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Synthesis of Acetyl-Substituted Heterocyclic Ketene Aminals and Their Deacetylation Reaction

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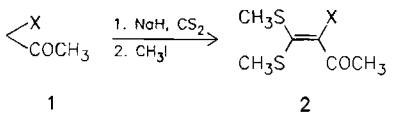
The acetyl-substituted heterocyclic ketene aminals **3**–**6** were synthesized by the reaction of ketene dithioacetals **2** with diamines. The deacetylation of heterocyclic diacetyl ketene-aminals by alkali was studied, and the corresponding monoacetyl derivatives were obtained.

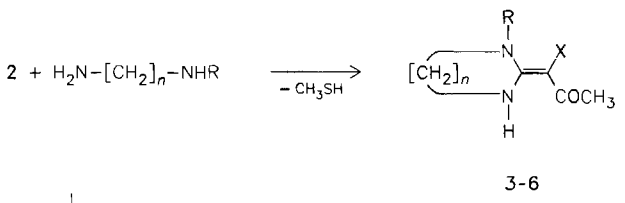
Heterocyclic ketene aminals are versatile starting materials for the synthesis of a wide variety of fused heterocycles, and recently, their synthesis and reactions have attracted much attention[1–23]. However, the synthesis of acetyl-substituted heterocyclic ketene aminals has only been studied in a few cases[14]. Here, we describe the synthesis of acetyl-substituted heterocyclic ketene aminals and their deacetylation reaction.

The acetyl-substituted heterocyclic ketene aminals **3**–**6** were synthesized by the reaction of ketene dithioacetals **2** with diamines in boiling toluene. The starting materials **2** were prepared by the reaction of active methylene compounds **1** with sodium hydride and carbon disulfide, followed by methyl iodide treatment in a one-pot reaction.

It has been reported that when 4,5-dihydro-2-(methylthio)-1*H*-imidazole was treated with **1a**–**c**, the products were **4d** and **7a**, **b**, respectively. This is due to the attack of methanethiol, produced during the reaction, on the carbonyl group of the initially formed ketene aminals **4a**–**c**[14]. This result would be expected to be useful for the synthesis of **3**–**6d** directly from the reaction of **2a** with amines, especially in a closed system. The experimental facts are contrary to our expectations; when **2a** reacted with 1,2-ethanediamine, 1,3-propanediamine or *N*-methyl-1,3-propanediamine, **3a**, **5a**, or **6a** were obtained, irrespective of whether the reaction proceeded in a normal manner or in a closed system. However, when **2a** reacted with *N*-methyl-1,2-ethanediamine in a closed system, **4d** was obtained in moderate yield. Similarly, **7a** or **7b** were obtained directly from the reaction of **2b** or **2c** with *N*-methyl-1,2-ethanediamine. **4a**–**c** could be obtained from the reaction of **2a**–**c** with *N*-methyl-1,2-ethanediamine only when nitrogen was bubbled through the reaction mixture to remove the methanethiol as soon as it was formed.



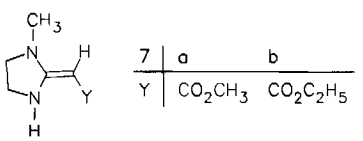
1 2



3-6

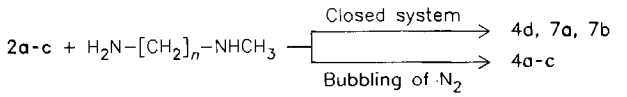
1-6	a	b	c	d
X	$COCH_3$	CO_2CH_3	$CO_2C_2H_5$	H

3-6	3	4	5	6
R	H	CH_3	H	CH_3
n	2	2	3	3



7

7	a	b
Y	CO_2CH_3	$CO_2C_2H_5$



The acetyl-substituted heterocyclic ketene aminals were easily deacetylated by treatment with alkali. This deacetylation reaction occurs not only for heterocyclic ketene N,N-acetals, but also for heterocyclic ketene N,O-acetals **8a**, **b** and N,S-acetals **9a**, **b**. It is a rather general synthetic method

