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Synthesis of Ketene Aminals with an Imidazolidine Ring by Condensation of 4,5-Dihydro-2-(methylthio)-1*H*-imidazoles with Active Methylene Compounds and Some Addition and Cyclocondensation Reactions

*Zhi-tang Huang** and *Lu-hang Tzai*

Institute of Chemistry, Academia Sinica,
Beijing, PR China

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The 4,5-dihydro-2-(methylthio)-1*H*-imidazoles **1a, b** react with active methylene compounds **2a–f** to afford the corresponding substituted methyleneimidazolidines **3a–f** and **4c–f** by elimination of methanethiol. The reaction of compounds **2g–j**, which contain a more active carbonyl group, with **1a** gives **3g–i** by elimination of a methylthio group as well as an acyl group, too. **3a, g–i** react with esters of α,β-unsaturated acids to afford the corresponding imidazo[1,2-*a*]pyridines **5, 6**, and **7** in an addition and cyclocondensation reaction sequence, but with diethyl azodicarboxylate only to give the addition product **8**.

Synthese von Ketenaminalen mit Imidazolidinring durch Kondensation von 4,5-Dihydro-2-(methylthio)-1*H*-imidazolen mit CH-aciden Methylenverbindungen und einige Additions- und Cyclokondensations-Reaktionen

4,5-Dihydro-2-(methylthio)-1*H*-imidazole **1a, b** reagieren mit aktiven Methylenverbindungen **2a–f** unter Eliminierung von Methanthiol zu den entsprechend substituierten Methylenimidazolidinen **3a–f** und **4c–f**. Die Verbindungen **2g–j**, die eine aktivere Carbonylgruppe enthalten, ergeben mit **1a** unter Eliminierung einer Methylthio- und Acylgruppe **3g–i**. **3a, g–i** reagieren mit Estern ungesättigter Säuren in einer Additions- und Cyclokondensations-Sequenz zu den entsprechenden Imidazo[1,2-*a*]pyridinen **5, 6** und **7**, ergeben aber mit Azodicarbonsäure-diethylester nur die Additionsprodukte **8**.

Ketene aminals with an imidazolidine ring have been reported in the literature only in few cases[1–6]. The α-carbon atom has high electron density, consequently the ketene aminals can act as nucleophiles and they are useful synthons, especially for the synthesis of fused heterocycles[7–12].

Here, a method by condensation of 4,5-dihydro-2-(methylthio)-1*H*-imidazoles **1** with active methylene compounds **2** is reported. The reaction of *S*-alkylated isothiourea with nitromethane for the synthesis of nitroketene aminals has been reported once in the literature[2]. We extended this method to the reaction of *S*-alkylated isothiourea derivatives containing a heterocyclic ring with various active methylene compounds and to the synthesis of some new ketene aminals.

1a reacts with the active methylene compounds **2a–f** at 100°C to yield crystalline products. MS and elemental analyses indicate that in fact an addition

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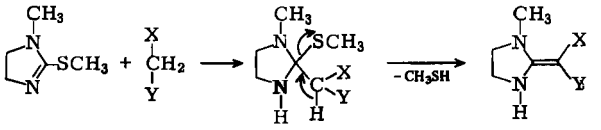
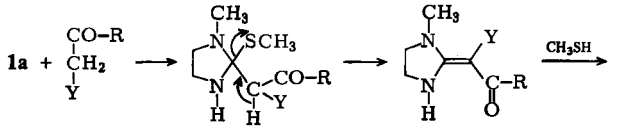
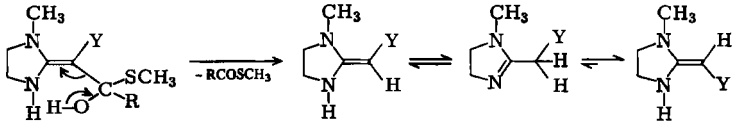
Scheme 1



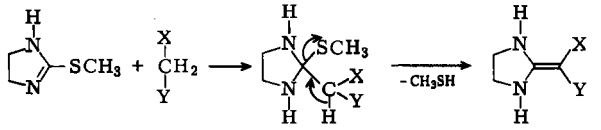
1a **2a-f** **3a-f**



2g-j



3g-i



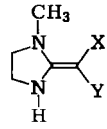
1b **2c-f** **4c-f**

2,3,4	a	b	c	d	e	f
X	H	E'	CN	CN	CN	CN
Y	NO_2	E'	CN	E	E'	CO_2Bu

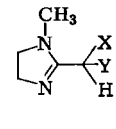
2,3	g	h	i	j
X(2)	Ac	Ac	Ac	COC_6H_5
Y	Ac	E	E'	E'

E = CO_2CH_3
E' = $CO_2C_2H_5$

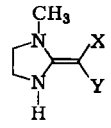
reaction took place accompanied with loss of methanethiol, and the corresponding substituted methyleneimidazolidines **3a–f** were formed. If compounds **2** contain a more active carbonyl group (such as acetyl or benzoyl; **2g–j**), compounds **3g–i** are formed by elimination of both a methylthio and an acyl group. This is caused by the methanethiol produced during the reaction. CH_3SH attacks the more active carbonyl group of the primarily formed ketene aminals, a finding which is supported by the following experimental fact: If **1a** reacts with **2i** under rapid bubbling of nitrogen gas through the solution to blow away the methanethiol as soon as it is formed, the main product is **3k** in which the acetyl has survived.



