An efficient synthesis of γ-imino- and γ-amino-β-enamino esters

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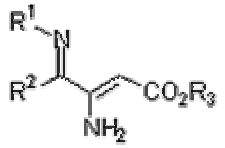
Dedicated to Professor Jim Coxon on the occasion of his 65th anniversary

Abstract
Condensation of ethyl 3-azido-4-oxopentanoate, easily accessible from ethyl 3-chloro-4-oxopentanoate, with primary amines was found to produce ethyl 4-imino-3-amino-2-pentenoates. In addition, ethyl 4-imino-3-amino-2-pentenoates were reduced chemoselectively to the corresponding ethyl 4-alkylamino-3-amino-2-pentenoates upon hydrogenation.

Keywords: Functionalized enamino esters, 1-aza-1,3-butadienes, γ-amino esters, functionalized ketimines

Introduction

β-Enamino esters are important building blocks in organic synthesis because they offer easy access to biologically active compounds such as β-amino acids[1] and heterocycles.[2] However, β-enamino esters with an imino functionality in γ-position (**1**) are virtually unknown,[3] but may be important synthons for the preparation of biologically active acyclic and heterocyclic compounds, since they contain both the functionalized enamino ester moiety and the 1-aza-1,3-butadiene skeleton.[4] Furthermore, the corresponding reduced γ-amino-β-enamino esters (**2**) have already proven to be useful in the synthesis of statine analogues as residues in renin inhibitors,[5] and the Bohlmann-Ratz synthesis of pyridine derivatives, as part of the renin inhibitor cyclothiazomycin,[6] with intracellular calcium ion concentration reducing effect,[7] or for use in library synthesis.[8] For these reasons, we wish to report our results on the synthesis of γ-imino-β-enamino esters through condensation of primary alkylamines with 3-azido-4-oxopentanoate and the subsequent reduction to the corresponding γ-amino-β-enamino esters.



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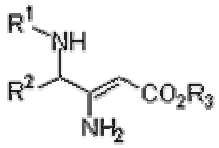

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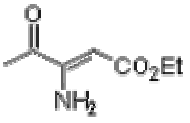
Results and Discussion

The required ethyl 3-azido-4-oxopentanoate **5** has already been reported in the literature. A first method involves nucleophilic substitution of ethyl 3-bromo-4-oxopentanoate with azide in acetone in the presence of triethylamine.[9] The β-azido ester **5**, however, could only be isolated if the time of heating was limited, since prolonged heating resulted in elimination of molecular nitrogen giving ethyl 3-amino-4-oxo-2-pentenoate **3**. A more efficient method involves substitution of ethyl 3-[(4-nitrophenyl)sulfonyloxy]-4-oxopentanoate with azide under mild reaction conditions.[10] Ethyl 3-azido-4-oxopentanoate **5** was however also easily prepared from reaction of readily available ethyl 3-chloro-4-oxopentanoate **4**,[11] with excess sodium azide in acetone under reflux (Scheme 1). The reaction was complete after reflux overnight with four equivalents of sodium azide and the only detectable side-product (<5%) was ethyl 4-oxo-2-pentenoate **6** resulting from elimination of hydrogen chloride.



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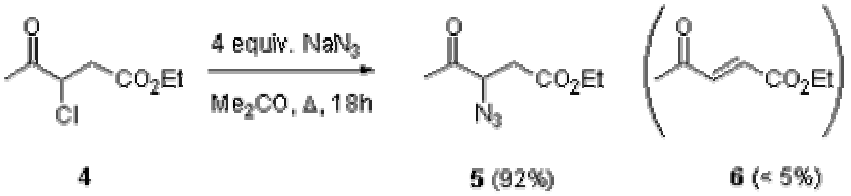
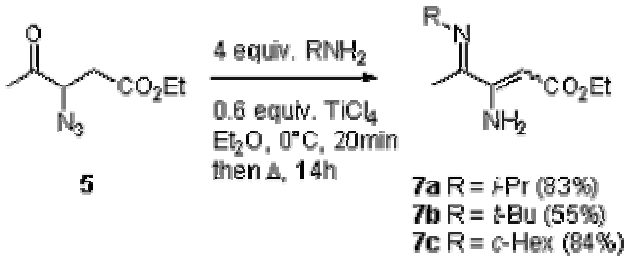


