtered under reduced pressure. Yield: 0.150 g (25%); mp 254–264 °C (decomp). ESI-MS: *m*/*z* = 593.1 (MH$^+$). ^{1}H NMR (DMSO-d_6): δ 2.53 (3H, s, N*Me*); 2.78 (3H, s, N*Me*); 2.93 (3H, s, N*Me*); 3.05 (3H, s, N*Me*); 3.13 (3H, s, N*Me*); 3.31 (3H, s, N*Me*); 3.59 (3H, s, COO*Me*); 3.61 (3H, s, COO*Me*); 3.73 (1H, d, *J* = 12.3 Hz, C*H*); 3.93 (1H, dd, *J* = 7.0, 11.6 Hz, C*H*); 4.19 (1H, d, *J* = 11.6 Hz, C*H*); 4.20 (1H, dd, *J* = 6.9, 12.3 Hz, C*H*). Anal. Calcd for $C_{24}H_{28}N_6O_{12}$. Found: C, 48.82; H, 4.66; N, 14.29, C, 48.65; H, 4.76; N, 14.18.) ν_{max} (KBr) 2957, 1790, 1743, 1734, 1696, 1684, 1671, 1455, 1428, 1382, 1339, 1289, 1224, 1181, 755 cm^{-1}.

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