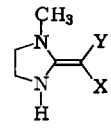
3a–i, k



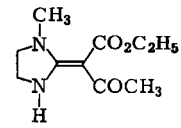
A



E isomer



Z isomer



3k, *Z* isomer

X = H or CN, Y = NO_2, $COCH_3$, CO_2R

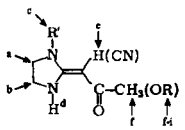
The ketene aminals **3a–i, k** are not contaminated with their tautomer **A** (amidine form) since there is only one set of signals in the ^1H and ^{13}C NMR spectra. The NH signals in the IR (3180–3480 cm^{-1}) and ^1H NMR spectra (δ = 6.00–9.60) and the ethylenic proton signal in the ^1H NMR spectra (in case of X = H) exclude the amidine form **A**. In the case of X ≠ Y, the stereochemical problem, *E* or *Z* isomerism, is still unsolved. Only the *E* isomer can form an intramolecular hydrogen bond, and in general compounds with intramolecular hydrogen bonds are more stable. The downfield shift (δ = 7.35–9.60) of the NH ^1H NMR signal proves the existence of an intramolecular hydrogen bond and confirms the proposed constitution of the ketene aminals (*E* isomer at present). In the case of **3k** the situation is more complex because the intramolecular hydrogen bond can be formed with both the acetyl and ethoxycarbonyl group. But the tendency towards formation of a hydrogen bond is stronger for the acetyl group than for the ethoxycarbonyl group, and the spectral data of NH of **3k** (ν_{NH} = 3180 cm^{-1}, δ_{NH} = 9.60) are similar to those of **3g** and different from those of **3i**, therefore the *Z* form is the accepted constitution for **3k**.

When **1b** reacts with **2** the results are different from those for **1a**, only the α-cyano-substituted methylene group is active enough to proceed the reaction. Hence, only **4c–f** are isolated, and the spectroscopic data are consistent with the constitution of the ketene aminal form as above. Scheme 1 shows a reasonable path for the reaction between **1** and **2**.

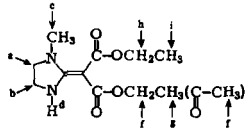
The ^1H and ^{13}C NMR data of **3a–i, k** and **4c–f** are listed in Tables 1 and 2. From these results it seems worthwhile to notice the smaller value of C-5 (δ = 28.1–95.9) which indicates that the electron density is higher at this carbon and nucleophilic attack of this carbon to electron deficient groups can be expected. The much smaller value of C-5 in **3c** and **4c** arose doubts about the correctness of their constitution, but the singlet in the ^1H off-resonance-decoupled ^{13}C NMR spectrum indicates that the ketene aminal form for **3c** and **4c** is unquestionable. The downfield shift of H^d is due to an intramolecular hydrogen bond as mentioned above.

The bathochromic shift of the carbonyl absorption (1570–1590 cm^{-1} in **3g, k**, 1638–1750 cm^{-1} in **3b, d–f, h, i, k** and **4d–f**) and ethylenic absorption

Tab. 1. ^{1}H NMR data (δ values) of **3a–i, k** in $CDCl_3$ and **4c–f** in [D_6]DMSO with TMS as internal standard



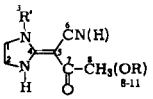
3a, c–i, 4c–f



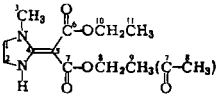
3b, k

No.	H^a	H^b	H^c	H^d	H^e	H^f	H^g	H^h	H^i
3a	3.64–3.80 m		2.86 s	8.49 s	6.50 s				
3b	3.62 s		2.84 s	8.26 s		4.15 q	1.30 t	4.15 q	1.30 t
3c	3.58–3.74 m		3.23 s	6.00 s					
3d	3.64 s		3.28 s	8.35 s		3.71 s			
3e	3.62 s		3.28 s	8.40 s		4.15 q	1.25 t		
3f	3.61 s		3.28 s	8.38 s		4.10 t	1.64 quint	1.42 sext	0.94 t
3g	3.36–3.61 m		2.79 s	9.10 s	4.59 s	2.02 s			
3h	3.30–3.55 m		2.74 s	7.35 s	3.99 s	3.59 s			
3i	3.33–3.52 m		2.74 s	7.36 s	3.99 s	4.08 q	1.25 t		
3k	3.68 s		2.84 s	9.60 s		2.33 s		4.15 q	1.30 t
4c	3.56 s		7.96 s						
4d	3.55 s		7.94 s			3.52 s			
4e	3.47 s		7.94 s			3.96 q	1.10 t		
4f	3.44 s		7.80 s			3.89 t	1.45 quint	1.23 sext	0.80 t

Table 2. ^{13}C NMR data (δ values) of **3a–i, k** in $CDCl_3$ and **4c–f** in [D_6]DMSO with TMS as internal standard