4 5 (92%) 6 (< 5%)

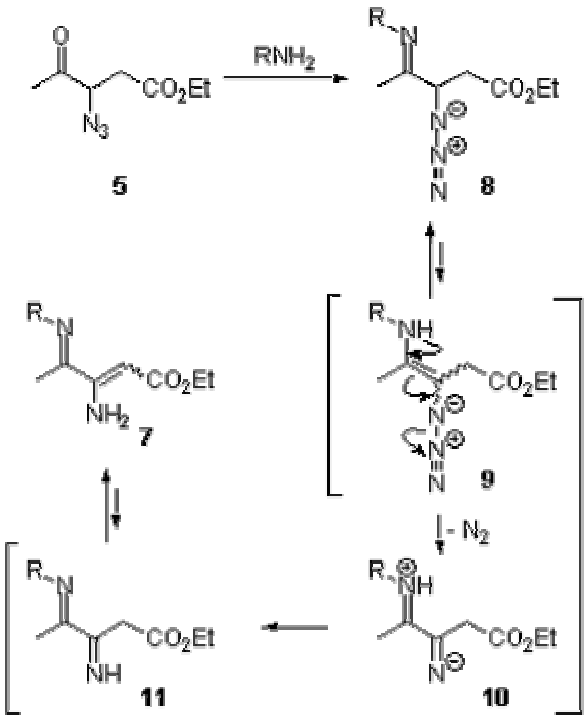
Scheme 1

From earlier research,[12] it is known that condensation of unfunctionalized α-azido ketones with primary amines produces mixtures of α-diimines and α-azido ketimines, depending on the reaction conditions and the steric hindrance in the substrate. However, in contrast to these results, reaction of ethyl 3-azido-4-oxopentanoate **5** with primary amines in the presence of titanium(IV) chloride[13] overnight at reflux temperature afforded the 4-alkylimino-3-amino-2-pentenoates **7a-c**, as single stereoisomers of undefined *E/Z* stereochemistry, in 55-84% yield

(Scheme 2). These results show the great influence of the additional ester function in β-position of the α-azido ketone **5** in the course of the reaction. From a mechanistic point of view, it is assumed that the intermediate α-azido imine **8**, which is in tautomeric equilibrium with the enamine **9**, generates the α-diimine **11** with elimination of molecular nitrogen (Scheme 3). Besides the already mentioned report on the synthesis of ethyl 3-amino-4-oxo-2-pentenoate from ethyl 3-azido-4-oxopentanoate **5**,[9] some other transformations of α-azido ketones under basic,[14] acidic[15] or thermolytic[16] conditions to α-imino ketones or α-enamino ketones have been described. Finally, the unstable NH-imine **11** is stabilized by tautomerization to the stable 4-alkylimino-3-amino-2-pentenoates **7**, and no further transimination occurs by condensation with an excess of the primary amine.

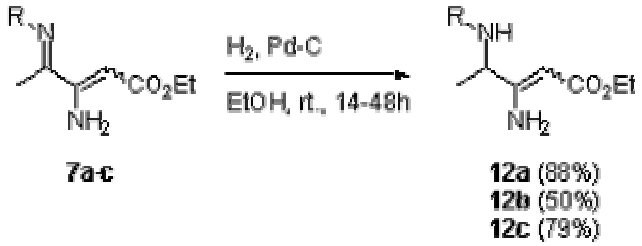


Scheme 2



Scheme 3

Subsequently, the hydrogenation of 4-alkylimino-3-amino-2-pentenoates **7a-c** was performed under catalysis of palladium on carbon. This catalytic hydrogenation resulted in the chemoselective reduction of the 4-imino function to the corresponding 4-alkylamino-3-amino-2-pentenoates **12a-c**, as single stereoisomers, in 50-88% yield (Scheme 4), without reduction of the enamino ester moiety.



