Alkylation of Heterocyclic Ketene Aminals with Benzyl Chloride and Ethyl Bromoacetate. Synthesis of Heterobicycles Containing γ-Lactam-Fused Diazaheterocycles

Zhi-tang Huang* and Zhi-rong Liu

Institute of Chemistry, Academia Sinica,
Beijing, PR of China

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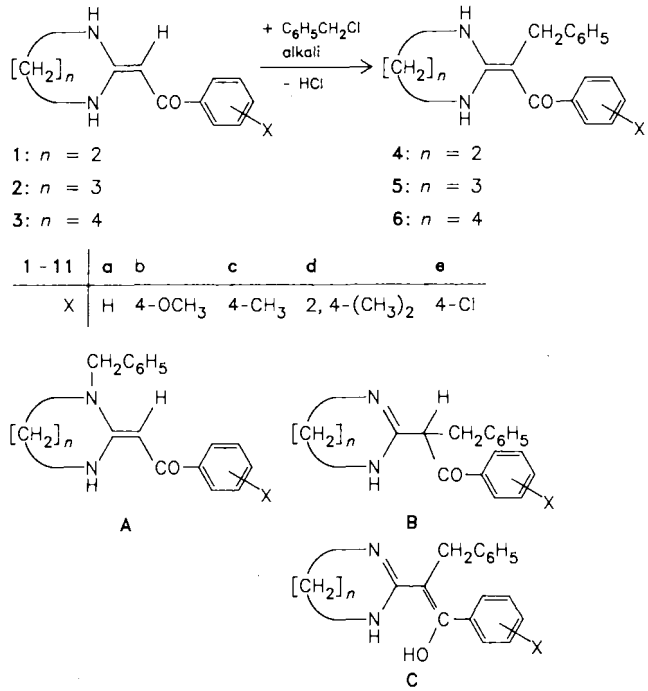
Heterocyclic ketene aminals **1**–**3** react with benzyl chloride to give the benzyl-substituted compounds **4**–**6**. With ethyl bromoacetate, **1**–**3** react smoothly, and γ-lactam-fused heterobicycles **9**–**11** are obtained by further cyclocondensation of the alkylation products.

Alkylierung von heterocyclischen Keten-aminalen mit Benzylchlorid und Bromessigsäure-ethylester. Synthese von Heterobicyclen bestehend aus γ-Lactam-verknüpften Diazaheterocyclen

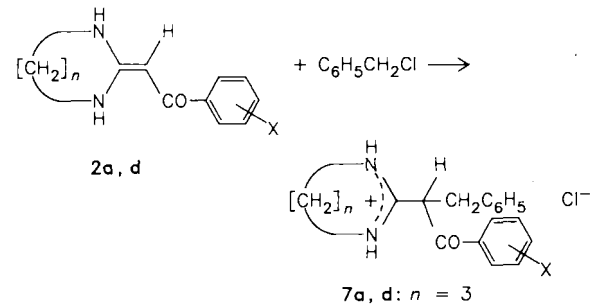
Heterocyclische Keten-aminale **1**–**3** reagieren mit Benzylchlorid zu den Benzyl-substituierten Verbindungen **4**–**6**. Bromessigsäure-ethylester liefert analoge Alkylierungsprodukte, die zu den γ-Lactamen **9**–**11** cyclisieren.

Heterocyclic ketene aminals are versatile starting materials for the synthesis of a wide variety of fused heterocycles. Recently, the addition and cyclization reaction of heterocyclic ketene aminals with esters of α,β-unsaturated acids have been reported[1–5], and heterobicycles containing δ-lactam-fused diazaheterocycles were synthesized by this reaction sequence. But the alkylation of heterocyclic ketene aminals has not been reported yet. Here we describe the alkylation of heterocyclic ketene aminals with benzyl chloride and ethyl bromoacetate. From the latter reaction the heterobicycles containing γ-lactam-fused diazaheterocycles were synthesized by further cyclocondensation reactions.



Heterocyclic ketene aminals **1**–**3** reacted with benzyl chloride in refluxing acetonitrile to give the benzyl-substituted heterocyclic ketene aminals **4**–**6** in moderate to good yields after treatment of the reaction mixture with alkali.

The starting materials **1**–**3** were prepared from ketene mercaptals and the corresponding diamines. The reaction of benzophenones with sodium hydride and carbon disulfides followed by treatment with methyl iodide served well to synthesize the mercaptals in a one-pot reaction[6]. The constitutions of **4**–**6** were determined by MS and elemental analyses. The existence of two NH signals and the absence of ethylenic or methine proton signals in the ^{1}H-NMR spectra exclude both the *N*-benzylation product **A** and the tautomer of ketone-amidine form **B**. The presence of a ketone carbonyl carbon signal in the ^{13}C-NMR spectra also excludes the tautomer of enol-amidine form **C**. The ^{1}H- and ^{13}C-NMR data are listed in Table 1 and 2, respectively. The reaction products confirmed as **4**–**6** were formed by *C*-benzylation similar to alkylation of enamines[7–10].



