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Heterocyclic β-Enamino Esters, 34[1)]

New Types of Spiro Compounds by Addition and Cyclization Reactions of 3-(2-Imidazolidinylidene)- and 3-(Tetrahydro-2(1*H*)-pyrimidinylidene)dihydro-2(3*H*)-furanones with Methyl Acrylate and Dimethyl Acetylenedicarboxylate

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The 2(3*H*)-furanones **1a** – **e** react with methyl acrylate in benzene or dioxane solution to afford the spiro compounds **2a** – **e** in an addition and cyclocondensation reaction sequence. With dimethyl acetylenedicarboxylate **1a, b** give merely the addition products **3a, b**, while **1c** – **e** yield the spiro compounds **4a** – **c** in a related addition-cyclocondensation step.

Heterocyclische β-Enaminoester, 34 [1)]

Neue Typen von Spiro-Verbindungen durch Additions- und Ringschlußreaktionen von 3-(2-Imidazolidinyliden)- und 3-(Tetrahydro-2(1*H*)-pyrimidinyliden)dihydro-2(3*H*)-furanonen mit Acrylsäure-methylester und Acetylendicarbonsäure-dimethylester

Die 2(3*H*)-Furanone **1a** – **e** reagieren mit Acrylsäure-methylester in Benzol- oder Dioxanlösung in einer Additions- und Cyclokondensations-Sequenz zu den Spiro-Verbindungen **2a** – **e**. **1a, b** ergeben mit Acetylendicarbonsäure-dimethylester die Additionsprodukte **3a, b**; hingegen resultieren aus **1c** – **e** in einer verwandten Additions-Cyclokondensationssequenz die Spiro-Verbindungen **4a** – **c**.

Recently, the formation of 3-(2-imidazolinylidene)- and 3-(tetrahydro-2(1*H*)-pyrimidinylidene)dihydro-2(3*H*)-furanones (**1a** – **e**)[3)], the addition and cyclization reaction of these title compounds with methyl propiolate as well as the addition of bromine, chlorine, and hydrochloric acid have been reported[1)]. Now we describe addition and cyclization reactions of **1a** – **e** with methyl acrylate and dimethyl acetylenedicarboxylate.

A variety of enamines react smoothly with methyl acrylate[4)] and dimethyl acetylenedicarboxylate[5)] to afford stable cyclobutane or labile cyclobutene adducts, respectively. The latter reaction sequence (cycloaddition-ring enlargement) represents a rather versatile procedure to build up 7-, 8-, and 9-membered carbocyclic and heterocyclic compounds, e. g. starting with 2-(iminotriphenylphosphoranylidene)enamino esters[6)]. However, it is also well known that at proper experimental conditions enamines react with methyl acrylate to afford alkylation products in good yields[7)].

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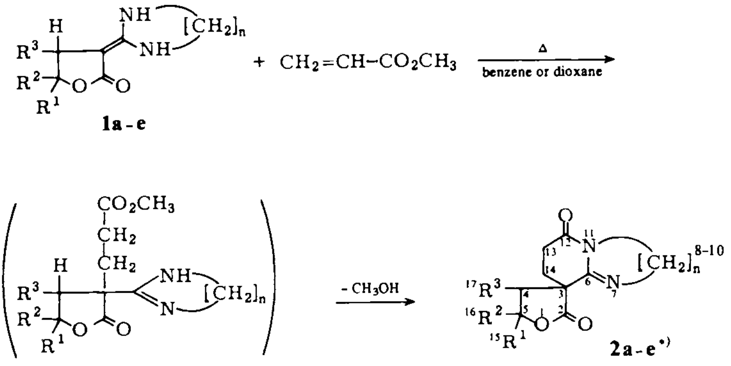
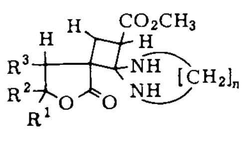
At room temperature the α-hetero-substituted dihydro-2(3*H*)-furanones **1a – e** do not show any reaction with methyl acrylate, but undergo rapid addition upon refluxing both components in benzene or dioxane solution with formation of a crystalline product. Spectra and elemental analyses indicate that in fact an addition of methyl acrylate takes place which is accompanied, however, by a condensation reaction with loss of methanol. A characteristic AA'BB' pattern in the ^1H NMR spectrum excludes the formation of a cyclobutane adduct, like **A**. Alternatively, **1a – e** may react with methyl acrylate *via* *N*-addition and subsequent condensation to give **B**. But in this case the chemical shift of one part of the AA'BB' signal must be larger (> 3 ppm); on the other hand, in the IR spectrum no ketone but instead an amide absorption is visible, and, thus, also **B** was excluded.