3a, c–i, 4c–f

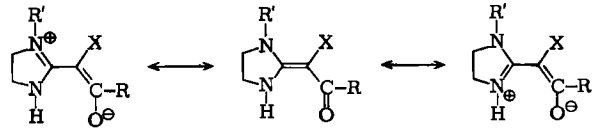


3b, k

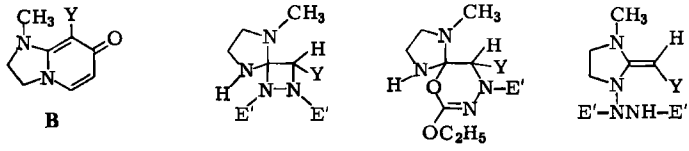
No.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11
3a	50.4	42.1	32.0	159.1	95.9						
3b	52.3	41.4	36.4	165.9	73.4	168.2	168.2	59.4	14.5	59.4	14.5
3c	53.4	41.2	34.2	165.2	30.8	117.3	117.3				
3d	52.2	41.2	34.5	163.9	52.7	119.8	169.7	51.2			
3e	52.2	41.2	34.6	164.1	53.0	119.8	169.5	59.8	14.6		
3f	52.2	41.2	34.6	164.1	53.2	119.6	169.6	63.7	30.9	19.1	14.8
3g	49.7	41.7	32.0	163.4	74.9		190.6	28.5			
3h	50.4	41.9	32.5	163.9	59.8		170.9	49.6			
3i	50.4	42.0	31.6	164.1	60.2		170.7	58.0	14.8		
3k	51.6	41.5	36.4	166.6	86.7	168.2	192.7	29.5		59.2	14.5
4c	43.7			166.4	28.1	117.3	117.3				
4d	40.2			165.1	51.7	118.6	167.5	50.8			
4e	43.3			165.2	51.9	119.0	167.0	58.5	14.7		
4f	43.2			165.2	51.8	118.6	166.9	62.1	30.6	18.5	13.3

(1528 – 1595 cm^{-1}) as compared with α,β-unsaturated ketones or esters can be rationalized according to Scheme 2.

Scheme 2



The ketene aminals **3a, g–i** react with the esters of α,β-unsaturated acids to afford imidazo[1,2-*a*]pyridines in an addition and cyclocondensation reaction sequence. When **3a, g–i** is treated with methyl propiolate in methanol on refluxing, the crystalline products **5a–d** are obtained in fair to good yields. Spectra and elemental analyses indicate that in fact addition of methyl propiolate takes place. This step is followed, however, by a cyclocondensation reaction with loss of methanol. The amide carbonyl carbon signal (δ = 160.2–161.2) in the ^{13}C NMR spectra excludes the constitution **B** which is formed *via* N-addition and subsequent cyclocondensation. The reaction of **3g** with methyl propiolate in benzene at room temperature indicates that the adduct with *trans* olefinic protons, confirmed by the coupling constant of 15.5 Hz, is formed at first and then isomerization to the *cis* form and subsequent cyclocondensation takes place in boiling methanol. This is similar to the reaction between ketene aminals with a γ-lactone substituent and methyl propiolate as reported in the literature[11]. Therefore, a reasonable reaction path and constitutional proposal for the products formed from **3a, g–i** and methyl propiolate can be rationalized in terms of Scheme 3.



B **C** **D** **E**

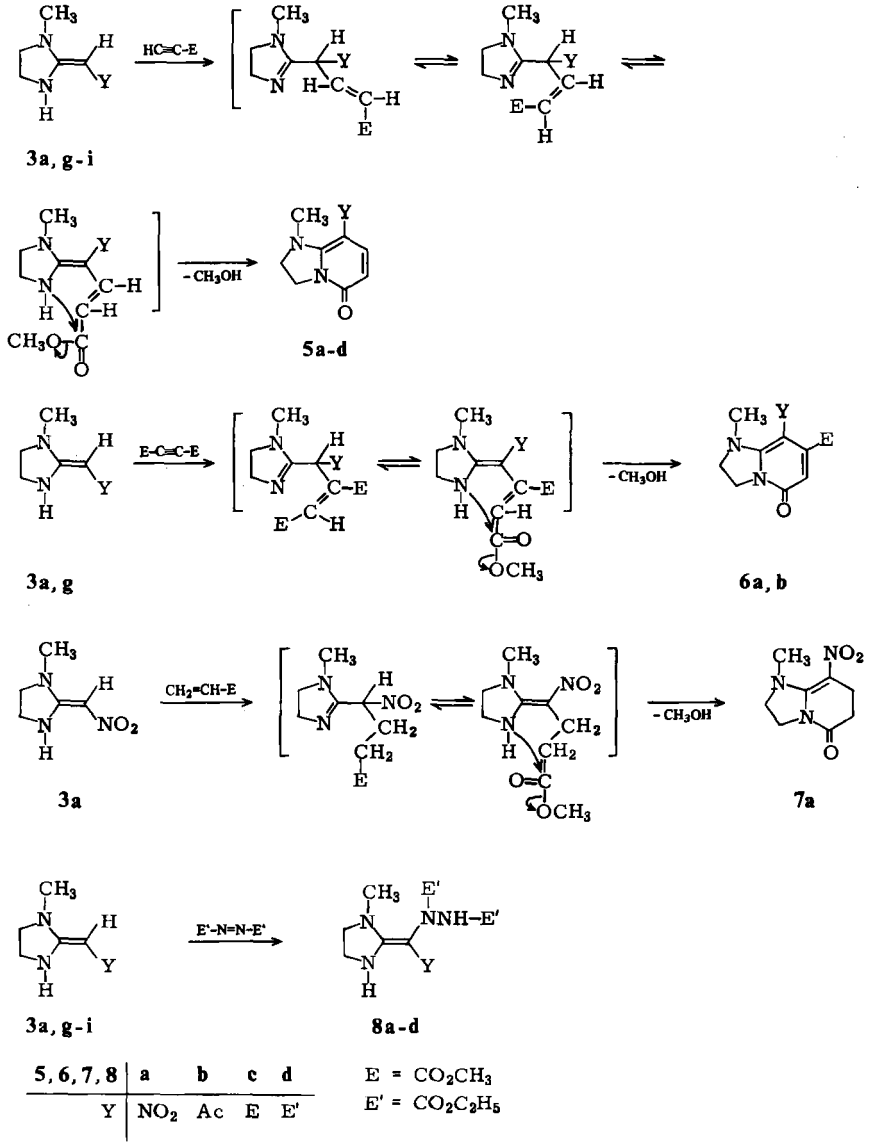
E' = $CO_2C_2H_5$

Furthermore, **3a, g** react with dimethyl acetylenedicarboxylate under similar conditions. Spectra and elemental analyses indicate that one molecule of acetylene ester has added. After loss of methanol the imidazo[1,2-*a*]pyridines **6a, b** are formed. Similarly, **7a** is obtained by refluxing of **3a** with methyl acrylate in methanol. The reaction paths of both reactions are also shown in Scheme 3.