Scheme 4

Although unsatisfactorily, the use of the 4-alkylamino-3-amino-2-pentenoates **12** in heterocyclic synthesis was demonstrated by transformation of γ-amino-β-enamino ester **12a** into the cyclic urea derivative **13** containing an ethoxycarbonylmethylene chain. The synthesis of related imidazolidin-2-ones with a 4-(alkoxycarbonyl)methylene substitution is only scarcely reported in literature. One report involved palladium-catalyzed oxidative cyclization-alkoxycarbonylation of acetylenic ureas.[17] A second example consisted of the cyclization reaction of a cyclic β-enamino ester with an amino function in γ-position to the imidazolidin-2-one upon reaction with trifosgene.[18] Related to the latter report, cyclization of diamino ester **12a** was attempted with different cyclization reagents, such as dimethyl- or diethylcarbonate, ethyl chloroformate, difosgene, urea and thiourea, under different conditions of temperature and solvent. The best result, with disappointingly low reproducibility and low yield, was obtained upon use of urea in toluene under reflux conditions (Scheme 5), while the other conditions gave either no reaction or complex reaction mixtures.

Scheme 5

In conclusion, the present disclosure describes a convenient entry to γ-imino- and γ-amino-β-enamino esters **7a-c** and **12a-c** by condensation of ethyl 3-azido-4-oxopentanoate **5** with primary amines and further reduction by heterogeneous hydrogenation. These functionalized β-

enamino esters **7** and **12** may be important synthons in organic synthesis for the preparation of biologically active compounds such as β- and/or γ-amino acids and heterocycles.

Experimental Section

General Procedures. NMR spectra were recorded on a Jeol JNM-EX 270 NMR spectrometer (270 MHz for ^{1}H NMR, 68 MHz for ^{13}C NMR). IR spectra were obtained using a Perkin Elmer Spectrum One FT-spectrophotometer. Mass spectra were recorded on a Varian MAT 112 mass spectrometer (EI 70 eV) or on an Agilent 1100 series VL mass spectrometer (ES 70 eV). Flash chromatography was performed with ACROS silica gel (particle size 0.035–0.070 mm, pore diameter ca. 6 nm) using a glass column. Diethyl ether was dried and distilled from sodium wire. CAUTION: use safety screens for all reactions with sodium azide or organic azides.

Synthesis of ethyl 3-azido-4-oxopentanoate (5). To a solution of ethyl 3-chloro-4-oxopentanoate (**4**)[11] (12.50 g, 70 mmol) in acetone (40 mL) was added sodium azide (18.21 g, 280 mmol). After 18h of stirring at reflux temperature, the reaction mixture was concentrated to 10% of the volume under reduced pressure, poured into water (100 mL) and extracted three times with diethyl ether (150 mL). The combined organic layers were dried over magnesium sulfate. After filtration and evaporation of the solvent, 11.92 g (92%) of ethyl 3-azido-4-oxopentanoate (**5**) was obtained as a crude light yellow oil of sufficient purity (> 95%) to be used in the next reaction step. The spectroscopic data matched completely the data reported in the literature.[10]

General procedure for the synthesis of ethyl 4-imino-3-amino-2-pentenoates (7). To a stirred ice-cooled solution of ethyl 3-azido-4-oxopentanoate (**5**) (2.28 g, 12.3 mmol) in 50 mL of dry diethyl ether, the alkylamine (49.2 mmol) was added, followed by the dropwise addition of a solution of titanium(IV) chloride (0.81 mL, 7.38 mmol) in pentane over a period of 20 minutes [CAUTION: exothermic reaction].[13] After the addition is complete, the solution was heated under reflux for 14h. The mixture was then filtrated over Celite®, poured in aqueous 0.5 N sodium hydroxide (100 mL) and extracted with diethyl ether (3x50 mL). The combined extracts were dried ($MgSO_4$), filtrated and concentrated under reduced pressure to give the pure ethyl 4-imino-3-amino-2-pentenoates **7a-c**.

