HETEROCYCLES, Vol. 60 , No. 6, 2003, pp. 1317 - 1328
Received, 27th January, 2003, Accepted, 20th March, 2003, Published online, 24th March, 2003

HYDROLYSIS OF *N,N*-DIMETHYLENAMINES. STEREOSPECIFIC SYNTHESIS OF THEIR ENOL AND ENOL ESTER DERIVATIVES

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Abstract – Stereospecific conversions of dimethylaminomethylidene group in various (*Z*)-alkyl 2-[(2,2-disubstituted ethenyl)amino]-3-dimethylaminopropenoates into their hydroxymethylidene and benzoyloxy methylidene derivatives were achieved in moderate to good yields. The difference between pathway to enol esters and (fused)pyrrole-2-carboxylate derivatives is clarified.

INTRODUCTION

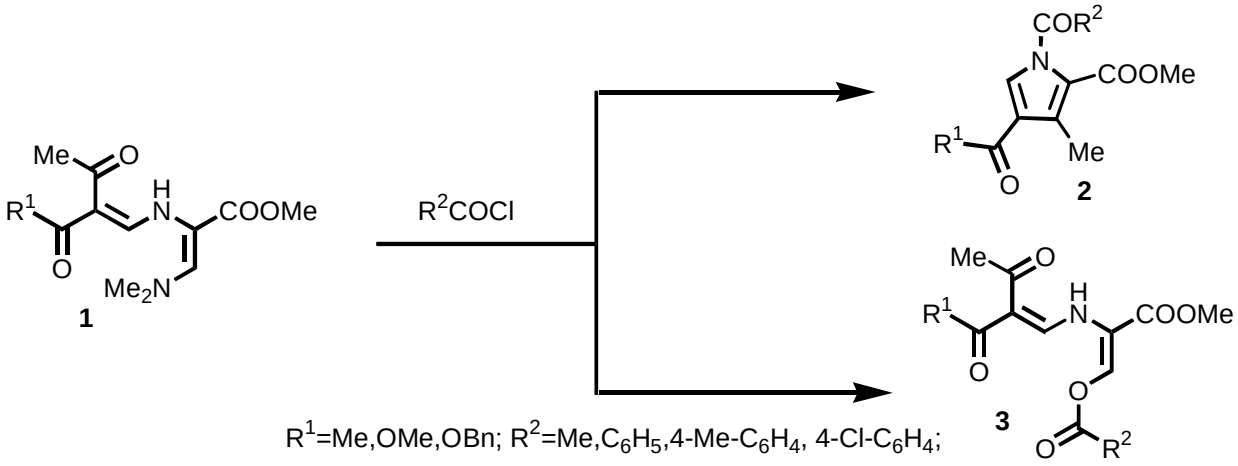
Enol esters have proven to be extremely valuable intermediates in organic synthesis. The most widely practised techniques involve the treatment of aldehydes and ketones under either acid or basic conditions with the appropriate acid anhydride or chloride and the addition of carboxylic acids to alkynes, which can be catalysed by mercury and palladium complexes.[1]

They are accessible *via* acylation of enolates,[2] transvinylation from vinyl or isopropenyl acetate in the presence of mercury(II), ruthenium(II), or palladium(II) catalysts,[3] or from vinylmercurials, obtained by acetoxymercuration of alkynes.[4]

The best routes appear to be based on ruthenium-catalysed synthesis *via* selective addition of carboxylic acids to alkynes,[5-10] including selective synthesis of (*Z*)-enol esters.[11]

Recently, (*Z*)-alkyl 2-acylamino-3-dimethylaminopropenoates, (*Z*)-alkyl 2-[(2,2-disubstituted ethenyl)-amino]-3-dimethylaminopropenoates (**1**) and related compounds, have been prepared and employed as valuable synthons in the synthesis of diverse groups of heterocycles, such as pyranones and fused

pyranones, fused pyridones, fused pyrimidinones, pyrroles, pyrazoles, imidazoles, 1,2,4-oxadiazoles[12] and derivatives of alkaloid aplysinopsin.[13,14]

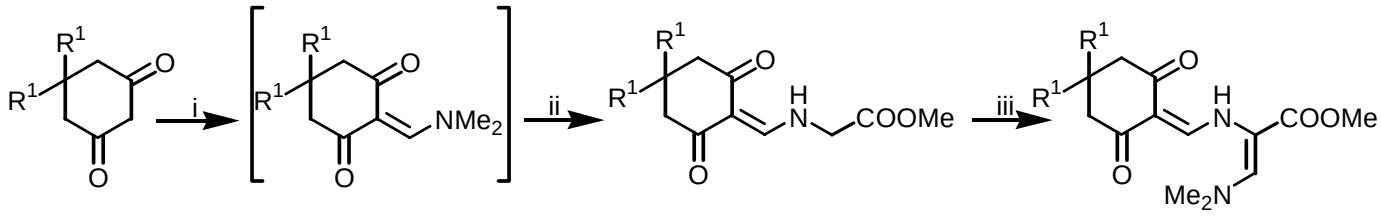


Scheme 1

As a part of this investigation, conversion of the dimethylaminomethylidene group into enol ester derivatives (**3**) has been recently described.[15] Similar procedures were employed for the condenzation of **1** into pyrrole-2-carboxylates (**2**).[16,17] (Scheme 1).