This reaction proceeds through the intermediate immonium salt, since the immonium salts **7a,d** were isolated from the reaction of **2a,d** with benzyl chloride in good yields when the reaction mixture was not worked up with alkali.

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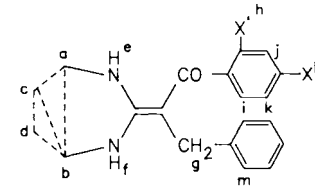
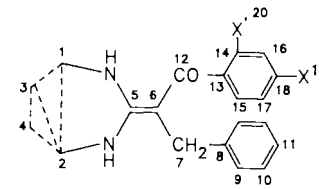
Table 1. ^{1}H-NMR data (δ values) of **4**–**6** in $CDCl_3$ with TMS as internal standard



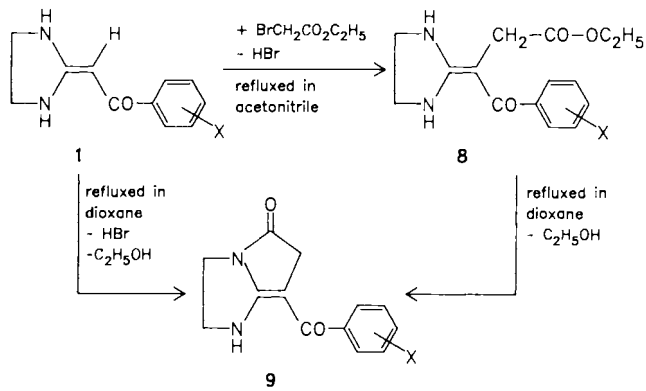
	H^a	H^b	H^c	H^d	H^e	H^f	H^g	H^h	H^i	H^j	H^k	H^l	H^m
4a	3.44t				10.10s	7.10s	3.44s			6.87-7.27m			
4b	3.50t				10.10s	7.07s	3.30s	7.08d		6.73d		3.70s	7.10-7.20m
4d	3.53t				10.00s	7.10s	3.33s	2.22s	6.77-7.10m			2.02s	6.77-7.10m
5a	3.21t		1.76quin		12.50s	7.10s	3.40s			7.10s			
5b	3.21t		1.75quin		12.80s	7.20s	3.46s	7.00d		6.68d		3.65s	7.10s
5d	3.14t		1.80quin		10.87s	7.10s	3.36s	2.37s	6.80-7.13m			2.27s	6.80-7.13m
5e	3.28t		1.77quin		12.40s	7.10s	3.40s	7.88d		7.36d			7.12-7.25m
6c	3.10t		1.60quin		12.23s	4.60s	3.60s		6.90-7.20m			2.23s	6.90-7.27m
6d	2.90-3.33m		1.62quin		12.30s	4.47s	3.43s	2.25s	6.83-7.20m			2.22s	6.83-7.20m

Table 2. ^{13}C-NMR data (δ values) of **4**–**6** in $CDCl_3$ with TMS as internal standard



	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18	C-19	C-20
4a	32.7				165.4	84.8	42.6	143.8	127.5	125.9	124.9	187.5	142.5	127.3		127.1		128.9		
4b	32.9				165.5	84.7	42.7	142.7	127.7	127.4	125.0	187.1	136.2	127.7		112.6		158.6	54.8	
4d	33.5				165.7	87.5	43.1	139.9	128.2	127.6	125.7	190.6	133.7	136.6	130.6	131.0	127.1	141.7	18.9	21.1
5a	37.9		19.9		159.5	86.2	31.9	144.4	127.8	126.0	125.1	184.8	142.6	127.3		126.8		127.4		
5b	38.0		20.0		159.7	86.1	32.1	142.7	127.7	127.5	125.2	184.6	137.1	127.9		112.7		158.4	55.0	
5d	37.6		20.1		159.3	82.1	32.9	136.8	130.7	127.0	125.5	185.4	130.5	134.6	127.3	128.3	125.7	141.2	19.8	20.9
5e	37.7		19.6		159.4	85.9	31.6	139.2	127.6	127.2	125.0	183.0	130.5	128.1		127.8		142.2		
6c	45.5		28.1		169.4	91.0	34.7	140.6	128.6	126.5	126.1	190.2	137.7	128.4		127.5		141.6	21.2	
6d	45.3		28.0		169.0	91.2	33.9	140.3	128.3	127.3	125.5	190.4	133.4	136.4	130.6	130.9	125.7	141.4	19.1	21.0

The reaction of **1**–**3** with ethyl bromoacetate proceeded smoothly in refluxing acetonitrile. In the case of **1**, the *C*-alkylation products **8** were obtained in good yields. But in the case of **2** and **3**, a further cyclization occurred, and cyclocondensation products **10** and **11**, respectively, were isolated. **8** could be further cyclized in a higher boiling solvent, such as dioxane, and cyclocondensation products **9** were obtained in good yields. If the reaction of **1** and ethyl bromo-