Table 1. Results of the deacetylation reaction

Starting material	Product	Yield (%)
3a	**3d**	89
4a	**4d**	83
5a	**5d**	64
8a	**8c**	72
8b	**8d**	90
9a	**9c**	97[24]
9b	**9d**	94[25]
4b	**7a**	73

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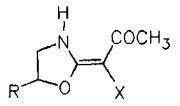
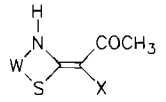
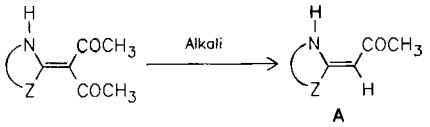
for heterocyclic ketene aminals of type **A** from diacetyl-substituted heterocyclic ketene aminals. The results of deacetylation of heterocyclic ketene aminals are summarized in Table 1.



8	a	b	c	d
R	H	CH_3	H	CH_3
X	$COCH_3$	$COCH_3$	H	H



9	a	b	c	d
W	$[CH_2]_2$		$[CH_2]_2$	
X	$COCH_3$	$COCH_3$	H	H

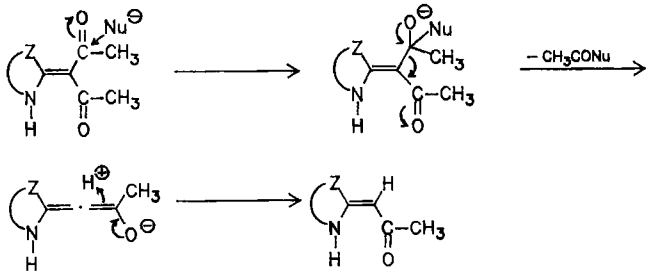


A

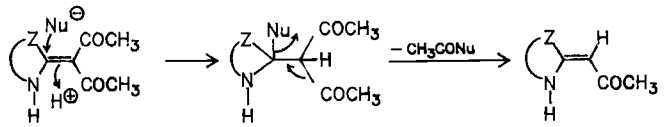
Z = NH, NCH_3, O, S

The mechanism of deacetylation may be explained by one of the following two routes. In the first one, the nucleophile attacks the carbonyl carbon atom of the acetyl group, and the product is then formed through the allenic enolate after elimination of CH_3CONu. In the second alternative, the nucleophile attacks the more positive carbon atom of the double bond; and elimination of CH_3CONu then takes place to form the product. The debromination reaction has been observed by Junjappa et al.[26] in the reaction of bromoketene

Route 1:



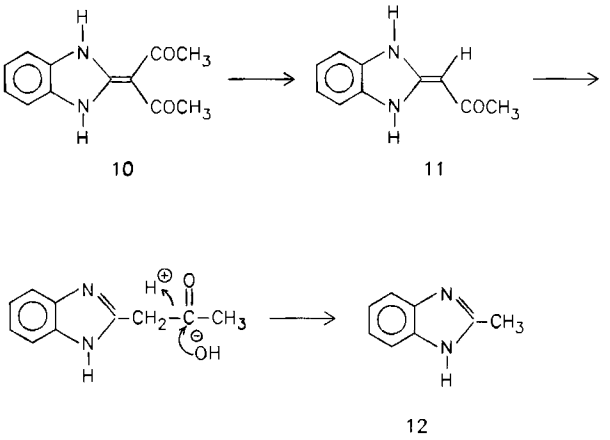
Route 2:



dithioacetal with morpholine, and the mechanism proposed is similar to that of the above-mentioned first route. We think that the deacetylation of acetyl-substituted heterocyclic ketene aminals is one type of decarbonylation of 1,3-diketones, and we therefore prefer the first route as the mechanism for deacetylation.

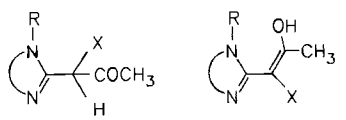
When 2-(diacetylmethylene)benzimidazoline (**10**) reacted with alkali under the same conditions the product isolated was not the monoacetyl-substituted compound **11**, but 2-methylbenzimidazole (**12**). This results from further deacetylation as follows shown in Scheme 1.

Scheme 1



The ^{1}H-NMR data and other spectral data of compounds **3**–**7** and **10** are listed in Table 2 and the experimental part, respectively.