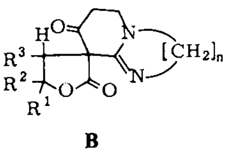
Therefore, a reasonable reaction path and constitutional proposal of the products formed from **1a – e** and methyl acrylate can be rationalized in terms of Scheme 1.

Scheme 1





A



B

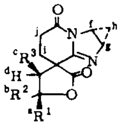
1,2	R¹	R²	R³	n
a	CH_3	H	H	2
b	CH_3	CH_3	H	2
c	CH_3	H	CH_3	2
d	CH_3	CH_3	H	3
e	CH_3	H	CH_3	3

*) ^{13}C NMR assignments

The ^1H and ^{13}C NMR data of **2a – e** are listed in Tables 1 and 2. The ^{13}C shift of C-8 in **2c** turned out to be remarkably large. Therefore this spectrum was measured employing the gated decoupling technique, the results being listed in Table 3. These results are compatible with the constitution of **2c** and the greater ^{13}C shift of C-8 can be obviously attributed to the steric factor of the C-4 methyl group.

Furthermore, **1a – e** react smoothly with dimethyl acetylenedicarboxylate at 0 – 10 °C in benzene or dioxane solution. From **1a, b** the reaction products were isolated as viscous oils. From their spectra and elemental analyses these products can be

Table 1. ^1H NMR Spectra of **2a – e** in $CDCl_3$ (δ in ppm; J in [Hz])

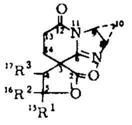


2a-e

	H^a	H^b	H^c	H^d	H^f	H^g	H^h	$H^{i,j}$
2a	1.53 d[a] (6.0)	4.75[a]	2.30[a]	2.86[a]	3.91 t (3.0)			2.09 – 2.91 m
2b	1.54 s	1.60 s	2.08 d (13.5)	2.95 d (13.5)	3.90 t (2.5)			2.17 – 2.67 m
2c	1.45 d (6.8)	4.79 dq (6.8; 7.9)	1.05 d (7.4)	2.73 qui (7.4)	3.93 t (4.0)	3.95 t (4.0)		1.88 – 2.64 m
2d	1.49 s	1.54 s	2.02 d (13.2)	2.74 d (13.2)	3.49 t (6.0)	3.73 t (6.0)	1.80 qui (6.0)	2.25 – 2.91 m
2e	1.39 d (6.8)	4.75 dq (6.8; 8.6)	1.07 d (7.3)	2.67 qui (7.3)	3.53 t (6.0)	3.75 t (6.0)	1.82 qui (6.0)	2.37 – 2.93 m

[a] $J_{ab} = J_{ac} = 6.0$, $J_{bd} = 9.3$, $J_{cd} = 13.1$.

Table 2. ^{13}C NMR Spectra of **2a – e** in $CDCl_3$ (δ in ppm)