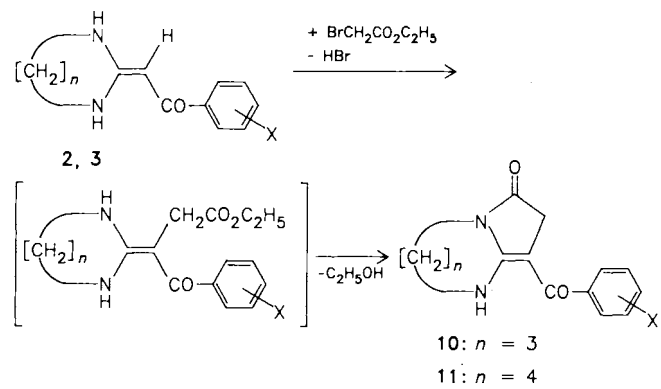
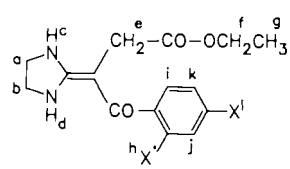


Table 3. ^{1}H-NMR data (δ values) of **8**, **10**, **11** in $CDCl_3$ and **9** in [D_6]DMSO with TMS as internal standard



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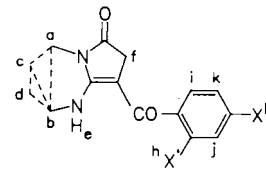
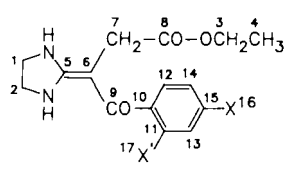


9 - 11

	H^a	H^b	H^c	H^d	H^e	H^f	H^g	H^h	H^i	H^j	H^k	H^l
8a	3.62s		6.10s	7.70s	3.07s	4.10q	1.24t			7.32s		
8d	3.58s		6.70s	7.80s	2.92s	3.97q	1.17t	2.25s		6.85s		2.17s
8e	3.67s		6.80s	8.06s	3.07s	4.13q	1.24t	7.36d		7.30d		
9a	3.82t	3.73t			8.10s	3.62s				7.23-7.65m		
9b	4.01t	3.84t			8.08s	3.68s		7.63d		6.91d		3.80s
9c	3.92t	3.82t			8.05s	3.70s		7.05d		6.74d		2.43s
9e	4.10t	4.00t			7.70s	3.87s		7.97d		7.73d		
10a	3.60t	3.40t	2.00quin		9.87s	3.40s				7.17-7.67m		
10b	3.57t	3.40t	1.96quin		9.60s	3.43s		7.57d		6.68d		3.77s
10c	3.62t	3.45t	2.00quin		9.67s	3.46s		7.52d		7.15d		2.34s
10d	3.56t	3.40t	2.05quin		9.50s	3.08s		2.32s		6.83-7.10m		2.32s
10e	3.70t	3.52t	2.05quin		9.93s	3.48s		7.68d		7.43d		
11a	3.84t	3.57t	1.86-2.16m		10.80s	3.47s				7.23-7.70m		
11c	3.80t	3.50t	1.84-2.10m		10.74s	3.47s		7.43d		7.10d		2.43s

Table 4. ^{13}C-NMR data (δ values) of **8**, **10**, **11** in $CDCl_3$ and **9** in [D_6]DMSO with TMS as internal standard



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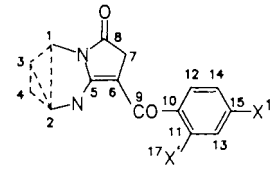

9 - 11

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16	C-17
8a	43.6		60.9	14.2	167.1	92.1	34.6	174.6	190.9	142.6	127.9		127.1		128.4		
8d	43.4		60.7	14.1	167.4	92.0	34.1	173.5	190.1	133.7	137.1	126.1	130.8	125.9	139.2	18.9	21.2
8e	43.6		61.1	14.2	167.3	92.1	34.5	174.4	192.2	131.2	128.7		128.2		139.4		
9a	49.3	41.0			161.4	98.8	38.3	174.8	186.4	139.6	127.9		127.0		129.6		
9b	49.3	41.4			161.8	98.9	38.4	176.7	187.5	133.0	129.0		113.4		160.9	55.2	
9c	48.8	40.7			161.4	98.3	37.9	175.7	186.8	138.9	128.1		126.6		140.4	20.3	
9e	49.0	40.4			161.7	98.4	37.9	176.5	187.0	135.4	128.5		127.7		139.3		
10a	38.6	37.3	20.1		158.5	84.5	35.5	174.3	184.4	142.9	128.2		127.1		129.8		
10b	38.5	37.2	20.0		158.2	84.2	35.7	174.4	182.9	133.4	128.9		113.4		160.9	55.3	
10c	38.5	37.2	20.0		158.2	84.4	35.6	174.4	183.9	138.1	128.8		127.1		140.0	21.4	
10d	38.3	37.1	20.0		157.2	85.5	34.6	174.4	187.9	132.2	134.2	126.2	131.2	125.9	138.0	19.2	21.1
10e	38.6	37.2	20.0		158.7	84.5	35.3	174.1	182.5	135.6	128.5		128.4		139.4		
11a	42.4	40.4	27.1	24.8	164.4	86.2	35.7	175.0	184.4	140.9	127.9		126.8		129.5		
11c	42.6	40.5	27.3	25.0	164.5	86.3	36.0	175.3	184.5	138.3	128.8		127.1		139.9	21.4	