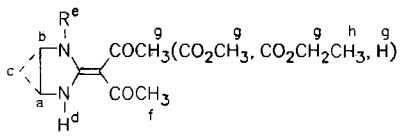
The constitution of the products **3**–**7** and **10** was confirmed by elemental analysis and mass spectrometry. Only one set of signals was observed in the NMR spectra of the products, indicating that these compounds are not mixtures. The absence of methine or methylene proton signals and the presence of nitrogen proton signals in the ^{1}H-NMR spectra of the products exclude the structure of tautomer **B**. The presence of the ketonic carbonyl carbon signal in the ^{13}C-NMR spectra of the products also excludes the structure of tautomer **C**.



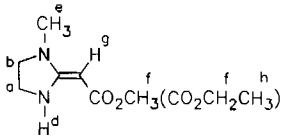
B C

The stereochemical problem of distinguishing the (*E*) or (*Z*) isomer of **4**, **6**, and **7** is solved by the intramolecular hydrogen bond formation. In general, compounds with intramolecular hydrogen bonds are more stable. Intramolecular hydrogen bond formation in **4**, **6**, and **7** is proven by the downfield shift of the NH signal in the ^{1}H-NMR spectra (δ = 7.28–11.20, see Table 2). This suggests that **4d**, **6d**, **7a**, and **7b** might be in (*E*) configuration. Because the ten-

Table 2. ^{1}H-NMR data (δ values) of **3**–**7** and **10** in $CDCl_3$ with TMS as internal standard



3 – 6



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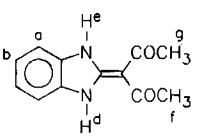

10

	H^a	H^b	H^c	H^d	H^e	H^f	H^g	H^h
3a	— 3.67 (s) —		–	— 9.69 (s) —		— 2.41 (s) —		–
3b	— 3.69 (s) —		–	9.50 (s)	8.50 (s)	2.36 (s)	3.65 (s)	–
3c	— 3.64 (s) —		–	9.68 (s)	8.66 (s)	2.38 (s)	4.17 (q)	1.30 (t)
3d	— 3.43 (s) —		–	8.90 (s)	7.08 (s)	1.73 (s)	4.51 (s)	–
4a	— 3.78 (s) —		–	9.41 (s)	2.89 (s)	— 2.22 (s) —		–
4b	— 3.62 (s) —		–	9.56 (s)	2.83 (s)	2.28 (s)	3.65 (s)	–
4d	3.44 (t)	3.47 (t)	–	9.10 (s)	2.76 (s)	1.98 (s)	4.55 (s)	–
5a	— 3.33 (dt) —		1.94 (quint)	— 11.00 (s) —		— 2.35 (s) —		–
5b	— 3.34 (dt) —		1.97 (quint)	10.59 (s)	7.23 (s)	2.33 (s)	3.67 (s)	–
5d	— 3.16 (t) —		1.82 (quint)	10.58 (s)	7.05 (s)	1.65 (s)	4.28 (s)	–
6a	— 3.45 (t) —		2.03 (quint)	9.21 (s)	3.02 (s)	— 2.08 (s) —		–
7a	3.43 (t)	3.48 (t)	–	7.28 (s)	2.72 (s)	3.57 (s)	3.97 (s)	–
7b	3.43 (t)	3.48 (t)	–	7.36 (s)	2.73 (s)	4.03 (q)	3.98 (s)	1.23 (t)
10	7.33 (d)	7.29 (d)	–	— 13.00 (s) —		— 2.35 (s) —		–

dency towards formation of a hydrogen bond is stronger for the acetyl group than for the alkoxycarbonyl group, **4b** might therefore be (*Z*)-configurated.

From the spectral data, the bathochromic shift of the carbonyl and double bond absorptions in the IR spectra are due to conjugation of the carbonyl group with the double bond and two nitrogen atoms. Two signals for NH in the ^{1}H-NMR spectra and two absorptions in the IR spectra were observed for compounds **3b**–**d**, **5b**, and **5d**; the further downfield signal and lower wave-number absorption are assigned to the NH *cis*-positioned to the acetyl group, due to the intramolecular hydrogen bond formation.