The purpose of this investigation was to establish relations between these reactions: whether they share the same intermediate or whether they are formed from **1** by completely different pathways.

RESULTS AND DISCUSSION



4a: R^1=Me
4b: R^1=H

5a: R^1=Me
5b: R^1=H

6a: R^1=Me (94%)
6b: R^1=H (92%)

7a: R^1=Me (24%)
7b: R^1=H (34%)

i) DMFDMA, PhMe; ii) $MeOOCCH_2NH_2 \cdot HCl$, AcOH; iii) DMFDMA, MeCN

Scheme 2

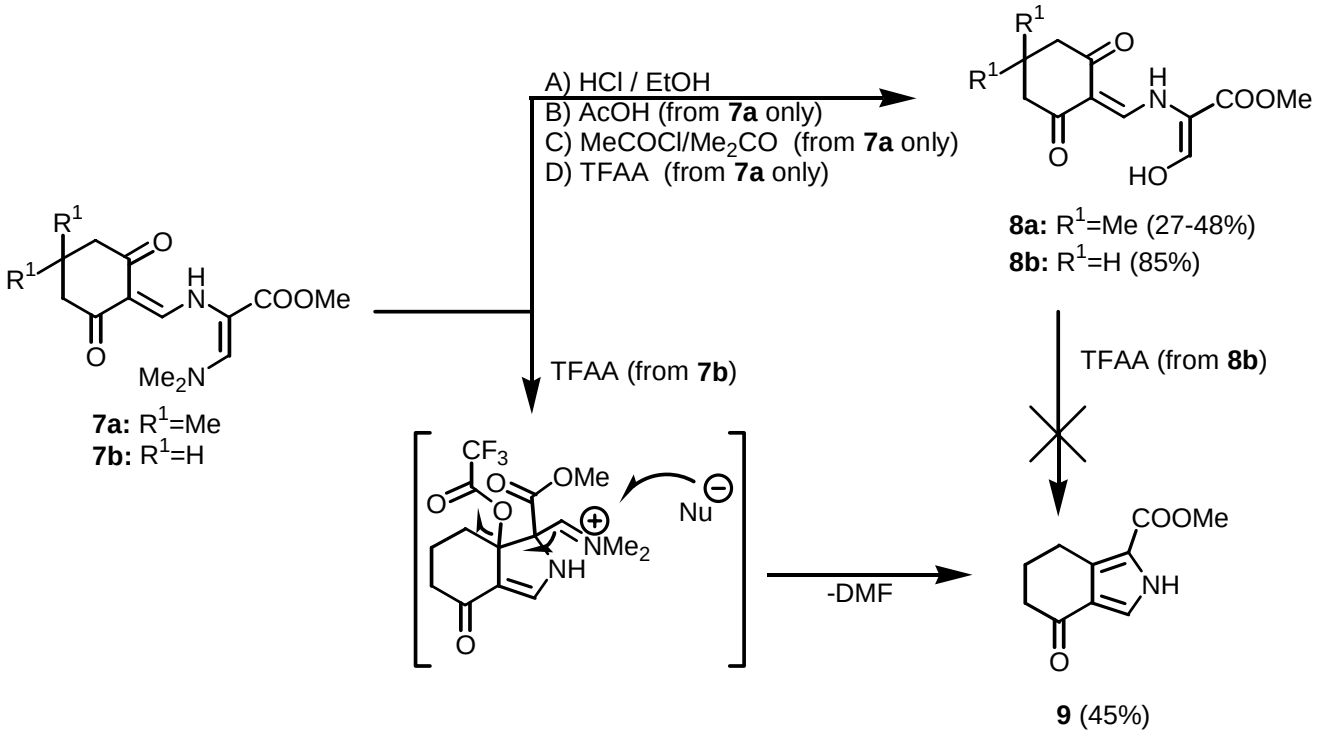
Methyl 2-[[(1,3-dioxocyclohexane-2-ylidene)methyl]amino]-3-dimethylaminopropenoates (**7**) were prepared in a three step synthesis from dimedone (**4a**) and 1,3-cyclohexanedione (**4b**) in 23% and 31% overall yields, respectively (Scheme 2), using standard protocols.[12,14]

It has been shown that all alkyl 2-[(2,2-disubstituted ethenyl)amino]-3-dimethylaminopropenoates (**1**), synthesized to date, exist in the *Z* form.[12c,14,18] The chemical shift of the H-C(3) in ^{1}H-NMR spectrum

(DMSO-d_6) of these compounds is always found in the narrow interval of δ=7.27-7.33 ppm. Compounds (**7a**) and (**7b**) exhibit the H-C(3) at δ=7.31 and 7.30 ppm, respectively, so we can assume that they also exist in the *Z* form.

In a continuation of this study, compounds (**7**) were hydrolysed with the solution of HCl in ethanol to give their enol derivatives (**8a**) and (**8b**), in 27 and 85% yields (method A), respectively. The hydrolysis of **7** with acetic acid gave **8a** in 48% yield, and no **8b** (method B). The reaction of **7** with acetyl chloride in acetone gave only **8a** again in 48% yield, and no **8b** (method C) and finally, the reaction of **7** with trifluoroacetic anhydride (TFAA) led to **8a** in 48% yield from **7a**, while **7b** gave isoindole derivative (**9)** in 45% yield. Compound (**9**) was not formed (or detected with TLC) from **8b** and TFAA under the same reaction conditions, suggesting that enol forms are not intermediates in the condensation reaction (Scheme 3).