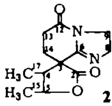


2a-e

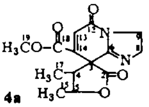
	2a	**2b**	**2c**	**2d**	**2e**
C-2 (s)	174.2	174.2	175.3	175.7	176.6
C-3 (s)	46.4	46.8	48.8	52.1	53.1
C-4	53.2 t	53.1 t	42.2 d	46.3 t	42.3 d
C-5	74.9 d	83.2 s	78.0 d	82.6 s	77.7 d
C-6 (s)	157.6	158.5	156.3	151.9	150.2
C-8 (t)	43.9	45.9	53.2	44.9	44.8
C-9 (t)	40.9	43.7	42.9	40.1	39.7
C-10 (t)				20.8	21.0
C-12 (s)	167.1	167.3	166.9	168.9	168.7
C-13 (t)	27.5	28.9	28.6	29.0	28.6
C-14 (t)	28.8	30.4	29.5	29.0	29.0
C-15 (q)	20.8	30.2	16.3	30.8	16.4
C-16 (q)		29.3		29.0	
C-17 (q)			12.2		12.9

considered as 1 : 1-adducts. As ^1H signals of olefinic protons as well as normal lactone absorptions are observed, the [2 + 2] cycloadduct **C** and the *N*-addition product **D** could be ruled out. The spectroscopic data are consistent with the constitution of the addition products **3a, b**.

Table 3. ^{13}C Chemical Shifts and Coupling Constants of **2c** and **4a** in $CDCl_3$ (w. r. = weakly resolved, l. r. = long range)



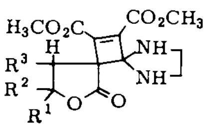
2c



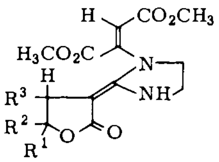
4a

ppm		J_{CH}	$^2J_{CH}$ or $^3J_{CH}$	C-Atom	ppm		J_{CH}	$^2J_{CH}$ or $^3J_{CH}$	C-Atom
175.3	w. r. m			2	171.6	d		5.5	2
	(l. r.)					(l. r.)			
166.9	w. r. m.			12	165.2	td		3.5; 4.5	12
	(l. r.)					(l. r.)			
156.3	w. r. m.			6	160.5	w. r. m.			6
	(l. r.)					(l. r.)			
78.0	d	151.2		5	159.8	d		12.5	18
	qd (l. r.)		4.7; 8.8			(l. r.)			
53.2	t	145.8		8	142.8	t		4.0	14
	dd (l. r.)		2.9; 4.4			(l. r.)			
48.8	w. r. m.			3	126.3	d	163.4		13
	(l. r.)								
42.9	t	147.4		9	79.2	d	150.3		5
	dd (l. r.)		1.5; 4.0			qd (l. r.)		5.0; 9.9	
42.2	d (w. r.)	132.0		4	61.1	t	147.6		8
	m (l. r.)					dd (l. r.)		2.1; 5.0	
29.5	t	133.2		14	54.2	sept		3.8	3
	td (l. r.)		6.0; 3.0			(l. r.)			
28.6	t	130.8		13	52.7	q	148.0		19
	dd (l. r.)		3.2; 6.0						
16.3	q	127.2		15	45.3	d	132.0		4
	d (l. r.)		3.6			qui (l. r.)		3.8	
12.2	q	127.2		17	40.7	t	150.0		9
	d (l. r.)		3.0			dd (l. r.)		1.8; 5.0	
					16.7	q	127.2		15
						d (l. r.)		4.8	
					9.7	q	127.2		17
						d (l. r.)		3.6	