acetate was conducted in refluxing dioxane, **9** was isolated directly in moderate yields. The structures of **8**–**11** were proved by the spectroscopic data and elemental analyses. The ^{1}H- and ^{13}C-NMR data of **8**–**11** are listed in Tables 3 and 4, respectively.

By this reaction we provide a new and convenient method for the synthesis of heterobicycles containing γ-lactam-fused diazaheterocycles. The experiments described above prove γ-lactam annulation to be more efficient with six- and seven-membered heterocyclic ring systems than with the five-membered imidazolidine ring.

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Experimental

IR spectra: Perkin-Elmer 782. – ^{1}H-NMR spectra: Varian EM-360L. – ^{13}C-NMR spectra: Jeol FX-100. – MS: AEI MS-50. – UV spectra: Hitachi 340. – Melting points are not corrected. – Elemental analyses: Analytical Laboratory of the Institute.

2-[1-Benzoyl-2-phenylethylidene]imidazolidine (**4a**): A mixture of 546 mg (3.0 mmol) of **1a** and 380 mg (3.0 mmol) of benzyl chloride in 15 ml of acetonitrile was refluxed for 48 h. After removal of solvent, the residue was dissolved in water, the solution was neutralized with sodium hydroxide solution and extracted with chloroform, and the extract dried with sodium sulfate. The crude product obtained after removal of chloroform was recrystallized from ethanol. Yield 350 mg (42%), m.p. 178–180°C. – IR (KBr): 3180 cm^{-1} (NH), 1585 (C=O), 1565, 1513. – UV (ethanol): λ_{max} (lg ε) = 310 nm (3.51), 230 (4.05). – MS: *m/z* = 278 (M^+).

$C_{18}H_{18}N_2O$ (278.3) Calcd. C 77.67 H 6.52 N 10.07
Found C 77.09 H 6.61 N 9.88

2-[1-(4-Methoxybenzoyl)-2-phenylethylidene]imidazolidine (**4b**): Similar to **4a**, 450 mg (49%) of **4b** was obtained from 654 mg (3.0 mmol) of **1b** and 380 mg (3.0 mmol) of benzyl chloride, m.p. 177–179°C. – IR (KBr): 3180 cm^{-1} (NH), 1580 (C=O), 1515. – UV (ethanol): λ_{max} (lg ε) = 314 nm (4.11), 250 (3.99). – MS: *m/z* = 308 (M^+).

$C_{19}H_{20}N_2O_2$ (308.4) Calcd. C 74.00 H 6.54 N 9.09
Found C 73.95 H 6.47 N 9.16

2-[1-(2,4-Dimethylbenzoyl)-2-phenylethylidene]imidazolidine (**4d**): Like **4a** 420 mg (69%) of **4d** was obtained from 432 mg (2.0 mmol) of **1d** and 253 mg (2.0 mmol) of benzyl chloride, m.p. 168–170°C. – IR (KBr): 3190 cm^{-1} (NH), 1588 (C=O), 1516. – UV (ethanol): λ_{max} (lg ε) = 304 nm (4.15), 240 (3.63). – MS: *m/z* = 306 (M^+).

$C_{20}H_{22}N_2O$ (306.4) Calcd. C 78.39 H 7.24 N 9.14
Found C 78.48 H 7.21 N 9.13

2-[1-Benzoyl-2-phenylethylidene]hexahydropyrimidine (**5a**): Analogously to **4a**, 420 mg (48%) of **5a** was obtained from 606 mg (3.0 mmol) of **2a** and 380 mg (3.0 mmol) of benzyl chloride, m.p. 179–182°C. – IR (KBr): 3240 cm^{-1} (NH), 1602 (C=O), 1570, 1509. – UV (ethanol): λ_{max} (lg ε) = 308 nm (4.01), 234 (4.01). – MS: *m/z* = 292 (M^+).