3a, g–i smoothly react with diethyl azodicarboxylate in benzene at ambient temperature. From their spectra and elemental analyses the products can be considered as 1 : 1 adducts. The two NH signals both in the IR and ^1H NMR spectra exclude the [2 + 2] cycloaddition product **C**, [2 + 4] cycloaddition product **D**, and also the N-addition product **E**. The spectroscopic data are consistent with the constitutions of the addition products **8a–d** as shown in Scheme 3.

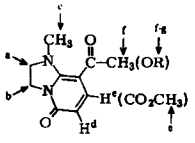
8 cannot undergo further cyclocondensation reaction on refluxing in ethanol. The stereochemical problem of **8** is solved by the above-mentioned reason, and consequently the *E* form for **8a** and *Z* form for **8b, 8c,** and **8d** is assumed. This is ascertained by the ^{1}H NMR NH-signal of **8** which is very near to the corresponding signal in the raw materials **3**.

Scheme 3

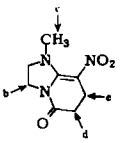


The ^1H and ^{13}C NMR data of **5**, **6**, **7**, and **8** are listed in Tables 3 and 4.

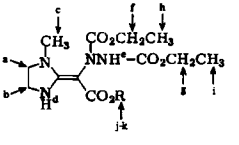
Table 3. ^1H NMR data (δ values) of **5**, **6**, **7**, and **8** in $CDCl_3$ with TMS as internal standard



5, 6



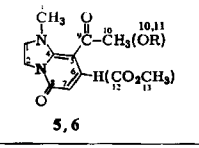
7a



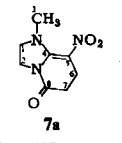
8

	H^a	H^b	H^c	H^d	H^e	H^f	H^g	H^h	H^i	H^j	H^k
5a	3.90 t	4.18 t	3.19 s	5.91 d	7.77 d						
5b	3.81 t	4.13 t	3.04 s	5.78 d	7.60 d	2.40 s					
5c	3.78 t	4.13 t	3.13 s	5.79 d	7.71 d	3.77 s					
5d	3.76 t	4.11 t	3.12 s	5.77 d	7.70 d	4.21 q	1.33 t				
6a	3.96 t	4.16 t	3.11 s	5.83 s	3.89 s						
6b	3.75 t	4.11 t	2.88 s	6.15 s	3.85 s	2.35 s					
7a	3.84–3.99 m		3.23 s	3.19 t	2.64 t						
8a	3.76 s		3.38 s	8.94 s	7.54 s	4.09–4.27 m		1.27 m			
8b	3.48 s		3.11 s	9.84 s	6.84 s	4.15 q	4.03 q	1.20 t	1.96 s		
8c	3.40–3.56 m		3.33 s	7.83 s	6.95 s	4.15–4.20 m		1.26 m	3.62 s		
8d	3.52 s		3.32 s	7.89 s	6.91 s	4.22–4.28 m		1.25 m	4.26 q	1.25 t	

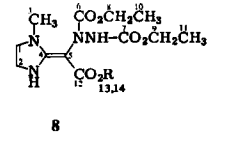
Table 4. ^{13}C NMR data of **5**, **6**, **7**, and **8** in $CDCl_3$ with TMS as internal standard



5, 6



7a



8

	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
5a	52.5	42.4	39.0	150.8	115.1	137.8	107.2	160.2						
5b	51.9	42.2	38.9	154.6	99.9	142.3	105.6	160.8	191.9	27.7				
5c	51.9	42.3	38.6	154.9	89.4	142.9	106.2	161.1	164.5	51.3				
5d	51.9	42.3	38.7	154.8	89.8	143.1	106.2	161.2	164.2	60.2	14.4			
6a	52.6	42.2	38.4	150.3	111.2	142.4	107.2	158.7				165.3	53.3	
6b	51.6	42.2	37.5	151.3	99.0	143.5	107.5	159.5	197.5	32.2		166.6	59.2	
7a	52.0	40.9	39.5	152.2	103.9	22.7	31.4	160.3						
8a	53.3	41.5	35.0	155.7	113.0	157.7	156.7	63.7	61.8	14.4				
8b	52.8	41.5	35.1	156.0	99.0	162.1	157.3	63.0	61.7	14.7	14.5	190.6	24.9	
8c	53.0	41.3	34.8	155.6	84.4	160.7	158.8	62.8	61.3	14.4		168.0	50.0	
8d	53.0	41.3	34.9	154.8	84.6	160.0	158.3	62.8	61.3	14.6	14.5	166.9	58.8	14.9

It is well-known in the literature that a variety of enamines afford [2 + 2] or [2 + 4] cycloaddition products with propiolates[13], acetylenedicarboxylates[14], acrylates[15], or azodicarboxylates[16]. However, the reactions of ketene aminals with an imidazolidine ring, like **3a**, **g**–**i**, with these α,β-unsaturated carbonyl compounds afford solely the Michael-type adducts.