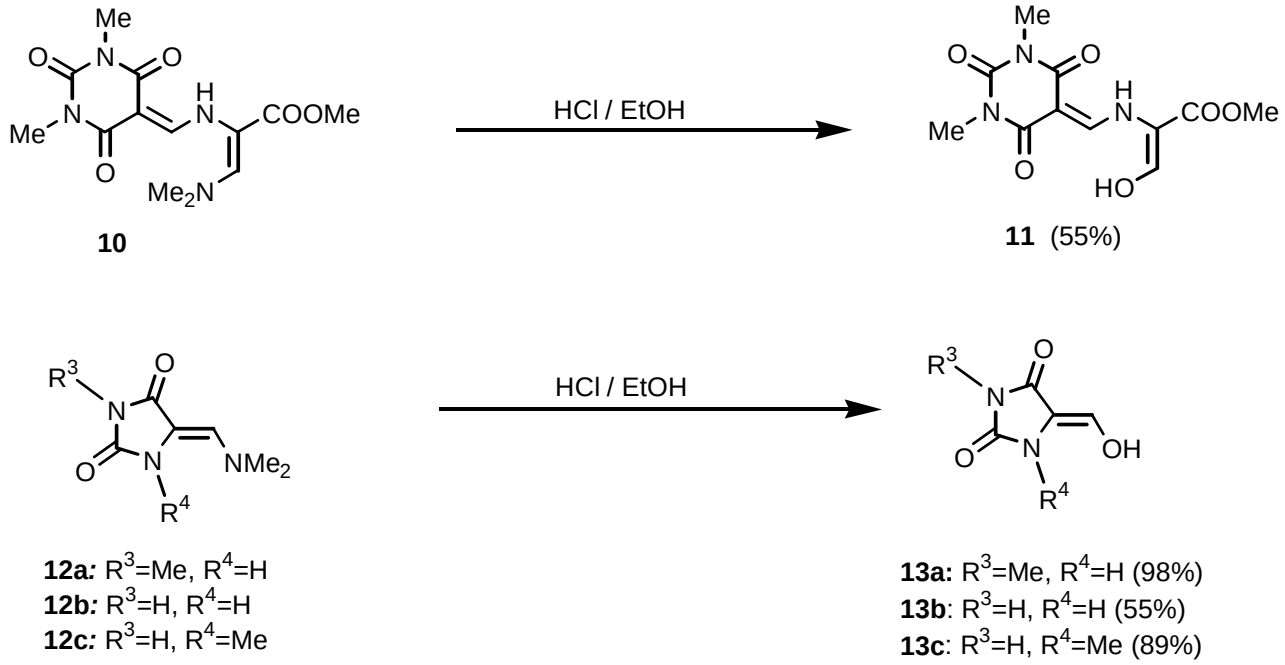
While the signal for the hydroxyl group is not detectable in the NMR spectrum, IR spectra for compounds (**8**) exhibit a strong peak at 3430 cm^{-1} belonging to this group.



Scheme 3

The proposed pathway for formation of **9** includes the formation of an intermediate (Scheme 3), which is upon hydrolysis converted into **9** and DMF. The latter was detected with the NMR spectroscopy of mother liquor, from which **9** was isolated. Pathway is analogous to already described condensation of alkyl 2-[(2,2-disubstituted ethenyl)amino]-3-dimethylaminopropenoates into pyrrole-2-carboxylates.[16,17] From the structure of the intermediate is obvious, that isoindole derivative can not be formed from **7a** due to a steric repulsion between methyl and trifluoroacetate group (Scheme 3).

Upon further investigation, we were able to prepare four other stable enols, employing hydrolysis in ethanolic HCl. Namely, methyl 2-[[(1,3-dimethyl-2,4,6-trioxohexahydropyrimidin-5-ylidene)methyl]-amino]-3-hydroxypropenoate (**11**) was prepared from compound (**10**) in 55% yield, and 5-[hydroxy-methylidene]imidazolidine-2,4-diones (**13**) were prepared from compounds (**12**) in 98, 55 and 89% yields, respectively (Scheme 4). Signals for hydroxyl groups are present in the NMR spectra for compounds (**13a**) and (**13b**), at 10.76 and 10.53 ppm, respectively. IR spectra show peaks for hydroxyl group at 3440 cm^{-1} for compound (**11**) and at 3160 - 3210 cm^{-1} for compounds (**13**).



10

11 (55%)

12a: R^3=Me, R^4=H
12b: R^3=H, R^4=H
12c: R^3=H, R^4=Me

13a: R^3=Me, R^4=H (98%)
13b: R^3=H, R^4=H (55%)
13c: R^3=H, R^4=Me (89%)

Scheme 4

Because compounds (**8**, **11** and **13**) were all prepared from (*Z*)- precursors, we expected the orientation around double bond in these compounds to remain the same. The issue was addressed with comparison of the experimental and calculated chemical shift of the olefinic proton. Shifts were calculated using the standard equation for trisubstituted olefins: $\delta_H=5.25+Z_{gem}+Z_{cis}+Z_{trans}$.[19]