$C_{19}H_{20}N_2O$ (292.4) Calcd. C 78.05 H 6.90 N 9.58
Found C 77.48 H 6.90 N 9.71

Hexahydro-2-[1-(4-methoxybenzoyl)-2-phenylethylidene]pyrimidine (**5b**): According to **4a**, 650 mg (67%) of **5b** was obtained from 696 mg (3.0 mmol) of **2b** and 380 mg (3.0 mmol) of benzyl chloride, m.p. 168–170°C. – IR (KBr): 3220 cm^{-1} (NH), 1590 (C=O), 1565. – UV (ethanol): λ_{max} (lg ε) = 304 nm (4.49), 224 (4.42). – MS: *m/z* = 322 (M^+).

$C_{20}H_{22}N_2O_2$ (322.4) Calcd. C 74.50 H 6.88 N 8.69
Found C 73.62 H 6.86 N 8.79

2-[1-(2,4-Dimethylbenzoyl)-2-phenylethylidene]hexahydropyrimidine (**5d**): According to **4a**, 350 mg (55%) of **5d** was obtained from 460 mg (2.0 mmol) of **2d** and 253 mg (2.0 mmol) of benzyl chloride, m.p. 198–200°C. – IR (KBr): 3250 cm^{-1}, 3170 (NH), 1630 (C=O), 1585, 1530. – UV (ethanol): λ_{max} (lg ε) = 300 nm (4.65), 234 (4.41). – MS: *m/z* = 320 (M^+).

$C_{21}H_{24}N_2O$ (320.4) Calcd. C 78.71 H 7.55 N 8.74
Found C 78.23 H 7.52 N 8.74

2-[1-(4-Chlorobenzoyl)-2-phenylethylidene]hexahydropyrimidine (**5e**): Like to **4a**, 350 mg (54%) of **5e** was obtained from 473 mg (2.0 mmol) of **2e** and 253 mg (2.0 mmol) of benzyl chloride, m.p. 187–190°C. – IR (KBr): 3240 cm^{-1} (NH), 1596 (C=O), 1580, 1510. – UV (ethanol): λ_{max} (lg ε) = 320 nm (3.22), 242 (4.11). – MS: *m/z* = 326 (M^+).

$C_{19}H_{19}ClN_2O$ (326.8) Calcd. C 69.82 H 5.86 N 8.57
Found C 69.59 H 6.10 N 8.74

Hexahydro-2-[1-(4-methylbenzoyl)-2-phenylethyliden]-1H-1,3-diazepine (**6c**): Similar to **4a**, 240 mg (75%) of **6c** was obtained from 213 mg (1.0 mmol) of **3c** and 127 mg (1.0 mmol) of benzyl chloride, m.p. 159–161°C. – IR (KBr): 3330 cm^{-1} (NH), 1610 (C=O), 1540. – UV (ethanol): λ_{max} (lg ε) = 324 nm (4.20), 236 (3.94). – MS: *m/z* = 320 (M^+).

$C_{21}H_{24}N_2O$ (320.4) Calcd. C 78.71 H 7.55 N 8.74
Found C 78.34 H 7.69 N 8.61

2-[1-(2,4-Dimethylbenzoyl)-2-phenylethylidene]hexahydro-1H-1,3-diazepine (**6d**): Similar to **4a**, 265 mg (79%) of **6d** was obtained from 244 mg (1.0 mmol) of **3d** and 127 mg (1.0 mmol) of benzyl chloride, m.p. 189–191°C. – IR (KBr): 3300 cm^{-1} (NH), 1600 (C=O), 1540. – UV (ethanol): λ_{max} (lg ε) = 318 nm (4.35), 240 (3.80). – MS: *m/z* = 344 (M^+).

$C_{22}H_{26}N_2O$ (334.5) Calcd. C 79.00 H 7.84 N 8.38
Found C 78.83 H 7.85 N 8.28

2-[1-Benzoyl-2-phenylethyl]-3,4,5,6-tetrahydropyrimidinium Chloride (**7a**): A mixture of 404 mg (2.0 mmol) of **2a** and 253 mg (2.0 mmol) of benzyl chloride in 20 ml of acetonitrile was refluxed for 36 h. After partial removal of solvent, **7a** crystallized as colorless crystals. Yield 570 mg (87%), m.p. 200–202°C. – IR (KBr): 3140 cm^{-1}, 2740 (NH, =N$^+$H), 1680 (C=O), 1653 (C=N), 1610. – ^{1}H-NMR ($CDCl_3$/TMS): δ = 1.70 (quint, 2H), 3.33 (t, 6H), 5.92 (t, 1H), 7.08–8.17 (m, 10H), 10.30 (s, 2H). – ^{13}C-NMR ($CDCl_3$/TMS): δ = 17.8, 36.9, 38.7, 50.1, 126.8, 128.3, 128.7, 129.2, 129.3, 133.8, 135.0, 135.7, 160.3, 195.4.