Ethyl 3-amino-4-(*N*-isopropylimino)-2-pentenoate (7a). Yield 83%, oil. ^{1}H NMR ($CDCl_3$) δ 1.15 (6H, d, J = 6.3 Hz, $\underline{Me}_2CH$), 1.29 (3H, t, J = 7.1 Hz, $C\underline{H}_3CH_2$), 2.01 (3H, s, $\underline{Me}C=N$), 3.81 (1H, septet, J = 6.3 Hz, $C\underline{H}Me_2$), 4.17 (2H, q, J = 7.1 Hz, $C\underline{H}_2CH_3$), 5.05 (1H, s, $C\underline{H}C=O$), 6.50 (1H, broad s, $N(\underline{H})H$), 7.50 (1H, broad s, $N(H)\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 12.7 ($\underline{Me}C=N$), 14.6 ($\underline{C}H_3CH_2$), 23.3 ($\underline{Me}_2CH$), 51.1 ($\underline{C}HMe_2$), 59.0 ($\underline{C}H_2CH_3$), 84.9 ($\underline{C}HC=O$), 155.9 and 157.3 (CNH_2 and C=N), 170.6 (C=O); IR (NaCl) 3462, 3340, 1736, 1672, 1598 cm^{-1}; MS (EI) *m/z* (%) 198 (M^+, 31), 183 (100), 153 (15), 137 (23), 111 (28), 109 (72), 84 (32), 68 (21), 44 (22), 43 (34), 42 (98). Calcd. for $C_{10}H_{18}N_2O_2$ 198.1368.

Ethyl 3-amino-4-(*N*-*tert*-butylimino)-2-pentenoate (7b). Yield 55%, oil. ^{1}H NMR ($CDCl_3$) δ 1.29 (3H, t, J = 7.26 Hz, C$\underline{H}_3$CH$_2$), 1.33 (9H, s, $\underline{Me}_3$C), 2.13 (3H, s, $\underline{Me}$C=N), 4.16 (2H, q, J = 7.26 Hz, C$\underline{H}_2$CH$_3$), 5.06 (1H, s, C$\underline{H}$C=O), 6.51 (1H, broad s, N($\underline{H}$)H), 7.49 (1H, broad s, N(H)$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 14.4 ($\underline{C}$H$_3$CH$_2$), 16.4 ($\underline{Me}$C=N), 30.0 ($\underline{Me}_3$C), 55.2 (Me$_3\underline{C}$), 58.8 ($\underline{C}$H$_2$CH$_3$), 83.8 ($\underline{C}$HC=O), 156.5 and 156.6 (CNH$_2$ and C=N), 170.6 (C=O); IR (NaCl) 3455, 3335, 1731 (weak), 1672, 1600 cm^{-1}; MS (EI) *m/z* (%) 212 (M$^+$, 98), 156 (39), 151 (37), 111 (53), 110 (34), 98 (26), 71 (27), 57 (100), 42 (29). Calcd. for $C_{11}H_{20}N_2O_2$ 212.1525.

Ethyl 3-amino-4-(*N*-cyclohexylimino)-2-pentenoate (7c). Yield 84%, oil. ^{1}H NMR ($CDCl_3$) δ 1.29 (3H, t, J = 7.0 Hz, C$\underline{H}_3$CH$_2$), 1.33-2.00 (10H, m, (CH$_2$)$_5$), 2.01 (3H, s, $\underline{Me}$C=N), 3.35-3.55 (1H, m, C$\underline{H}$(CH$_2$)$_5$), 4.16 (2H, q, J = 7.0 Hz, C$\underline{H}_2$CH$_3$), 5.06 (1H, s, C$\underline{H}$C=O), 6.48 (1H, broad s, N($\underline{H}$)H), 7.47 (1H, broad s, N(H)$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 12.2 ($\underline{Me}$C=N), 14.1 ($\underline{C}$H$_3$CH$_2$), 24.0 and 25.2 and 32.8 ((CH$_2$)$_5$), 58.4 ($\underline{C}$H$_2$CH$_3$), 58.8 ($\underline{C}$H(CH$_2$)$_5$), 84.4 ($\underline{C}$HC=O), 155.3 and 156.8 (CNH$_2$ and C=N), 170.0 (C=O); IR (NaCl) 3460, 3339, 1736 (weak), 1672, 1598 cm^{-1}; MS (EI) *m/z* (%) 238 (M$^+$, 25), 196 (19), 195 (100), 182 (16), 165 (15), 121 (12), 111 (18), 83 (19), 55 (14). Calcd. for $C_{13}H_{22}N_2O_2$ 238.1681.