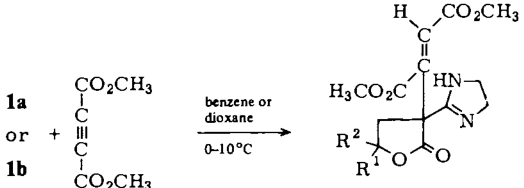
Scheme 2



C



D

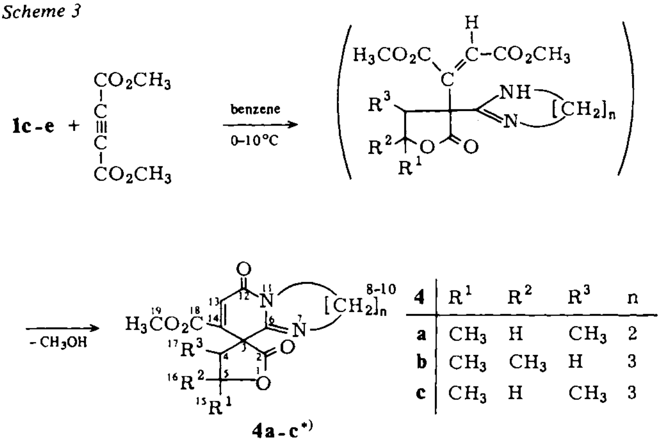


3a, b

3	R^1	R^2
a	CH_3	H
b	CH_3	CH_3

Although the chemical shift of the olefinic protons in **3a, b**, δ = 6.17 – 6.37 (Table 4), would support a *cis*-position of both ester groups, according to additive shielding parameters estimated for a number of examples[8], these increments, however, cannot be applied to these rather different and complex systems. Furthermore, several heterocyclic systems with significant discrepances are well known[8]. Thus, we assume that this nucleophilic attack to the triple bond results in fact in a normal *anti*-addition[9].

Scheme 3

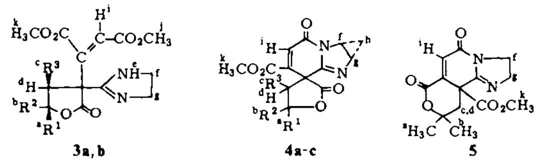


4	R^1	R^2	R^3	n
a	CH_3	H	CH_3	2
b	CH_3	CH_3	H	3
c	CH_3	H	CH_3	3

4a-c[*]

[*] ^{13}C NMR assignments

Table 4. ^{1}H NMR Spectra of **3a, b**, **4a – c** and **5** in $CDCl_3$ (δ in ppm; *J* in [Hz])

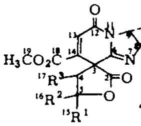


	H^a	H^b	H^c	H^d	H^f	H^g	H^h	H^i	H^j	H^k
3a	1.45 d[a] (6.2)	4.6 b[a]	2.21[a]	2.80[a]	3.73 t (4.5)			6.17 s	3.75 s	3.84 s
3b	1.46 s	1.50 s	2.61 d (13.8)	3.32 d (13.8)	3.71 t (4.0)			6.37 s	3.77 s	3.84 s
4a	1.61 d (6.8)	4.90 qui (6.8)	1.12 d (7.4)	2.97 qui (7.4)	3.79 (9.0)	4.39 (9.0)		6.30 s		3.88 s
4b	1.59 s	1.72 s	2.31 d (14.0)	2.96 d (14.0)	3.60 t (6.0)	3.72 (6.0)	1.88 qui (6.0)	6.31 s		3.89 s
4c	1.58 d (6.8)	4.80 dq (6.8; 8.4)	1.11 d (7.4)	2.92 qui (7.4)	3.64 t (6.0)	3.70 t (6.0)	1.87 qui (6.0)	6.32 s		3.89 s
5	1.67 s	1.77 s	2.47 d (12.6)	2.65 d (12.6)	3.78 (9.0)	4.39 (9.0)		6.89 s		3.83 s

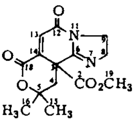
[a] J_{ab} = 6.2, J_{bc} = 6.6, J_{bd} = 9.8, J_{cd} = 13.0.

1c – e react with dimethyl acetylenedicarboxylate under similar conditions to afford crystalline products. Spectral and elemental data indicate that one molecule of acetylene ester has been added but accompanied by subsequent elimination of methanol, similar to the reaction with methyl acrylate. Constitutions **4a – c** were proposed for the products obtained showing a similar ^{13}C NMR pattern as **2a – e**. This smooth cyclization reaction again can be understood in terms of an *anti*-addition as shown in Scheme 3.