$C_{19}H_{21}ClN_2O$ (328.8) Calcd. C 69.39 H 6.44 N 8.52
Found C 69.37 H 6.40 N 8.47

2-[1-(2,4-Dimethylbenzoyl)-2-phenylethyl]-3,4,5,6-tetrahydropyrimidinium Chloride (**7d**): Similar to **7a**, 565 mg (79%) of **7d** was obtained from 460 mg (2.0 mmol) of **2d** and 253 mg (2.0 mmol) of benzyl chloride, m.p. 197–200°C. – IR (KBr): 3120 cm^{-1}, 2800 (NH, =N$^+$H), 1700 (C=O), 1680 (C=N), 1630. – ^{1}H-NMR ($CDCl_3$/TMS): δ = 1.55 (quint, 2H), 2.29 (s, 3H), 2.37 (s, 3H), 3.17 (t, 4H), 3.34 (d, 2H), 5.30 (t, 1H), 7.00–8.03 (m, 8H), 10.30 (s, 2H). – ^{13}C-NMR ($CDCl_3$/TMS): δ = 17.2, 20.0, 20.5, 34.4, 38.1, 53.4, 126.1, 126.4, 128.0, 128.6, 129.0, 132.1, 132.9, 136.5, 137.9, 142.0, 159.4, 196.9.

$C_{21}H_{25}ClN_2O$ (356.9) Calcd. C 70.67 H 7.06 N 7.85
Found C 70.62 H 7.04 N 7.69

Ethyl 3-Benzoyl-3-(2-imidazolidinylidene)propionate (**8a**): A mixture of 376 mg (2.0 mmol) of **1a** and 334 mg (2.0 mmol) of ethyl bromoacetate in 15 ml of acetonitrile was refluxed for 25 h. After removal of solvent, the viscous residue was dissolved in water and the solution neutralized with sodium hydroxide solution to weakly alkaline, then extracted with chloroform. The extract was dried with anhydrous sodium sulfate. The crude product was obtained after removal of chloroform and recrystallized from acetonitrile. Yield 330 mg (60%), m.p. 148–150°C. – IR (KBr): 3280 cm^{-1}, 3190 (NH), 1728, 1705 (ester C=O), 1640 (C=O), 1590, 1525. – UV (ethanol): λ_{max} (lg ε) = 310 nm (4.08), 234 (3.95). – MS: *m/z* = 274 (M^+).

$C_{15}H_{18}N_2O_3$ (274.3) Calcd. C 65.67 H 6.61 N 10.21
Found C 65.88 H 6.16 N 10.69

Ethyl 3-(2,4-Dimethylbenzoyl)-3-(2-imidazolidinylidene)propionate (**8d**): Like **8a**, 450 mg (75%) of **8d** was obtained from 432 mg (2.0 mmol) of **1d** and 334 mg (2.0 mmol) of ethyl bromoacetate, m.p. 158–160°C. – IR (KBr): 3200 cm^{-1}, 3140 (NH), 1725 (ester C=O), 1710 (C=O), 1595, 1525. – UV (ethanol): λ_{max} (lg ε) = 298 nm (4.31), 236 (3.70). – MS: *m/z* = 302 (M^+).

$C_{17}H_{22}N_2O_3$ (302.4) Calcd. C 67.52 H 7.34 N 9.27
Found C 66.93 H 7.24 N 9.15

Ethyl 3-(4-Chlorobenzoyl)-3-(2-imidazolidinylidene)propionate (**8e**): According to **8a**, 430 mg (70%) of **8e** was obtained from 445 mg (2.0 mmol) of **1e** and 334 mg (2.0 mmol) of ethyl bromoacetate, m.p. 245–248°C. – IR (KBr): 3190 cm^{-1}, 3090 (NH), 1730 (ester C=O), 1645 (C=O), 1590, 1525. – UV (ethanol): λ_{max} (lg ε) = 312 nm (4.01), 240 (4.01). – MS: *m/z* = 308 (M^+).

$C_{15}H_{17}ClN_2O_3$ (308.8) Calcd. C 58.35 H 5.55 N 9.07
Found C 58.44 H 5.45 N 9.17

8-Benzoyl-1,3,4,7-tetrahydropyrrolo[1,2-a]pyrimidin-6(2H)-one (**10a**): A mixture of 404 mg (2.0 mmol) of **2a** and 334 mg (2.0 mmol) of ethyl bromoacetate in 20 ml of acetonitrile was refluxed for 25 h. After removal of solvent, the residue was dissolved in water and the solution neutralized with sodium hydroxide solution, then extracted with chloroform. The extract was dried with anhydrous sodium sulfate. The crude product was obtained after removal of chloroform and was recrystallized from acetonitrile. Yield 350 mg (72%), m.p. 204–206°C. – IR (KBr): 3230 cm^{-1} (NH), 1718 (amide C=O), 1635 (C=O), 1575, 1525. – UV (ethanol): λ_{max} (lg ε) = 336 nm (4.21), 232 (4.04). – MS: *m/z* = 242 (M^+).