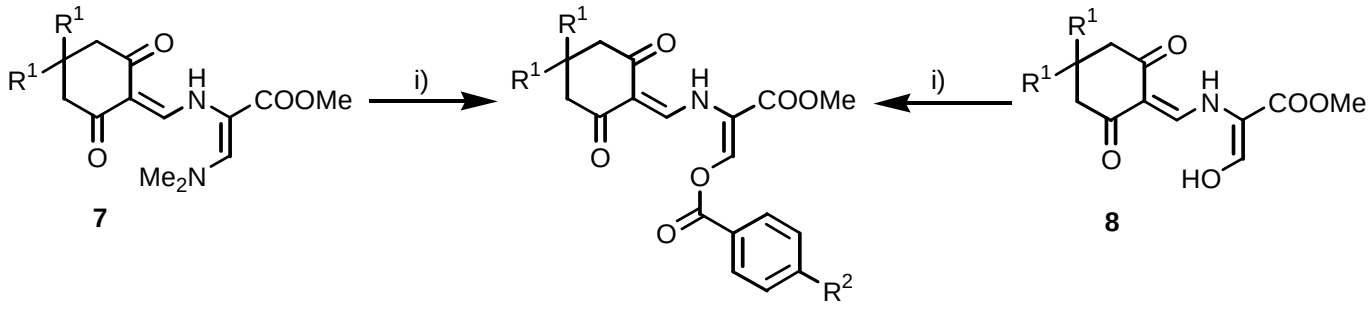
The Z_{trans} value for bis substituted ethenylamino group is not found in the Tables,[19] but can be easily calculated from the series of analoguous (*Z*)-alkyl 2-[(2,2-disubstituted ethenyl)amino]-3-dimethylamino-propenoates (**1**), for which the structure was confirmed with NOESY or/and HMBC spectroscopy.

Z_{trans} was found to be 0.06 ppm, calculated as an average from 9 compounds.[20-23] Thus the calculated shift for compounds (**8**) and (**11**) (7.71 ppm) is indeed in agreement with experimental values for those compounds (7.64-7.66 ppm).

Similarly, calculated shift for olefinic protons of compounds (**13**) (6.73 ppm), prepared from (*Z*)-precursors, is close to their experimental values 6.92 ppm, 6.81 ppm and 6.88 ppm for **13a**, **13b** and **13c**, respectively, while calculated shift for (*E*)- isomer (6.36 ppm) falls far out of range.

We may conclude from these data, that the described transformations of the dimethylaminomethylidene group into the hydroxymethylidene group indeed occurred with conservation of the orientation around double bond. Furthermore, in HMBC spectra of compounds (**8b**) and (**11**) the coupling constant $^{3}J_{C\text{-}H}$ between the carbonyl carbon and the proton at C-3 in the propenoate moiety was found to be less than 4 Hz, which proves the *Z* configuration beyond any doubt.

In a continuation of our studies, compounds (**7**) were heated with benzoyl chlorides in acetone, to give enol esters (**14**) in moderate yields. Under similar conditions, **14a** and **14b** were prepared from **8a** and **8b** in 87 and 50% yields, respectively, thus proving that the enol form is indeed intermediate in this reaction, as expected (Scheme 5).



7 **8**

i) R^2COCl / Me_2CO

14a: R^1=R^2=Me (25%)
14b: R^1=H; R^2=Me (93%)
14c: R^1=Me; R^2=H (34%)
14d: R^1=R^2=H (40%)

Scheme 5

The NMR spectra of compounds (**14**) recorded in $CDCl_3$ show one set of signals, with the signal for H-C(3) in δ=8.45–8.48 ppm region, which is in agreement with calculated shift for (*Z*)-isomer at 8.60 ppm. Some analogous enol esters with the (*Z*)- structure exhibit the signal for H-C(3) at 8.30-8.35 ppm.[15]

In the solution of DMSO-d_6, compounds (**14**) isomerize in the mixture of (*Z*)- and (*E*)- isomers (~3:2), exhibiting signals for H-C(3) at 8.10-8.23 ppm for (*Z*)- isomer and 7.64-7.82 ppm for (*E*)- isomer, which is again in agreement with data published earlier.[15]

CONCLUSION

In conclusion, various (*Z*)-alkyl 2-[(2,2-disubstituted ethenyl)amino]-3-dimethylaminopropenoates (**1**) can be stereospecifically converted to (*Z*)-benzoyloxymethylidene derivatives *via* (*Z*)-hydroxy-methylidene derivatives. The latter can be prepared and isolated from some (*Z*)-dimethylamino-methylidene compounds with generally applicable reaction using ethanolic solution of hydrochloric acid.

The acid catalyzed condensations of compounds (**1**) into pyrrole-2-carboxylates and their fused derivatives proceed *via* a different pathway and are strongly dependent on steric factors.

EXPERIMENTAL

Melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. NMR spectra were recorded on Varian VXR 300 at 300 MHz for ^{1}H and 75 MHz for ^{13}C nucleus, using DMSO-d_6 as a solvent. Microanalyses were performed on a Perkin Elmer 2400C instrument, MS spectra recorded on Autospec Q spectrometer and IR spectra on BIO-RAD FTS 60 spectrophotometer. NMR spectral data is summarized in Tables.