General procedure for the synthesis of ethyl 4-amino-3-amino-2-pentenoates (12). To a solution of ethyl 4-imino-3-amino-2-pentenoate **7** (5.69 mmol) in ethanol (10 mL) was added 10% palladium on carbon (20% for **7c**). After 14h (48h for **7c**) of stirring at room temperature under hydrogen atmosphere (6 bar), the reaction mixture was filtrated over Celite® and concentrated under reduced pressure to give the pure ethyl 4-amino-3-amino-2-pentenoates **12a-c**.

Ethyl 3-amino-4-(*N*-isopropylamino)-2-pentenoate (12a). Yield 88%, oil. ^{1}H NMR ($CDCl_3$) δ 0.93 and 0.96 (each 3H, each d, J = 6.27 Hz, $\underline{Me}_2$CH), 1.18 (3H, t, J = 7.0 Hz, C$\underline{H}_3$CH$_2$), 1.18 (3H, d, J = 6.60 Hz, $\underline{Me}$CH), 2.63 (1H, septet, J = 6.27 Hz, C$\underline{H}$Me$_2$), 3.23 (1H, q, J = 6.60 Hz, C$\underline{H}$Me), 4.03 (2H, q, J = 7.0 Hz, C$\underline{H}_2$CH$_3$), 4.44 (1H, s, C$\underline{H}$C=O), 6.12 (1H, broad s, N($\underline{H}$)H), 7.61 (1H, broad s, N(H)$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 14.7 ($\underline{C}$H$_3$CH$_2$), 22.7 and 23.8 ($\underline{Me}_2$CH), 23.3 ($\underline{Me}$CH), 47.6 ($\underline{C}$HMe$_2$), 55.2 ($\underline{C}$HMe), 58.5 ($\underline{C}$H$_2$CH$_3$), 80.7 ($\underline{C}$HC=O), 167.6 (CNH$_2$), 170.6 (C=O); IR (NaCl) 3449, 3330, 1735 (weak), 1665, 1611 cm^{-1}; MS (ES) *m/z* (%) 201 (M+H$^+$, 100). Calcd. for $C_{10}H_{20}N_2O_2$ 200.1525.

Ethyl 3-amino-4-(*N*-*tert*-butylamino)-2-pentenoate (12b). Yield 50%, oil. ^{1}H NMR ($CDCl_3$) δ 1.05 (9H, s, $\underline{Me}_3$C), 1.24-1.29 (6H, m, C$\underline{H}_3$CH$_2$ and $\underline{Me}$CH), 3.39 (1H, q, J = 7.0 Hz, C$\underline{H}$Me), 4.10 (2H, q, J = 7.0 Hz, C$\underline{H}_2$CH$_3$), 4.49 (1H, s, C$\underline{H}$C=O), 6.50 (1H, broad s, N($\underline{H}$)H), 7.77 (1H, broad s, N(H)$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 14.3 ($\underline{C}$H$_3$CH$_2$), 24.6 ($\underline{Me}$CH), 28.8 ($\underline{Me}_3$C), 50.8 ($\underline{C}$HMe), 50.9 (Me$_3\underline{C}$), 58.0 ($\underline{C}$H$_2$CH$_3$), 78.8 ($\underline{C}$HC=O), 169.0 and 170.4 (CNH$_2$ and C=O); IR (NaCl) 3442, 3329, 1736, 1663, 1607 cm^{-1}; MS (EI) *m/z* (%) 215 (M+H$^+$, 100), 159 (31). Calcd. for $C_{11}H_{22}N_2O_2$ 214.1681.