$C_{14}H_{14}N_2O_2$ (242.3) Calcd. C 69.40 H 5.82 N 11.58
Found C 69.90 H 5.81 N 11.46

1,3,4,7-Tetrahydro-8-(4-methoxybenzoyl)pyrrolo[1,2-a]pyrimidin-6(2H)-one (**10b**): Like **10a**, 510 mg (94%) of **10b** was obtained from 464 mg (2.0 mmol) of **2b** and 334 mg (2.0 mmol) of ethyl bromoacetate, m.p. 180–182°C. – IR (KBr): 3240 cm^{-1} (NH), 1725 (amide C=O), 1625 (C=O), 1595, 1525. – UV (ethanol): λ_{max} (lg ε) = 342 (3.90), 257 (4.11). – MS: *m/z* = 272 (M^+).

$C_{15}H_{16}N_2O_3$ (272.3) Calcd. C 66.16 H 5.92 N 10.29
Found C 66.08 H 6.03 N 9.94

1,3,4,7-Tetrahydro-8-(4-methylbenzoyl)pyrrolo[1,2-a]pyrimidin-6(2H)-one (**10c**): Similar to **10a**, 252 mg (66%) of **10c** was obtained from 324 mg (1.5 mmol) of **2c** and 251 mg (1.5 mmol) of ethyl bromoacetate, m.p. 185–188°C. – IR (KBr): 3240 cm^{-1} (NH), 1720 (amide C=O), 1645 (C=O), 1525. – UV (ethanol): λ_{max} (lg ε) = 338 nm (4.18), 242 (3.85). – MS: *m/z* = 256 (M^+).

$C_{15}H_{16}N_2O_2$ (256.3) Calcd. C 70.29 H 6.29 N 10.93
Found C 70.03 H 6.16 N 10.80

8-(2,4-Dimethylbenzoyl)-1,3,4,7-tetrahydropyrrolo[1,2-a]pyrimidin-6(2H)-one (**10d**): Analogously to **10a**, 470 mg (87%) of **10d** was obtained from 460 mg (2.0 mmol) of **2d** and 334 mg (2.0 mmol) of ethyl bromoacetate, m.p. 159–161°C. – IR (KBr): 3240 cm^{-1} (NH), 1725 (amide C=O), 1635 (C=O), 1520. – UV (ethanol): λ_{max} (lg ε) = 325 nm (4.37), 244 (3.69). – MS: *m/z* = 270 (M^+).

$C_{16}H_{18}N_2O_2$ (270.3) Calcd. C 71.09 H 6.71 N 10.37
Found C 70.92 H 6.91 N 10.40

8-(4-Chlorobenzoyl)-1,3,4,7-tetrahydropyrrolo[1,2-a]pyrimidin-6(2H)-one (**10e**): According to **10a**, 400 mg (72%) of **10e** was obtained from 473 mg (2.0 mmol) of **2e** and 334 mg (2.0 mmol) of ethyl bromoacetate, m.p. 175–177°C. – IR (KBr): 3240 cm^{-1} (NH), 1725 (amide C=O), 1630 (C=O), 1565, 1520. – UV (ethanol): λ_{max} (lg ε) = 338 nm (4.21), 240 (4.04). – MS: *m/z* = 276 (M^+).

$C_{14}H_{13}ClN_2O_2$ (276.7) Calcd. C 60.76 H 4.73 N 10.13
Found C 60.56 H 4.71 N 10.12

9-Benzoyl-1,2,3,4,5,8-hexahydro-7H-pyrrolo[1,2-a]-1,3-diazepin-7-one (**11a**): According to **10a**, 200 mg (52%) of **11a** was obtained from 324 mg (1.5 mmol) of **3a** and 251 mg (1.5 mmol) of ethyl bromoacetate, m.p. 179–182°C. – IR (KBr): 3230 cm^{-1} (NH), 1715 (amide C=O), 1623 (C=O), 1535. – UV (ethanol): λ_{max} (lg ε) = 340 nm (4.17), 234 (4.00). – MS: *m/z* = 256 (M^+).

$C_{15}H_{16}N_2O_2$ (256.3) Calcd. C 70.29 H 6.29 N 10.93
Found C 69.98 H 6.18 N 10.70

1,2,3,4,5,8-Hexahydro-9-(4-methylbenzoyl)-7H-pyrrolo[1,2-a]-1,3-diazepin-7-one (**11c**): According to **10a**, 250 mg (62%) of **11c** was obtained from 345 mg (1.5 mmol) of **3c** and 251 mg (1.5 mmol) of ethyl bromoacetate, m.p. 146–148°C. – IR (KBr): 3240 cm^{-1} (NH), 1725 (amide C=O), 1620 (C=O), 1530. – UV (ethanol): λ_{max} (lg ε) = 343 nm (4.14), 241 (4.11). – MS: *m/z* = 270 (M^+).