The following compounds were prepared according to procedures already described in the literature: (*Z*)-methyl 2-[[1,3-dimethyl-2,4,6-trioxohexahydropyrimidin-5-ylidenemethyl]amino]-3-dimethylaminopropenoate (**10**),[14] (*Z*)-5-[dimethylaminomethylidene]imidazolidine-2,4-diones (**12a**),[13] (**12b**)[13] and (**12c**).[24]

General Procedure for the Synthesis of Glycinates (6). To the 135 mmol of compound (**4**) in toluene (100 mL), dimethylformamide dimethyl acetal (DMFDMA, 180 mmol, 26.3 mL) was added and the solution was heated at 90-100°C for 2 h. After that, the reaction mixture was evaporated *in vacuo* and 16.95 g (135 mmol) of methyl glycinate hydrochloride and 100 mL of glacial acetic acid were added, then heated at 90-100°C for another hour. The reaction mixture was then evaporated *in vacuo* and 2-propanol was added for crystallization. The precipitate was collected by filtration and recrystallized from 2-propanol. The following compounds were prepared according to this procedure:

Methyl *N*-[(5,5-Dimethyl-1,3-dioxocyclohexane-2-ylidene)methyl]glycinate (6a). This compound was prepared from **4a**, white crystals (94%); mp 152-154°C. Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found C, 60.65; H, 7.11; N, 5.65. ν_{max} (KBr) 3420, 3130, 2960, 1750, 1670, 1620, 1590 cm^{-1}.

Methyl *N*-[(1,3-Dioxocyclohexane-2-ylidene)methyl]glycinate (6b). This compound was prepared from **4b**, white crystals (92%); mp 110-111°C. Anal. Calcd for $C_{10}H_{13}NO_4$: C, 56.87; H, 6.20; N, 6.63. Found C, 56.68; H, 5.98; N, 6.64. ν_{max} (KBr) 3420, 3200, 2960, 1750, 1650, 1600, 1570 cm^{-1}.

General Procedure for the Synthesis of Propenoates (7). To the 19 mmol of compound (**6**) in acetonitrile (100 mL), DMFDMA (33 mmol, 5 mL) was added and the mixture was heated at 50°C for 3 h. After that, the reaction mixture was evaporated *in vacuo* and the mixture of 2-propanol and ether (1:1) was added for crystallization. These compounds were used in reactions without further purification. To

obtain correct microanalyses, the compounds were crystallized from 2-propanol with substantial loss in yield. The following compounds were prepared according to this procedure:

(*Z*)-Methyl 2-[(5,5-Dimethyl-1,3-dioxocyclohexane-2-ylidene)methyl]amino-3-dimethylaminopropenoate (7a). This compound was prepared from **6a,** yellow crystals (24%); mp 134-136 °C. Anal. Calcd for $C_{15}H_{22}N_2O_4$: C, 61.21; H, 7.53; N, 9.52. Found C, 61.14; H, 7.62; N, 9.33. ν_{max} (KBr) 3440, 3170, 2960, 1690, 1650, 1590 cm^{-1}.

(*Z*)-Methyl 2-[(1,3-Dioxocyclohexane-2-ylidene)methyl]amino-3-dimethylaminopropenoate (7b). This compound was prepared from **6b**, yellow crystals (34%); mp 135-137 °C. Anal. Calcd for $C_{13}H_{18}N_2O_4$: C, 58.63; H, 6.81; N, 10.52. Found C, 58.78; H, 6.78; N, 10.20. ν_{max} (KBr) 3450, 3120, 2950, 1680, 1650, 1580 cm^{-1}.

Table 1. ^{1}H and ^{13}C NMR Spectral Data for Compounds (**6**) and (**7**) (DMSO-d_6)

Compound	^{1}H NMR	^{13}C NMR
6a	0.95 (6 H, s, 2xMe), 2.24 and 2.30 (2 H, s, CH_2), 3.67 (3 H, s, COOMe). 4.36 (2 H, d, *J* 6.3 Hz, C<u>H</u>$_2$NH), 8.04 (1 H, d, *J* 14.3 Hz, C<u>H</u>NH), 10.82 (1 H, td, *J* 6.3, 14.3 Hz, NH).	28.1(2), 30.7, 50.0, 50.6, 51.0, 52.2, 107.2, 159.0, 169.5, 194.7, 197.7
6b	1.83 (2 H, tt, *J* 6.0, 6.0 Hz, CH_2), 2.31 and 2.38 (2 H, t, *J* 6.0 Hz, CH_2), 3.66 (s, 3H, COOMe). 4.37 (2 H, d, *J* 6.2 Hz, C<u>H</u>$_2$NH), 8.07 (1 H, d, *J* 14.4 Hz, C<u>H</u>NH), 10.88 (1 H, td, *J* 6.2, 14.4 Hz, NH).	19.5, 37.1, 37.5, 50.1, 52.2, 108.5, 159.5, 169.6, 195.3, 198.5
7a	0.96 (6 H, s, 2xMe), 2.25 and 2.32 (2 H, s, CH_2), 2.96 (6 H, s, NMe_2), 3.59 (3 H, s, COOMe), 7.31 (1 H, s, H-C(3)), 7.80 (1 H, d, *J* 14.0 Hz, C<u>H</u>NH), 11.55 (1 H, d, *J* 14.0 Hz, NH).	28.1(2), 30.7, 42.5(2), 50.8, 50.8, 51.1, 98.0, 107.1, 144.7, 158.8, 165.8, 194.6, 198.0
7b	1.85 (2 H, m, *J* 6.0 Hz, CH_2), 2.33 and 2.41 (2 H, t, *J* 6.0 Hz, CH_2), 2.96 (6 H, s, NMe_2), 3.58 (3 H, s, COOMe), 7.30 (1 H, s, H-C(3)), 7.84 (1 H, d, *J* 13.9, C<u>H</u>NH), 11.63 (1 H, d, *J* 13.9 Hz, NH).	19.4, 37.0, 37.4, 42.6(2), 51.1, 98.0, 108.4, 144.6, 159.3, 165.8, 195.1, 198.8

(*Z*)-Methyl 2-[(5,5-Dimethyl-1,3-dioxocyclohexane-2-ylidene)methyl]amino-3-hydroxypropenoate (8a).