Experimental Part

IR spectra: Shimadzu 430. – ^{1}H NMR spectra: Varian EM-360L and CAMECA RNM-250. – ^{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.

(E)-1-Methyl-2-(nitromethylene)imidazolidine (**3a**): A mixture of 19.5 g (0.15 mol) of **1a** and 18.3 g (0.30 mol) of nitromethane (**2a**) was stirred under bubbling of nitrogen through the solution at 100°C for 22 h until no more methanethiol could be smelled. After removal of excess nitromethane under diminished pressure, the solid residue was digested with cooled isopropyl alcohol and washed twice with cooled methanol. Yield 12.9 g (60%), m. p. 140–142°C, recrystallization from methanol, m. p. 143–144.5°C. – IR (KBr): 3350 (NH), 1578 (C=C), 1551, 1340 cm^{-1} (NO_2). – UV (ethanol): λ_{max} (lg ε) = 328 nm (4.42). – MS: *m/z* = 143 ($M^{\oplus}$). **3a** has been reported in the literature[17].

$C_5H_9N_3O_2$ (143.2) Calcd. C 41.95 H 6.34 N 29.35 Found C 42.05 H 6.44 N 29.33

Diethyl (1-methyl-2-imidazolidinylidene)malonate (**3b**): Similar to **3a**, a mixture of 8.9 g (0.067 mol) of **1a** and 10.7 g (0.067 mol) of diethyl malonate (**2b**) was heated for 54 h; 9.0 g (56%) of product was obtained by filtration, m. p. 76–78°C, recrystallization from ethyl acetate, m. p. 78–79.5°C. – IR (KBr): 3340 (NH), 1705 (ester C=O), 1560 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 270 nm (4.11). – MS: *m/z* = 197 ($M - OC_2H_5$)$^{\oplus}$, 169 ($M - CO_2C_2H_5$)$^{\oplus}$.

$C_{11}H_{18}N_2O_4$ (242.3) Calcd. C 54.54 H 7.49 N 11.56 Found C 54.58 H 7.89 N 11.53

(1-Methyl-2-imidazolidinylidene)malononitrile (**3c**): 2.60 g (0.02 mol) of **1a** was dropped into a solution of 1.32 g (0.02 mol) of malononitrile (**2c**) in 8 ml of dioxane under stirring. The solution was refluxed for 3 h; 2.16 g (73%) of solid product was obtained, m. p. 172–176°C, recrystallization from ethanol, m. p. 179–180°C. – IR (KBr): 3370 (NH), 2180 (CN), 1586 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 198 (4.25), 253 nm (4.35). – MS: *m/z* = 148 ($M^{\oplus}$).

$C_7H_8N_4$ (148.2) Calcd. C 56.44 H 5.44 N 37.81 Found C 56.91 H 5.48 N 37.35

Methyl (E)-(1-methyl-2-imidazolidinylidene)cyanoacetate (**3d**): According to **3a**, a mixture of 6.51 g (0.05 mol) of **1a** and 4.95 g (0.05 mol) of methyl cyanoacetate (**2d**) was heated at 100°C for 0.5 h. The reaction mass was digested with 10 ml of diethyl ether and filtered; 7.04 g (78%) of product was obtained, m. p. 157–159°C, recrystallization from methyl acetate, m. p. 159–161°C. – IR (KBr): 3370 (NH), 2210 (CN), 1650 (C=O), 1585 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 212 (4.23), 261 nm (4.37). – MS: *m/z* = 181 ($M^{\oplus}$).

$C_8H_{11}N_3O_2$ (181.2) Calcd. C 53.93 H 6.22 N 23.58 Found C 53.55 H 6.41 N 23.44

Ethyl (E)-(1-methyl-2-imidazolidinylidene)cyanoacetate (**3e**): According to **3d**, 6.51 g (0.05 mol) of **1a** and 5.66 g (0.05 mol) of ethyl cyanoacetate (**2e**) were heated for 1.5 h; yield 7.50 g (78%), m. p. 114–117°C, recrystallization from ethyl acetate, m. p. 114.5–116°C. – IR (KBr): 3330 (NH), 2170 (CN), 1650 (C=O), 1574 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 211 (4.25), 261 nm (4.40). – MS: *m/z* = 195 ($M^{\oplus}$).

$C_9H_{13}N_3O_2$ (195.2) Calcd. C 55.37 H 6.71 N 21.52 Found C 55.48 H 7.10 N 21.56

n-Butyl (E)-(1-methyl-2-imidazolidinylidene)cyanoacetate (**3f**): Analogously to **3d**, 1.75 g (13.5 mmol) of **1a** and 1.71 g (13.5 mmol) of *n*-butyl cyanoacetate (**2f**) were heated for 2.5 h; yield 2.08 g (73%), m. p. 99–106°C, recrystallization from butyl acetate, m. p.

105.5–107°C. – IR (KBr): 3370 (NH), 2200 (CN), 1654 (C=O), 1579 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 210 (4.31), 260 nm (4.46). – MS: *m/z* = 223 ($M^{\oplus}$).

$C_{11}H_{17}N_3O_2$ (223.3) Calcd. C 59.18 H 7.67 N 18.82 Found C 58.92 H 7.96 N 18.69

(E)-1-Methyl-2-(2-oxopropylidene)imidazolidine (**3g**): Similar to **3d**, 19.5 g (0.15 mol) of **1a** and 15.0 g (0.15 mol) of acetylacetone (**2g**) were heated for 25 h; yield 11.1 g (53%), m. p. 105–106°C, recrystallization from ethyl acetate, m. p. 104–105.5°C. – IR (KBr): 3290 (NH), 1590 (C=O), 1560 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 288 nm (4.43). – MS: *m/z* = 140 ($M^{\oplus}$).