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Experimental

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

2-(Diacetylmethylene)imidazolidine (**3a**): A mixture of 2.04 g (10 mmol) of **2a** and 0.78 g (13 mmol) of 1,2-ethanediamine in 25 ml of toluene was heated for 5 h at reflux. The solution was concentrated to about 5 ml; 1.35 g (80%) of **3a** was obtained on cooling (the same result was obtained in a closed system); m.p. 164–166°C. – IR (KBr): $\tilde{\nu}$ = 3310 cm^{-1}, 3285 (NH), 1600 (C=O), 1565, 1554. – UV (ethanol): λ_{max} (lg ε) = 270 nm (4.26), 222 (3.53). – MS: *m/z* = 168 [M^+].

$C_8H_{12}N_2O_2$ (168.2) Calcd. C 57.12 H 7.19 N 16.66
Found C 57.03 H 7.22 N 16.63

2-[Acetyl(methoxycarbonyl)methylene]imidazolidine (**3b**): As described for **3a**, 1.25 g (49%) of **3b**, m.p. 147–149°C, was obtained from 3.08 g (14 mmol) of **2b** and 1.02 g (17 mmol) of 1,2-ethanediamine. – IR (KBr): = 3362 cm^{-1}, 3290 (NH), 1645 (ester C=O), 1594 (C=O), 1565. – UV (ethanol): λ_{max} (lg ε) = 269 nm (4.22), 242 (4.23). – MS: *m/z* = 184 [M^+].

$C_8H_{12}N_2O_3$ (184.2) Calcd. C 52.16 H 6.57 N 15.21
Found C 52.25 H 6.63 N 15.05

2-[Acetyl(ethoxycarbonyl)methylene]imidazolidine (**3c**): As described for **3a**, 1.96 g (52%) of **3c**, m.p. 118–120°C, was obtained from 4.45 g (19 mmol) of **2c** and 1.44 g (24 mmol) of 1,2-ethanediamine. – IR (KBr): $\tilde{\nu}$ = 3390 cm^{-1}, 3310 (NH), 1645 (ester C=O), 1590 (C=O), 1570, 1535. – UV (ethanol): λ_{max} (lg ε) = 270 nm (4.22), 244 (4.23). – MS: *m/z* = 198 [M^+].

$C_9H_{14}N_2O_3$ (198.2) Calcd. C 54.53 H 7.12 N 14.14
Found C 54.49 H 7.12 N 14.18

2-(Acetylmethylene)imidazolidine (**3d**): (1) As described for **3a**, 1.83 g (58%) of **3d**, m.p. 147–149°C, was obtained from 4.05 g (25 mmol) of **2d** and 3.00 g (50 mmol) of 1,2-ethanediamine in 30 ml of toluene.

(2) A mixture of 100 mg (0.6 mmol) of **3a** and sodium methoxide solution (100 mg of sodium in 10 ml of methanol) was heated for 11 h at reflux. After removal of the solvent, the residue was dissolved in 2 ml of water, and the solution was neutralized and extracted with chloroform (3 × 5 ml). The extract was dried with anhydrous sodium sulfate; after removal of the solvent, 67 mg (89%) of **3d** was obtained. – IR (KBr): $\tilde{\nu}$ = 3260 cm^{-1}, 3100 (NH), 1595 (C=O), 1545. – UV (ethanol): λ_{max} (lg ε) = 290 nm (4.50), 235 (3.80). – MS: *m/z* = 126 [M^+].

$C_6H_{10}N_2O$ (126.2) Calcd. C 57.12 H 7.99 N 22.21
Found C 57.09 H 7.83 N 22.03

2-(Diacetylmethylene)-1-methylimidazolidine (**4a**): A mixture of 1.63 g (8 mmol) of **2a** and 0.81 g (11 mmol) of *N*-methyl-1,2-ethanediamine in 15 ml of toluene was heated at 50°C for 3 h under bubbling of nitrogen. On cooling, 1.20 g (82%) of **4a** was obtained, m.p. 157–160°C. – IR (KBr): $\tilde{\nu}$ = 3180 cm^{-1} (NH), 1605 (C=O),

1565, 1555. – UV (ethanol): λ_{max} (lg ε) = 287 nm (4.20), 251 (3.80). – MS: *m/z* = 182 [M^+].