Method A: 723 mg (2.46 mmol) of compound (**7a**) in the mixture of ethanol and concetrated HCl (5:1, 5 mL) was stirred at rt for 5 h. The precipitate was collected by filtration and recrystallized from 2-propanol to give the *title compound* (**8a**) (177 mg, 27%) as a yellow crystals; mp 201-207°C. Anal. Calcd for $C_{13}H_{17}NO_5$: C, 58.42; H, 6.41; N, 5.24. Found C, 58.65; H, 6.51; N, 4.96. ν_{max} (KBr) 3430, 2950, 2705, 2490, 1700, 1650, 1600, 1515 cm^{-1}.

Method B: 219 mg of compound (**7a**) was heated in glacial acetic acid (4 mL) at 80°C for 4 h. The reaction mixture was evaporated *in vacuo* and 2-propanol was added to precipitate the *title compound* (**8a**) (95 mg, 48%) as a yellow solid.

Method C: To a 228 mg of compound (**7a**) in acetone (5 mL), acetyl chloride (0.5 mL) was added and the mixture was heated at 40-50°C for 3 h. The reaction was left to cool at rt to give the *title compound* (**8a**) (99 mg, 48%) as a yellow solid.

Method D: To a 180 mg of compound (**7a**), TFAA (4 mL) was added and stirred at rt for 3.5 h. After that, reaction mixture was cooled in an ice bath and methanol was added dropwise, until all TFAA was transformed. The reaction mixture was evaporated *in vacuo* and 2-propanol was added to precipitate the *title compound* (**8a**) (78 mg, 48%) as a yellow solid.

(*Z*)-Methyl 2-[(1,3-Dioxocyclohexane-2-ylidene)methyl]amino-3-hydroxypropenoate (8b). 934 mg (3.51 mmol) of compound (**7b**) in the mixture of ethanol and concetrated HCl (5:1, 10 mL) was stirred at rt for 3 h. The precipitate was collected by filtration and recrystallized from acetonitrile to give the *title compound* (**8b**) (713 mg, 85%) as a white solid mp 215-219°C; *m/z* (EI): 239 (94, M^+), 224 (100%). Anal. Calcd for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48; N, 5.86. Found C, 55.21; H, 5.64; N, 5.82. ν_{max} (KBr) 3430, 2960, 2560, 1700, 1630, 1600, 1540 cm^{-1}.

(*Z*)-Methyl 2-[[(1,3-Dimethyl-2,4,6-trioxohexahydropyrimidin-5-ylidene)methyl]amino]-3-hydroxy-propenoate (11). The suspension of **10** (302 mg, 0.97 mmol) in the mixture of concentrated HCl and ethanol (1:5, 5 mL) was heated at 90-100°C for 5 min, then cooled to form a precipitate, which was collected by filtration and recrystallized from 2-propanol to give the *title compound* (**11**) (152 mg, 55%) as a white crystals; mp 246-248°C (decomp). Anal. Calcd for $C_{11}H_{13}N_3O_6$: C, 46.65; H, 4.63; N, 14.84. Found C, 46.41; H, 4.57; N, 14.73. ν_{max} (KBr) 3440, 2970, 2690, 1750, 1720, 1640, 1600 cm^{-1}.

3-Methyl-5-[hydroxymethylidene]imidazolidine-2,4-dione (13a). To the 787 mg (4.65 mmol) of compound (**12a**) in the mixture of concentrated HCl and ethanol (1:5, 6 mL) was heated at 80°C for 4 h. The solution was evaporated and treated with ethyl acetate to give the *title compound* (**13a**) (649 mg, 98%) as a white solid; mp 156-168°C; *m/z* (EI): 142 (98, M^+), 114 (100), 58 (94%). Anal. Calcd for $C_5H_6N_2O_3$: C, 42.26; H, 4.26; N, 19.71. Found C, 41.93; H, 4.06; N, 20.02. ν_{max} (KBr) 3210, 2710, 1790, 1750, 1720, 1650 cm^{-1}.

5-[Hydroxymethylidene]imidazolidine-2,4-dione (13b). This compound was prepared from **12b** in an analogous manner as **13a**, 3 h, 55% yield, white solid; mp 231-234°C; *m/z* (EI): 128 (37, M^+), 100 (100), 57 (35%). Anal. Calcd for $C_4H_4N_2O_3$: C, 37.51; H, 3.15; N, 21.87. Found C, 37.35; H, 3.10; N, 21.69. ν_{max} (KBr) 3160, 2720, 1700 cm^{-1}.

1-Methyl-5-[(hydroxy)methylidene]imidazolidine-2,4-dione (13c). This compound was prepared from **12c** in an analoguos manner as **13a**, 5 h, 89% yield, white solid; mp 278-284°C. Anal. Calcd for $C_5H_6N_2O_3$: C, 42.26; H, 4.26; N, 19.71. Found C, 42.33; H, 4.47; N, 19.92. ν_{max} 3160, 3020, 2700, 1680 (KBr) cm^{-1}.