Ethyl 3-amino-4-(*N*-cyclohexylamino)-2-pentenoate (12c). Yield 79%, oil. ^{1}H NMR ($CDCl_3$) δ 1.27 (3H, t, J = 7.0 Hz, C$\underline{H}_3$CH$_2$), 1.36 (3H, d, J = 7.0 Hz, $\underline{Me}$CH), 1.20-2.00 (10H, m, (CH$_2$)$_5$), 2.31-2.65 (1H, m, C$\underline{H}$(CH$_2$)$_5$), 3.45 (1H, q, J = 7.0 Hz, C$\underline{H}$Me), 4.11 (2H, q, J = 7.0 Hz, C$\underline{H}_2$CH$_3$), 4.52 (1H, s, C$\underline{H}$C=O), 6.40 (1H, broad s, N($\underline{H}$)H), 7.69 (1H, broad s, N(H)$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 14.6 ($\underline{C}$H$_3$CH$_2$), 22.1 ($\underline{Me}$CH), 24.9 and 25.1 and 25.7 and 32.2 and 33.5

($(CH_2)_5$), 54.9 (CHMe), 55.4 (CH$(CH_2)_5$), 58.7 (CH_2CH_3), 81.8 (CHC=O), 164.9 (CNH_2), 170.4 (C=O); IR (NaCl) 3446, 3326, 1733, 1667, 1607 cm^{-1}; MS (EI) *m/z* (%) 241 ($M+H^+$, 23). Calcd. for $C_{13}H_{24}N_2O_2$ 240.1838.

Synthesis of ethyl (1-isopropyl-5-methyl-2-oxoimidazolidin-4-ylidene)acetate (13). To a solution of ethyl 3-amino-4-(*N*-isopropylamino)-2-pentenoate **12a** (0.20 g, 1 mmol) in toluene (20 mL) was added urea (0.12 g, 2 mmol). After 17h of stirring at reflux temperature, the reaction mixture was concentrated under reduced pressure, poured into water (20 mL) and extracted three times with diethyl ether (20 mL). The combined organic layers were dried over magnesium sulfate. After filtration and evaporation of the solvent 0.16 g of a brown oil was obtained, which was purified by column chromatography (petroleum ether–EtOAc, 3:2, R_f = 0.41) to give 80 mg (35%) of pure ethyl (1-isopropyl-5-methyl-2-oxoimidazolidin-4-ylidene)acetate **13** as an oil. Data for **13**: ^{1}H NMR ($CDCl_3$) δ 1.20 (3H, t, J = 7.26 Hz, CH_3CH_2), 1.22 and 1.23 (each 3H, each d, J = 7.0 Hz, Me_2CH), 1.37 (3H, d, J = 6.60 Hz, MeCH), 3.97 (1H, septet, J = 7.0 Hz, $CHMe_2$), 4.09 (2H, q, J = 7.26 Hz, CH_2CH_3), 4.31 (1H, qxd, J_{vic} = 6.60 Hz, J_{allyl} = 1.32 Hz, CHMe), 4.76 (1H, d, J_{allyl} = 1.32 Hz, CHC=O), 8.97 (1H, broad s, NH); ^{13}C NMR ($CDCl_3$) δ 14.3 (CH_3CH_2), 19.6 and 22.0 (Me_2CH), 21.5 (MeCH), 44.5 ($CHMe_2$), 54.8 (CHMe), 59.6 (CH_2CH_3), 84.5 (CHC=O), 155.6 and 158.0 (N-C(=O)N and C=CH), 168.3 (C=O); IR (NaCl) 3393, 3322, 1732, 1682, 1635 cm^{-1}; MS (ES) *m/z* (%) 227 ($M+H^+$, 100), 181 (50). Calcd. for $C_{11}H_{18}N_2O_3$ 226.1317.

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