$C_9H_{14}N_2O_2$ (182.2) Calcd. C 59.32 H 7.74 N 15.38
Found C 59.43 H 7.76 N 15.36

(Z)-2-[Acetyl(methoxycarbonyl)methylene]-1-methylimidazolidine (**4b**): As described for **4a**, 1.60 g (81%) of **4b**, m. p. 101–103°C, was obtained from 2.20 g (10 mmol) of **2b** and 0.96 g (13 mmol) of *N*-methyl-1,2-ethanediamine. – IR (KBr): $\tilde{\nu}$ = 3370 cm^{-1} (NH), 1640 (ester C=O), 1590 (C=O), 1575, 1515. – UV (ethanol): λ_{max} (lg ε) = 270 nm (4.24), 245 (3.90). MS: *m/z* = 198 [M^+].

$C_9H_{14}N_2O_3$ (198.2) Calcd. C 54.53 H 7.12 N 14.14
Found C 54.05 H 7.13 N 14.18

(E)-2-(Acetylmethylene)-1-methylimidazolidine (**4d**): (1) As described for **3a**, 2.20 g (63%) of **4d**, m.p. 103–105°C (ref.[14] 104–105.5°C), was obtained from 4.05 g (25 mmol) of **2d** and 2.74 g (37 mmol) of *N*-methyl-1,2-ethanediamine.

(2) A mixture of 2.04 g (10 mmol) of **2a** and 0.89 g (12 mmol) of *N*-methyl-1,2-ethanediamine in 30 ml of toluene was heated at 110°C for 5 h in a closed system. The solution was concentrated to about 5 ml; 0.56 g (40%) of **4d** was obtained.

(3) As described for **3d** (2), 70 mg (83%) of **4d** was obtained from 109 mg (0.6 mmol) of **4a** and sodium methoxide solution (100 mg of sodium in 10 ml of methanol) on heating for 5 h at reflux. – The IR and UV spectra are identical to those reported in ref.[14].

$C_7H_{12}N_2O$ (140.2) Calcd. C 59.97 H 8.63 N 19.99
Found C 59.99 H 8.48 N 20.00

2-(Diacetylmethylene)hexahydropyrimidine (**5a**): As described for **3a**, 0.80 g (88%) of **5a**, m. p. 102–104°C, was obtained from 1.02 g (5 mmol) of **2a** and 0.44 g (6 mmol) of 1,3-propanediamine in 15 ml of toluene on heating for 2 h at reflux. – IR (KBr): $\tilde{\nu}$ = 3140 cm^{-1} (NH), 1600 (C=O), 1545. – UV (ethanol): λ_{max} (lg ε) = 282 nm (4.08), 265 (4.05), 219 (3.72). – ^{13}C-NMR ($CDCl_3$); δ = 197.4, 159.7, 102.1, 37.8, 32.5, 19.2. – MS: *m/z* = 182 [M^+].

$C_9H_{14}N_2O_2$ (182.2) Calcd. C 59.32 H 7.74 N 15.38
Found C 58.97 H 7.78 N 15.38

2-[Acetyl(methoxycarbonyl)methylene]hexahydropyrimidine (**5b**): As described for **3a**, 3.50 g (77%) of **5b**, m. p. 65–68°C, was obtained from 5.06 g (23 mmol) of **2b** and 2.22 g (30 mmol) of 1,3-propanediamine in 25 ml of toluene on heating for 1 h at reflux. – IR (KBr): $\tilde{\nu}$ = 3200 cm^{-1}, 3165 (NH), 1645 (ester C=O), 1595 (C=O), 1545. – UV (ethanol): λ_{max} (lg ε) = 270 nm (4.13), 248 (4.13), 220 (3.86). – MS: *m/z* = 198 [M^+].

$C_9H_{14}N_2O_3$ (198.2) Calcd. C 54.53 H 7.12 N 14.14
Found C 54.20 H 7.14 N 14.08

2-(Acetylmethylene)hexahydropyrimidine (**5d**): (1) As described for **3a**, 0.93 g (53%) of **5d**, m. p. 158–161°C, was obtained from 2.02 g (12.5 mmol) of **2d** and 1.33 (18 mmol) of 1,3-propanediamine in 15 ml of toluene on heating for 5 h at reflux.