$C_7H_{12}N_2O$ (140.2) Calcd. C 59.68 H 8.63 N 19.98 Found C 60.07 H 8.85 N 20.00

Methyl (E)-(1-methyl-2-imidazolidinylidene)acetate (**3h**): Analogously to **3d**, 13.0 g (0.10 mol) of **1a** and 11.6 g (0.10 mol) of methyl acetylacetate (**2h**) were heated for 25 h; yield 9.7 g (62%), m. p. 130–135°C, recrystallization from methanol, m. p. 140–141°C. – IR (KBr): 3480 (NH), 1640 (C=O), 1595 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 271 nm (4.46). – MS: *m/z* = 156 ($M^{\oplus}$).

$C_7H_{12}N_2O_2$ (156.2) Calcd. C 53.83 H 7.74 N 17.94 Found C 54.07 H 7.70 N 18.00

Ethyl (E)-(1-methyl-2-imidazolidinylidene)acetate (**3i**): Similar to **3d**, 19.5 g (0.15 mol) of **1a** and 19.5 g (0.15 mol) of ethyl acetylacetate (**2i**) were heated for 32 h; yield 16.0 g (63%), m. p. 98–101.5°C, recrystallization from diethyl ether, m. p. 101.5–102°C. – Similar to above, from 1.30 g (0.01 mol) of **1a** and 1.92 g (0.01 mol) of ethyl benzoylacetate (**2j**) 0.44 g of **3i** was obtained. – IR (KBr): 3480 (NH), 1638 (C=O), 1583 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 271 nm (4.40). – MS: *m/z* = 170 ($M^{\oplus}$).

$C_8H_{14}N_2O_2$ (170.2) Calcd. C 56.45 H 8.29 N 16.46 Found C 56.46 H 8.24 N 16.37

Ethyl (Z)-2-(1-methyl-2-imidazolidinylidene)acetoacetate (**3k**): A mixture of 2.0 g (0.0145 mol) of **1a** and 2.0 g (0.0145 mol) of ethyl acetylacetate (**2i**) was stirred under rapid bubbling of nitrogen through the solution (ca. 0.3 liter/min) at 100°C for 20 h; yield 1.53 g (47%), m. p. 112–114.5°C, recrystallization from diethyl ether, m. p. 113–114.5°C. – IR (KBr): 3180 (NH), 1676 (ester C=O), 1570 (C=O), 1528 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 249 nm (4.24). – MS: *m/z* = 212 ($M^{\oplus}$).

$C_{10}H_{16}N_2O_3$ (212.2) Calcd. C 56.59 H 7.60 N 13.20 Found C 56.85 H 7.57 N 13.10

(2-Imidazolidinylidene)malononitrile (**4c**): According to **3c**, from 1.16 g (0.01 mol) of **1b** and 0.66 g (0.01 mol) of **2c** in 10 ml of dioxane, 0.85 g (63%) of **4c** was obtained, m. p. >270°C (subl.); **4c** can be recrystallized from acetonitrile. In lit.[18] **4c** is prepared by the reaction of dicyanoketene ethylene acetal with ethylenediamine. – IR (KBr): 3260 (NH), 2170 (CN), 1595 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 198 (4.22), 248 cm^{-1} (4.33). – MS: *m/z* = 134 ($M^{\oplus}$).

$C_6H_6N_4$ (134.2) Calcd. C 53.72 H 4.51 N 41.77 Found C 53.58 H 4.44 N 41.18

Methyl (2-imidazolidinylidene)cyanoacetate (**4d**): Similar to **3c**, 2.52 g (0.02 mol) of **1b** and 1.98 g (0.02 mol) of **2d** in 15 ml of dioxane were refluxed for 5.5 h; yield 2.42 g (72%), recrystallization from dioxane, m. p. 232.5–234.5°C. – IR (KBr): 3390, 3290 (NH), 2210 (CN), 1665 (C=O), 1597 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 207 (4.24), 253 nm (4.52). – MS: *m/z* = 167 ($M^{\oplus}$).

$C_7H_9N_3O_2$ (167.2) Calcd. C 50.30 H 5.43 N 25.14 Found C 50.31 H 5.45 N 25.15

Ethyl (2-imidazolidinylidene)cyanoacetate (**4e**): Analogously to **3c**, 1.16 g (0.01 mol) of **1b** and 1.13 g (0.01 mol) of **2e** in 10 ml of dioxane were refluxed for 7 h; yield 1.56 g (86%), m. p. 184–186°C, recrystallization from dioxane, m. p. 185–186°C. – IR (KBr): 3340,

3260 (NH), 2180 (CN), 1654 (C=O), 1594 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 207 (4.24), 253 nm (4.42). – MS: *m/z* = 181 ($M^{\oplus}$).

$C_8H_{11}N_3O_2$ (181.2) Calcd. C 53.03 H 6.19 N 23.19 Found C 53.31 H 6.31 N 23.46

n-Butyl (2-imidazolidinylidene)cyanoacetate (**4f**): Similar to **3c**, 1.16 g (0.01 mol) of **1b** and 1.27 g (0.01 mol) of **2f** in 10 ml of dioxane were refluxed for 8.5 h; yield 1.08 g (52%), m. p. 137–139°C, recrystallization from butyl acetate, m. p. 138–140°C. – IR (KBr): 3340, 3260 (NH), 2180 (CN), 1655 (C=O), 1595 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 208 (4.25), 254 nm (4.40). – MS: *m/z* = 209 ($M^{\oplus}$).