Table 2. ^{1}H and ^{13}C NMR Spectral Data for Compounds (**8, 11, 13** and **9**) (DMSO-d_6)

Compound	^{1}H NMR	^{13}C NMR
8a	0.96 (6 H, s, 2xMe), 2.26 and 2.34 (2 H, s, CH_2), 3.71 (3 H, s, COOMe), 7.64 (1 H, s, H-C(3)), 8.70 (1 H, d, *J* 14.0 Hz, C<u>H</u>NH), 12.40 (1 H, d, *J* 14.0 Hz, NH).	28.1(2), 30.8, 50.6, 50.9, 51.9, 107.5, 108.2, 148.2, 153.0, 163.9, 194.5, 198.4
8b	1.85 (2 H, m, CH_2), 2.34 and 2.42 (2 H, t, *J* 6.5 Hz, CH_2), 3.71 (3 H, s, COOMe), 7.65 (1 H, s, H-C(3)), 8.70 (1 H, d, *J* 14.0 Hz, C<u>H</u>NH), 12.43 (1 H, d, *J* 14.0 Hz, NH).	19.4, 37.1, 37.4, 51.9, 108.1, 108.7, 148.4, 153.6, 169.9, 195.1, 199.1
11	3.13 and 3.15 (3 H, s, NMe), 3.73 (3 H, s, COOMe), 7.66 (1 H, s, H-C(3)), 8.85 (1 H, d, *J* 14.4 Hz, C<u>H</u>NH), 11.64 (1 H, d, *J* 14.4 Hz, NH).	26.8, 27.5, 52.0, 91.0, 108.1, 148.2, 151.5, 154.4, 161.8, 163.9, 164.1.
13a	2.83 (3 H, s, NMe), 6.92 (1 H, d, *J* 5.4, =C<u>H</u>-OH), 9.79 (1 H, s, NH), 10.76 (1 H, d, *J* 5.4, =CH-O<u>H</u>).	23.7, 111.3, 132.7, 153.4, 164.2
13b	6.81 (1 H, d, *J* 5.6, =CH-OH), 9.68 (1 H, s, NH), 10.51 (1 H, s, NH), 10.53 (1 H, d, *J* 5.6, =CH-OH).	112.6, 131.7, 153.8, 165.6
13c	3.17 (3 H, s, NMe), 6.88 (1 H, s, -CH=), 10.73 (1 H, br s, NH).	28.8, 113.5, 134.1, 154.5, 165.6
9	1.96 (2 H, m, CH_2), 2.36 and 2.88 (2 H, dd, *J* 6.1 Hz, CH_2), 3.77 (3 H, s, COOMe), 7.44 (1 H, d, *J* 3.6 Hz, H-C(3)), 12.45 (1 H, br s, NH).	22.1, 24.1, 38.5, 51.2, 117.8, 122.7, 123.7, 134.2, 160.9, 193.8

Methyl 4,5,6,7-Tetrahydro-4-oxo-2*H*-isoindole-1-carboxylate (9). To the 349 mg (1.31 mmol) of compound (**7b**), TFAA (4 mL) was added, and the solution was stirred at rt for 2.5 h. After that, the reaction mixture was cooled in an ice bath, and 2-propanol was added dropwise until all TFAA was transformed. The solution was evaporated and 2-propanol added for the crystallization to give the *title compound* (**9**) (114 mg, 45%) as a brown crystals; mp 190-194°C (2-propanol). Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.74; N, 7.25. Found C, 62.06; H, 5.72; N, 6.97. ν_{max} (KBr) 3190, 3120, 3000, 2950, 1690, 1650, 1560, 1505 cm^{-1}.

General Procedure for the Synthesis of Enol Esters (14). To a suspension of **7** (1 mmol) in acetone (5 mL), corresponding benzoyl chloride (0.5 –1 mL) was added and solution was heated at 50°C for several hours. After that the mixture was cooled to form a precipitate, which was collected by filtration and recrystallized from an appropriate solvent. The following compounds were prepared in this manner:

(*Z*)-Methyl 2-[(5,5-Dimethyl-1,3-dioxocyclohexane-2-ylidene)methyl]amino-3-(4-methylbenzoyl-oxy)propenoate (14a). This compound was prepared from **7a** and 4-methylbenzoyl chloride (1 mL, 7.41 mmol), 3.5 h, 97 mg (25%) of white crystals; mp 187-189°C (2-propanol/MeCN 1:1). Anal. Calcd for $C_{21}H_{23}NO_6$: C, 65.44; H, 6.02; N, 3.63. Found C, 65.49; H, 5.93; N, 3.41. ν_{max} (KBr) 3440, 3100, 2950, 1750, 1720, 1660, 1600, 1570 cm^{-1}. Analogous sample was prepared from **8a** (145 mg, 0.54 mmol) and 4-methylbenzoyl chloride (1 mL, 7.41 mmol) in acetone (4 mL), under reflux (30 min). After cooling, 182 mg (87%) of *title compound* (**14a**) was collected by filtration.