(2) As described for **3d** (2), 89 mg (64%) of **5d** was obtained from 182 mg (1 mmol) of **5a** and sodium methoxide solution (140 mg of sodium in 20 ml of methanol) on heating for 10 h at reflux. – IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1}, 3178 (NH), 1636 (C=O), 1588, 1528. – UV (ethanol): λ_{max} (lg ε) = 292 nm (4.34), 230 (3.65). – MS: *m/z* = 140 [M^+].

$C_7H_{12}N_2O$ (140.2) Calcd. C 59.97 H 8.63 N 19.99
Found C 59.70 H 8.64 N 20.01

2-(Diacetylmethylene)-1-methylhexahydropyrimidine (**6a**): As described for **3a**, 1.46 g (68%) of **6a**, m. p. 164–166°C, was obtained from 2.24 g (11 mmol) of **2a** and 1.32 g (15 mmol) of *N*-methyl-1,3-propanediamine in 20 ml of toluene on heating for 2 h at reflux. – IR (KBr): = 3208 cm^{-1} (NH), 1620, 1610 (C=O), 1570, 1520. – UV (ethanol): λ_{max} (lg ε) = 287 nm (4.25), 240 (3.90). – ^{13}C-NMR ($CDCl_3$): δ = 188.1, 165.8, 105.8, 47.5, 39.2, 38.6, 28.2, 19.3. – MS: *m/z* = 196 [M^+].

$C_{10}H_{16}N_2O_2$ (196.3) Calcd. C 61.20 H 8.22 N 14.28
Found C 60.92 H 8.15 N 14.35

(E)-1-Methyl-2-[(methoxycarbonyl)methylene]imidazolidine (**7a**): (1) As described for **4d** (2), 1.97 g (63%) of **7a**, m. p. 142–143°C (ref.[14] 140–141°C), was obtained from 4.40 g (20 mmol) of **2b** and 1.63 g (22 mmol) of *N*-methyl-1,2-ethanediamine.

(2) As described for **3d** (2), 115 mg (74%) of **7a** was obtained from 198 mg (1 mmol) of **4b** and sodium methoxide solution (50 mg of sodium in 10 ml of methanol). – IR (KBr): $\tilde{\nu}$ = 3380 cm^{-1} (NH), 1642 (ester C=O), 1590, 1520. – UV (ethanol): λ_{max} (lg ε) = 271 nm (4.46). – MS: *m/z* = 156 [M^+].

$C_7H_{12}N_2O_2$ (156.2) Calcd. C 53.83 H 7.75 N 17.94
Found C 53.51 H 7.78 N 17.67

(E)-2-[(Ethoxycarbonyl)methylene]-1-methylimidazolidine (**7b**): As described for **4d** (2), 0.78 g (54%) of **7b**, m. p. 102–105°C (ref.[14] m. p. 101.5–102°C), was obtained from 2.00 g (8.5 mmol) of **2c** and 0.74 g (10 mmol) of *N*-methyl-1,2-ethanediamine. – The IR and UV spectra are identical to those reported in ref.[14].

(E)-2-(Acetylmethylene)oxazolidine (**8c**): As described for **3d** (2), 55 mg (72%) of **8c**, m. p. 105–107°C (ref.[27] 106–108) was obtained from 101 mg (0.6 mmol) of **8a**[27] and sodium methoxide solution (100 mg of sodium in 10 ml of methanol) on heating for 8 h at reflux. – IR (KBr): $\tilde{\nu}$ = 3240 cm^{-1} (NH), 1625 (C=O), 1550, 1500. – UV (ethanol): λ_{max} (lg ε) = 288 nm (4.22). – ^{1}H NMR ($CDCl_3$); δ = 2.02 (s, 3H), 3.71, 4.11 (A_2B_2, *J* = 8.0 Hz), 4.90 (s, 1H), 9.20 (s, 1H). – MS: *m/z* = 127 [M^+].