$C_{16}H_{18}N_2O_2$ (270.3) Calcd. C 71.09 H 6.71 N 10.37
Found C 70.91 H 6.60 N 10.31

7-Benzoyl-1,2,3,6-tetrahydro-5H-pyrrolo[1,2-a]imidazol-5-one (**9a**): A solution of 200 mg of **8a** in 15 ml of dioxane was refluxed for 2 d. After removal of the solvent, the crude product was recrystallized from acetonitrile. Yield 135 mg (81%), m.p. 232 to 234°C. **9a** was obtained also by refluxing a mixture of 376 mg (2.0 mmol) of **1a** and 334 mg (2.0 mmol) of ethyl bromoacetate in 25 ml of dioxane for 40 h. The workup procedure was according to **8a**. Yield 120 mg (26%). – IR (KBr): 3290 cm^{-1} (NH), 1720 (amide C=O), 1645 (C=O), 1585, 1525. – UV (ethanol): λ_{max} (lg ε) = 330 nm (4.21), 236 (4.03). – MS: *m/z* = 228 (M^+).

$C_{13}H_{12}N_2O_2$ (228.3) Calcd. C 68.40 H 5.30 N 12.28
Found C 68.30 H 5.27 N 12.27

1,2,3,6-Tetrahydro-7-(4-methoxybenzoyl)-5H-pyrrolo[1,2-a]imidazol-5-one (**9b**): Like **9a**, 215 mg (41%) of **9b** was obtained from 436 mg (2.0 mmol) of **1b** and 334 mg (2.0 mmol) of ethyl bromoacetate in dioxane, m.p. 223–226°C. – IR (KBr): 3280 cm^{-1} (NH), 1715 (amide C=O), 1640 (C=O), 1590. – UV (ethanol): λ_{max} (lg ε) = 334 nm (4.26), 266 (3.89). – MS: *m/z* = 258 (M^+).

$C_{14}H_{14}N_2O_3$ (258.3) Calcd. C 65.10 H 5.46 N 10.85
Found C 64.93 H 5.56 N 10.62

1,2,3,6-Tetrahydro-7-(4-methylbenzoyl)-5H-pyrrolo[1,2-a]imidazol-5-one (**9c**): According to **9a**, 225 mg (47%) of **9c** was obtained from 404 mg (2.0 mmol) of **1c** and 334 mg (2.0 mmol) of ethyl bromoacetate in dioxane, m.p. 245–248°C. – IR (KBr): 3250 cm^{-1} (NH), 1710 (amide C=O), 1640 (C=O), 1595, 1565. – UV (ethanol): λ_{max} (lg ε) = 332 nm (4.32), 242 (4.08). – MS: *m/z* = 242 (M^+).

$C_{14}H_{14}N_2O_2$ (242.3) Calcd. C 69.40 H 5.82 N 11.58
Found C 69.54 H 5.90 N 11.62

7-(4-Chlorobenzoyl)-1,2,3,6-tetrahydro-5H-pyrrolo[1,2-a]imidazol-5-one (**9e**): Similar to **9a**, 125 mg (74%) of **9e** was obtained from 200 mg of **8e**, m.p. 244–246°C. 202 mg (39%) of **9e** was obtained also from 445 mg (2.0 mmol) of **1e** and 334 mg (2.0 mmol) of ethyl bromoacetate in dioxane. – IR (KBr): 3230 cm^{-1} (NH), 1720 (amide C=O), 1635 (C=O), 1590, 1515. – UV (ethanol): λ_{max} (lg ε) = 334 nm (4.42), 242 (4.12). – MS: *m/z* = 262 (M^+).

$C_{13}H_{11}ClN_2O_2$ (262.7) Calcd. C 59.43 H 4.22 N 10.67
Found C 59.20 H 4.25 N 10.63

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1a: 64944-80-5 / **1b**: 107195-10-8 / **1c**: 82100-23-0 / **1d**: 115890-18-1 / **1e**: 107165-82-2 / **2a**: 82100-30-9 / **2b**: 107165-84-4 / **2c**: 115859-76-2 / **2d**: 115859-68-2 / **2e**: 107165-83-3 / **3a**: 115859-77-3 / **3c**: 115859-69-3 / **3d**: 115859-70-6 / **4a**: 115859-60-4 / **4b**: 115859-61-5 / **4d**: 115859-62-6 / **5a**: 115859-63-7 / **5b**: 115859-64-8 / **5d**: 115912-12-4 / **5e**: 115859-65-9 / **6c**: 115859-66-0 / **6d**: 115859-67-1 / **7a** · HCl: 115859-71-7 / **7d** · HCl: 115859-72-8 / **8a**: 115859-73-9 / **8d**: 115859-74-0 / **8e**: 115859-75-1 / **9a**: 115859-85-3 / **9b**: 115890-19-2 / **9c**: 115859-86-4 / **9e**: 115859-87-5 / **10a**: 115859-78-4 / **10b**: 115859-79-5 / **10c**: 115859-80-8 / **10d**: 115859-81-9 / **10e**: 115859-82-0 / **11a**: 115859-83-1 / **11c**: 115859-84-2

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