$C_{10}H_{15}N_3O_2$ (209.3) Calcd. C 57.40 H 7.23 N 20.08 Found C 57.06 H 7.14 N 20.10

2,3-Dihydro-1-methyl-8-nitroimidazo[1,2-a]pyridin-5(1H)-one (**5a**): A solution of 0.085 g (1 mmol) of methyl propiolate in 5 ml of methanol was dropped into a solution of 0.14 g (1 mmol) of **3a** in 10 ml of methanol at room temperature. The mixture was refluxed for 20 h. After removal of the solvent, the crude product (0.19 g) was purified by silica gel column chromatography, and methanol was used as eluent. Yield 0.12 g (62%), m. p. 160–166°C, recrystallization from benzene, m. p. 160–162°C. – IR (KBr): 1670 (C=O), 1580 (C=C), 1540, 1314 cm^{-1} (NO_2). – UV (ethanol): λ_{max} (lg ε) = 211 (3.96), 264 (3.94), 312 (3.85), 378 nm (4.11). – MS: *m/z* = 195 ($M^{\oplus}$).

$C_8H_9N_3O_3$ (195.2) Calcd. C 49.23 H 4.65 N 21.53 Found C 49.00 H 4.79 N 21.44

8-Acetyl-2,3-dihydro-1-methylimidazo[1,2-a]pyridin-5(1H)-one (**5b**): Similar to **5a**, a mixture of 0.28 g (2 mmol) of **3g** and 0.17 g (2 mmol) of methyl propiolate in methanol was refluxed for 20 h; yield 0.28 g (73%), m. p. 80–95°C, recrystallization from diethyl ether, m. p. 99.5–100.5°C. – IR (KBr): 1670 (amide C=O), 1605 (C=O), 1569 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 233 (4.08), 327 nm (4.23). – MS: *m/z* = 192 ($M^{\oplus}$).

$C_{10}H_{12}N_2O_2$ (192.2) Calcd. C 62.48 H 6.29 N 14.57 Found C 62.38 H 5.83 N 14.67

Methyl 1,2,3,5-tetrahydro-1-methyl-5-oxoimidazo[1,2-a]pyridine-8-carboxylate (**5c**): Similar to **5a**, a mixture of 0.47 g (3 mmol) of **3h** and 0.25 g (3 mmol) of methyl propiolate in methanol was refluxed for 40 h; yield 0.44 g (70%), m. p. 132–133.5°C, recrystallization from methanol/diethyl ether, m. p. 132–133°C. – IR (KBr): 1695 (ester C=O), 1662 (amide C=O), 1559 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 285 (4.18), 322 nm (4.07). – MS: *m/z* = 208 ($M^{\oplus}$).

$C_{10}H_{12}N_2O_3$ (208.2) Calcd. C 57.69 H 5.81 N 13.45 Found C 57.70 H 5.77 N 13.36

Ethyl 1,2,3,5-tetrahydro-1-methyl-5-oxoimidazo[1,2-a]pyridine-8-carboxylate (**5d**): Similar to **5a**, a mixture of 0.17 g (1 mmol) of **3i** and 0.085 g (1 mmol) of methyl propiolate in methanol was refluxed for 20 h; yield 0.11 g (50%), m. p. 88–92°C, recrystallization from diethyl ether, m. p. 98.5–99.5°C. – IR (KBr): 1693 (ester C=O), 1655 (amide C=O), 1574 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 285 (4.18), 320 nm (4.08). – MS: *m/z* = 222 ($M^{\oplus}$).

$C_{11}H_{14}N_2O_3$ (222.2) Calcd. C 59.45 H 6.35 N 12.60 Found C 59.65 H 6.47 N 12.58

Methyl 1,2,3,5-tetrahydro-1-methyl-8-nitro-5-oxoimidazo[1,2-a]pyridine-7-carboxylate (**6a**): A solution of 0.14 g (1 mmol) of dimethyl acetylenedicarboxylate in 5 ml of methanol was dropped slowly into a solution of 0.14 g (1 mmol) of **3a** in 10 ml of methanol at room temperature. The mixture was refluxed for 3 h and the crude product was purified like **5a**; yield 0.18 g (77%), m. p. 166–173°C, recrystallization from methyl acetate, m. p. 171–173.5°C. – IR (KBr): 1745 (ester C=O), 1670 (amide C=O), 1597 (C=C), 1540,

1320 cm^{-1} (NO_2). – UV (ethanol): λ_{max} (lg ε) = 228 (4.05), 267 (3.86), 317 (3.80), 380 nm (4.30). – MS: *m/z* = 253 ($M^{\oplus}$).

$C_{10}H_{11}N_3O_5$ (253.2) Calcd. C 47.43 H 4.38 N 16.59 Found C 47.32 H 4.35 N 16.39

Methyl 8-acetyl-1,2,3,5-tetrahydro-1-methyl-5-oxoimidazo[1,2-a]pyridine-7-carboxylate (**6b**): Similar to **6a**, a mixture of 0.14 g (1 mmol) of **3g** and 0.14 g (1 mmol) of dimethyl acetylenedicarboxylate in methanol was refluxed for 4 h; yield 0.20 g (80%), m. p. 100–105°C, recrystallization from methanol/diethyl ether, m. p. 111–112°C. – IR (KBr): 1725 (ester C=O), 1650 (amide C=O), 1635 (C=O), 1570 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 302 (3.77), 346 nm (3.85). – MS: *m/z* = 250 ($M^{\oplus}$).