$C_6H_9NO_2$ (127.1) Calcd. C 56.68 H 7.14 N 11.02
Found C 56.64 H 7.23 N 10.80

(E)-2-(Acetylmethylene)-5-methyloxazolidine (**8d**): As described for **3d** (2), 70 mg (90%) of **8d**, m. p. 45–47°C, was obtained from 100 mg (0.55 mmol) of **8b**[27] and sodium methoxide solution (100 mg of sodium in 10 ml of methanol) on heating for 5 h at reflux. – IR (KBr): $\tilde{\nu}$ = 3240 cm^{-1} (NH), 1620 (C=O), 1540. – UV (ethanol): λ_{max} (lg ε) = 284 nm (3.89). – ^{1}H-NMR ($CDCl_3$): δ = 1.47 (d, 3H), 2.01 (s, 3H), 3.29, 3.81, 4.72 (ABX, *J* = 9.0, 8.0, 7.0 Hz), 4.86 (s, 1H), 9.23 (s, 1H). – MS: *m/z* = 141 [M^+].

$C_7H_{11}NO_2$ (141.2) Calcd. C 59.56 H 7.86 N 9.92
Found C 59.92 H 7.95 N 9.52

2-(Diacetylmethylene)-2,3-dihydro-1H-benzimidazole (**10**): A mixture of 1.53 g (7.5 mmol) of **2a** and 0.81 g (7.5 mmol) of 1,2-phenylenediamine in 20 ml of dimethylformamide was heated for 5 h at reflux. After removal of the solvent, the residue was recrystallized from ethanol; 0.89 (55%) of **10** was obtained, m. p. 204–207°C. – IR (KBr): $\tilde{\nu}$ = 3190 cm^{-1} (NH), 1596 (C=O), 1545. – UV (ethanol): λ_{max} (lg ε) = 328 nm (4.37), 315 (4.32), 287 (4.02), 258 (4.02). – MS: *m/z* = 216 [M^+].

$C_{12}H_{12}N_2O_2$ (216.3) Calcd. C 66.65 H 5.60 N 12.96
Found C 66.19 H 5.56 N 12.95

Deacetylation of **10**: A mixture of 2.16 g (10 mmol) of **10** and 0.48 g (12 mmol) of sodium hydroxide in 30 ml of ethanol was heated for 12 h at reflux under nitrogen. The workup procedure was similar to **3d** (2). 0.83 g of **12** was obtained by recrystallization from ethyl acetate/petroleum ether (1:1), m. p. 174–176°C (ref.[28] 176°C). – ^{1}H NMR ($CDCl_3$): δ = 2.76 (s, 3H), 7.13–7.80 (m, 4H), 13.17 (s, 1H).

CAS Registry Numbers

2a: 15908-50-6 / **2b**: 29866-43-1 / **2c**: 54893-95-7 / **2d**: 17649-86-4 / **3a**: 86919-74-6 / **3b**: 126978-94-7 / **3c**: 70835-55-1 / **3d**: 126978-95-8 / **4a**: 126978-96-9 / (*Z*)-**4b**: 127002-11-3 / (*E*)-**4d**: 101998-53-2 / **5a**: 126978-97-0 / **5b**: 126978-98-1 / **5d**: 126978-99-2 / **6a**: 126979-00-8 / (*E*)-**7a**: 101998-54-3 / (*E*)-**7b**: 101998-55-4 / **8a**: 121373-62-4 / **8b**: 121373-72-6 / (*E*)-**8c**: 121373-71-5 / (*E*)-**8d**: 126979-01-9 / **9a**: 35587-98-5 / **9b**: 123150-21-0 / (*E*)-**9c**: 126979-03-1 / (*E*)-**9d**: 123150-31-2 / **10**: 126979-02-0 / **12**: 615-15-0 / $H_2N[CH_2]_2NHMe$: 109-81-9 / $H_2N[CH_2]_3NH_2$: 109-76-2 / $H_2N[CH_2]_3NHMe$: 6291-84-5 / *o*-$C_6H_4(NH_2)_2$: 95-54-5 / $H_2N[CH_2]_2NH_2$: 107-15-3 / AcMe: 67-64-1

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