(*Z*)-Methyl 2-[(1,3-Dioxocyclohexane-2-ylidene)methyl]amino-3-(4-methylbenzoyloxy)propenoate (14b). This compound was prepared from **7b** and 4-methylbenzoyl chloride (1 mL, 7.41 mmol), 3 h, 332 mg (93%) of yellow crystals; mp 153-164°C (2-propanol). Anal. Calcd for $C_{19}H_{19}NO_6$: C, 63.86; H, 5.36; N, 3.92. Found C, 63.63; H, 5.39; N, 4.27. ν_{max} (KBr) 3440, 3100, 2950, 1750, 1670, 1600, 1570 cm^{-1}. Analogous sample was prepared from **8b** (201 mg) and 4-methylbenzoyl chloride (1 mL) in acetone (5 mL), under reflux (2 h). After cooling, 150 mg (50%) of *title compound* (**14b**) was collected by filtration.

Table 3. ^{1}H and ^{13}C NMR Spectral Data for Compounds (**14**) ($CDCl_3$)

Compound	^{1}H NMR	^{13}C NMR
14a	1.10 (6 H, s, 2xCH_3), 2.46 (3 H, s, C<u>H</u>$_3$-Ph), 2.47 and 2.49 (2 H, s, CH_2), 3.93 (3 H, s, $COOCH_3$), 7.41 (2 H, d, *J* 7.9 Hz, Ph), 8.19 (2 H, d, *J* 7.9 Hz, Ph), 8.48 (1 H, s, H-C(3)), 9.09 (1 H, d, *J* 13.6 Hz, C<u>H</u>NH), 12.82 (1 H, d, *J* 13.6 Hz, NH).	21.8, 28.6(2), 31.1, 51.4, 51.7, 53.0, 109.7, 114.7, 123.9, 129.9(2), 130.9(2), 134.5, 146.2, 153.3, 161.4, 162.8, 196.2, 200.0
14b	2.04 (2 H, m, *J* 6.2 Hz, CH_2), 2.45 (3 H, s, C<u>H</u>$_3$-Ph), 2.56 and 2.60 (2 H, t, *J* 6.2 Hz, 2xCH_2), 3.92 (3 H, s, $COOCH_3$), 7.39 (2 H, d, *J* 8.1, Ph), 8.18 (2 H, d, *J* 8.1 Hz, Ph), 8.45 (1 H, s, H-C(3)), 9.07 (1 H, d, *J* 13.6 Hz, C<u>H</u>NH), 12.82 (1 H, d, *J* 13.6 Hz, NH).	19.5, 21.8, 37.6, 38.0, 52.9, 110.8, 114.6, 123.8, 129.8(2), 130.8(2), 134.6, 146.1, 153.8, 161.3, 162.7, 196.6, 200.5
14c	1.10 (6 H, s, 2x CH_3), 2.44 and 2.49 (2 H, s, CH_2), 3.91 (3 H, s, $COOCH_3$), 7.57-7.62 (2 H, m, Ph), 7.67-7.78 (1 H, m, Ph), 8.24-8.32 (2 H, m, Ph), 8.47 (1 H, s, H-C(3)), 9.06 (1 H, d, *J* 13.6 Hz, C<u>H</u>NH), 12.80 (1 H, d, *J* 13.6 Hz, NH).	27.8(2), 30.4, 50.7, 51.5(2), 107.4, 108.2, 128.2(2), 128.9(2), 130.7, 132.4, 147.8, 152.9, 163.6, 167.0, 194.1, 198.0
14d	2.05 (2 H, m, *J* 5.9 Hz, CH_2), 2.56 and 2.61 (2 H, m, *J* 5.9 Hz, 2xCH_2), 3.92 (3 H, s, $COOCH_3$), 7.57-7.62 (2 H, m, Ph), 7.66-7.76 (1 H, m, Ph), 8.25-8.34 (2 H, m, Ph), 8.46 (1 H, s, H-C(3)), 9.05 (1 H, d, *J* 13.6 Hz, C<u>H</u>NH), 12.83 (1 H, d, *J* 13.6 Hz, NH).	19.5, 37.7, 38.1, 53.0, 110.9, 115.0, 126.7, 129.1(2), 130.8(2), 134.5, 134.9, 153.9, 161.4, 162.7, 196.6, 200.6

(*Z*)-Methyl 2-(5,5-Dimethyl-1,3-dioxocyclohexane-2-ylidene)methyl]amino-3-benzoyloxypropenoate (14c). This compound was prepared from **7a** and benzoyl chloride (0.5 mL), 3 h, 126 mg (34%) of off white crystals; mp 167-168°C (2-propanol). Anal. Calcd for $C_{20}H_{21}NO_6.{}^{1}/_{2}H_2O$: C, 63.15; H, 5.83; N, 3.68. Found C, 63.25; H, 5.67; N, 3.77. ν_{max} (KBr) 3440, 3100, 2960, 1750, 1650, 1600, 1570 cm^{-1}.

(*Z*)-Methyl 2-[(1,3-Dioxocyclohexane-2-ylidene)methyl]amino-3-benzoyloxypropenoate (14d). This compound was prepared from **7b** and benzoyl chloride (0.5 mL), 5 h, 137 mg (40%) of pale yellow crystals; mp 174-176°C (2-propanol/MeCN 1:1). Anal. Calcd for $C_{18}H_{17}NO_6$: C, 62.97; H, 4.99; N, 4.08. Found C, 62.78; H, 4.92; N, 4.21. ν_{max} (KBr) 3440, 3140, 2960, 1750, 1720, 1670, 1600, 1570 cm^{-1}.

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