$C_{12}H_{14}N_2O_4$ (250.3) Calcd. C 57.59 H 5.64 N 11.19 Found C 57.25 H 5.60 N 11.11

2,3,6,7-Tetrahydro-1-methyl-8-nitroimidazo[1,2-a]pyridin-5(1H)-one (**7a**): A mixture of 0.43 g (3 mmol) of **3a** and 0.26 g (3 mmol) of methyl acrylate in 15 ml of methanol was refluxed for 30 h. The crude product was purified like **5a**; yield 0.19 g (32%), m. p. 167–169°C. – IR (KBr): 1685 (C=O), 1612 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 366 nm (4.27). – MS: *m/z* = 197 ($M^{\oplus}$).

$C_8H_{11}N_3O_3$ (197.2) Calcd. C 48.73 H 5.62 N 21.31 Found C 49.00 H 5.67 N 21.05

Diethyl (E)-1-[(1-methyl-2-imidazolidinylidene)nitromethyl]-1,2-hydrazinedicarboxylate (**8a**): A solution of 0.53 g (3 mmol) of diethyl azodicarboxylate in 30 ml of benzene was dropped slowly into a solution of 0.43 g (3 mmol) of **3a** in 20 ml of benzene at room temperature under stirring, and the mixture was stirred further at room temperature for 26 h. After removal of the solvent, the residue was digested with diethyl ether; yield 0.91 g (96%), m. p. 98–101°C. – IR (KBr): 3310, 3370 (NH), 1730, 1750 (C=O), 1573 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 330 nm (4.27). – MS: *m/z* = 317 ($M^{\oplus}$).

$C_{11}H_{19}N_5O_6$ (317.3) Calcd. C 41.64 H 6.04 N 22.07 Found C 41.92 H 6.07 N 21.80

Diethyl (Z)-1-[acetyl(1-methyl-2-imidazolidinylidene)methyl]-1,2-hydrazinedicarboxylate (**8b**): Similar to **8a**, from 0.42 g (3 mmol) of **3g** and 0.53 g (3 mmol) of diethyl azodicarboxylate, 0.91 g (96%) of **8b** was obtained, m. p. 98–100°C. – IR (KBr): 3250, 3330 (NH), 1740, 1718 (ester C=O), 1685 (C=O), 1590 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 340 nm (4.20). – MS: *m/z* = 314 ($M^{\oplus}$).

$C_{13}H_{22}N_4O_5$ (314.3) Calcd. C 49.67 H 7.06 N 17.82 Found C 48.73 H 7.02 N 17.51

Diethyl (Z)-1-[methoxycarbonyl(1-methyl-2-imidazolidinylidene)methyl]-1,2-hydrazinedicarboxylate (**8c**): Similar to **8a**, from 0.47 g (3 mmol) of **3h** and 0.53 g (3 mmol) of diethyl azodicarboxylate, 0.90 g (91%) of **8c** was obtained, m. p. 128.5–130°C. – IR (KBr): 3290 (NH), 1739 cm^{-1} (C=O). – UV (ethanol): λ_{max} (lg ε) = 273 nm (4.35). – MS: *m/z* = 257 ($M - CO_2C_2H_5)^{\oplus}$, 242 ($M - NHCO_2C_2H_5)^{\oplus}$.

$C_{13}H_{22}N_4O_6$ (330.3) Calcd. C 47.27 H 6.71 N 16.96 Found C 47.24 H 6.57 N 16.85

Diethyl (Z)-1-[ethoxycarbonyl(1-methyl-2-imidazolidinylidene)methyl]-1,2-hydrazinedicarboxylate (**8d**): Similar to **8a**, from 0.51 g (3 mmol) of **3i** and 0.53 g (3 mmol) of diethyl azodicarboxylate, 0.76 g (74%) of **8d** was obtained, m. p. 82–85°C. – IR (KBr): 3300 (NH), 1744, 1705 (C=O), 1575 cm^{-1} (C=C). – UV (ethanol): λ_{max} (lg ε) = 273 nm (4.39). – MS: *m/z* = 344 ($M^{\oplus}$).

$C_{14}H_{24}N_4O_6$ (344.4) Calcd. C 48.83 H 7.02 N 16.27 Found C 48.74 H 7.04 N 16.12

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1a: 52839-23-3 / **1b**: 20112-79-2 / **2a**: 75-52-5 / **2b**: 105-53-3 / **2c**: 109-77-3 / **2d**: 105-34-0 / **2e**: 105-56-6 / **2f**: 5459-58-5 / **2g**: 123-54-6 / **2h**: 105-45-3 / **2i**: 141-97-9 / **2j**: 94-02-0 / **3a**: 94662-65-4 / **3b**: 101998-48-5 / **3c**: 101998-49-6 / **3d**: 101998-50-9 / **3e**: 101998-51-0 / **3f**: 101998-52-1 / **3g**: 101998-53-2 / **3h**: 101998-54-3 / **3i**: 101998-55-4 / **3k**: 101998-56-5 / **4c**: 5624-24-8 / **4d**: 91912-29-7 / **4e**: 101998-57-6 / **4f**: 101998-58-7 / **5a**: 101998-59-8 / **5b**: 101998-60-1 / **5c**: 101998-61-2 / **5d**: 101998-62-3 / **6a**: 101998-63-4 / **6b**: 101998-64-5 / **7a**: 101998-65-6 / **8a**: 101998-66-7 / **8h**: 101998-67-8 / **8c**: 101998-68-9 / **8d**: 102046-57-1 / HC≡CE: 922-67-8 / EC ≡ CE: 762-42-5 / H_2C=CHE: 96-33-3 / E'N=NE': 1972-28-7

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