Table 5. ^{13}C NMR Spectra of **4a – c** and **5** in $CDCl_3$ (δ in ppm)



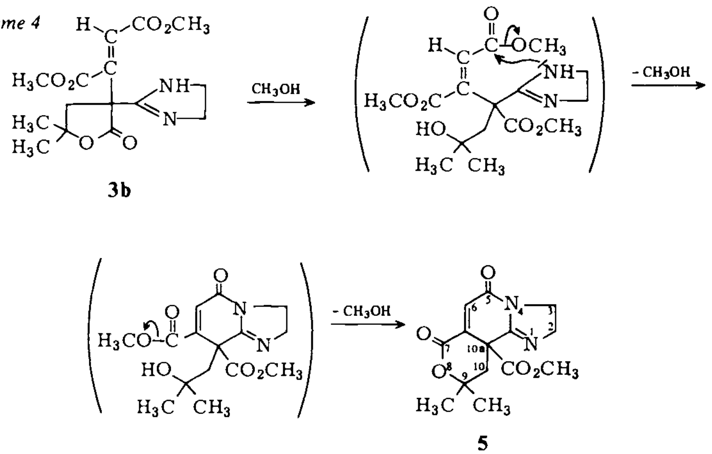
4



5

	4a	**4b**	**4c**	**5**
C-2 (s)	171.6	172.4	173.0	164.8
C-3 (s)	54.2	55.7	57.5	52.3
C-4	45.3 d	46.6 t	46.0 d	61.3 t
C-5	79.2 d	83.4 s	79.1 d	84.3 s
C-6 (s)	160.5	154.0	150.4	161.1
C-8 (t)	61.1	45.2	45.1	45.6
C-9 (t)	40.7	38.5	38.5	41.1
C-10 (t)		19.2	19.2	
C-12 (s)	165.2	165.5	165.5	165.5
C-13 (d)	126.4	124.7	125.9	122.6
C-14 (s)	142.8	138.9	138.2	151.1
C-15 (q)	16.7	30.4	16.9	28.6
C-16 (q)		28.9		28.1
C-17 (q)	9.7		9.5	
C-18 (s)	159.8	163.6	163.9	170.2
C-19 (q)	52.7	52.8	52.6	52.6

Scheme 4



The ^1H and ^{13}C NMR data of **3a**, **b** and **4a** – **c** are listed in Tables 4 and 5. And, once again, **4a** shows a remarkably large chemical shift for C-8 comparable to that in **2c**. Again the gated decoupling technique was employed (Table 3).

When **3b** is refluxed with alcohols a crystalline product is formed. The spectral and elemental analyses indicate that cyclization with loss of one molecule of methanol took place, but the pattern of the NMR spectra was rather different from structural types of **4a** – **c**, especially with regard to the olefinic signals as well as to the signals of C-4 and C-14 in ^{13}C NMR (see Tables 4 and 5). Based on these results constitution **5** was proposed for this reaction product, and the reaction mechanism given in Scheme 4 might be assumed.

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Experimental Part

IR spectra: Perkin-Elmer 157-G. – ^1H- and ^{13}C NMR spectra: Bruker WH-90. – MS: MS-30 of the AEI. – Melting points: not corrected. – Elemental analyses: Analytical Laboratory of the Institute.

2',3',4,5,6',7'-Hexahydro-5-methylspiro[furan-3(2H),8'(5'H)-imidazo[1,2-a]pyridine]-2,5'-dione (**2a**): A mixture of 0.17 g (1.0 mmol) of **1a**, 0.090 g (1.0 mmol) of methyl acrylate, and 20 ml of benzene or dioxane was refluxed under stirring for 12 h. After removal of the solvent, the solid residue was recrystallized from methylene chloride. Yield 0.19 g (83%), m.p. 170 – 175 °C. – IR (KBr): 1764 (lactone C = O), 1672 (amide C = O), 1630 cm^{-1} (C = N).

$C_{11}H_{14}N_2O_3$ (222.2)	Calcd.	C 59.44	H 6.35	N 12.61	
	Found	C 59.22	H 6.04	N 12.63	M.W. 222 (MS)

2',3',4,5,6',7'-Hexahydro-5,5-dimethylspiro[furan-3(2H),8'(5'H)-imidazo[1,2-a]pyridine]-2,5'-dione (**2b**): Similar to **2a** from 0.18 g (1.0 mmol) of **1b** and 0.090 g (1.0 mmol) of methyl acrylate; yield 0.21 g (88%), m.p. 171 – 173 °C. – IR (KBr): 1754 (lactone C = O), 1680 (amide C = O), 1635 cm^{-1} (C = N).

$C_{12}H_{16}N_2O_3$ (236.3)	Calcd.	C 61.00	H 6.83	N 11.86	
2b:	Found	C 60.71	H 6.57	N 11.83	M.W. 236 (MS)
2c:	Found	C 60.72	H 6.50	N 11.91	M.W. 236 (MS)

2',3',4,5,6',7'-Hexahydro-4,5-dimethylspiro[furan-3(2H),8'(5'H)-imidazo[1,2-a]pyridine]-2,5'-dione (**2c**): Like **2a** from 0.18 g (1.0 mmol) of **1c** and 0.090 g (1.0 mmol) of methyl acrylate; yield 0.19 g (79%), m.p. 139 – 142 °C. – IR (KBr): 1765 (lactone C = O), 1675 (amide C = O), 1635 cm^{-1} (C = N).

3',4,4',5,7',8'-Hexahydro-5,5-dimethylspiro[furan-3(2H),9'(6'H)-[2H]pyrido[1,2-a]pyrimidine]-2,6'-dione (**2d**): Similar to **2a** from 0.10 g (0.50 mmol) of **1d** and 0.040 g (0.50 mmol) of methyl acrylate; yield 0.12 g (96%), m.p. 145 – 148 °C. – IR (KBr): 1754 (lactone C = O), 1682 (amide C = O), 1634 cm^{-1} (C = N).

$C_{13}H_{18}N_2O_3$ (250.3)	Calcd.	C 62.38	H 7.25	N 11.20	
2d:	Found	C 62.23	H 7.37	N 11.11	M.W. 250 (MS)
2e:	Found	C 61.60	H 7.40	N 11.04	M.W. 250 (MS)

3',4,4',5,7',8'-Hexahydro-4,5-dimethylspiro[furan-3(2H),9'(6'H)-[2H]pyrido[1,2-a]pyrimidine]-2,6'-dione (**2e**): Like **2a** from 0.10 g (0.50 mmol) of **1e** and 0.040 g (0.50 mmol) of methyl acrylate in a yield of 0.12 g (96%); m.p. 141 – 144 °C. – IR (KBr): 1754 (lactone C=O), 1678 (amide C=O), 1628 cm^{-1} (C=N).

Dimethyl (E)-2-[Tetrahydro-3-(2-imidazolin-2-yl)-5-methyl-2-oxo-3-furanyl]-2-butenedioate (**3a**): 0.14 g (1.0 mmol) of dimethyl acetylenedicarboxylate in 5 ml of benzene or dioxane was added dropwise to a solution of 0.17 g (1.0 mmol) of **1a** in 20 ml of benzene or dioxane under stirring during 1 h at 0 – 10 °C. Then the mixture was stirred at 0 – 10 °C for 6 h. After removal of the solvent, **3a** was obtained as a viscous oil; yield 0.31 g (100%). – IR (film): 3390 (NH), 1762 (lactone C=O), 1725 (ester C=O), 1640, 1610 cm^{-1} (C=C, C=N).

$C_{14}H_{18}N_2O_6$ (310.3)	Calcd.	C 54.19	H 5.85	N 9.03	
	Found	C 54.15	H 5.45	N 9.20	M.W. 310 (MS)

Dimethyl (E)-2-[Tetrahydro-3-(2-imidazolin-2-yl)-5,5-dimethyl-2-oxo-3-furanyl]-2-butenedioate (**3b**): Similar to **3a** from 0.18 g (1.0 mmol) of **1b** and 0.14 g (1.0 mmol) of dimethyl acetylenedicarboxylate in benzene or dioxane solution; **3b** was obtained as a viscous oil; yield 0.32 g (100%). – IR (film): 3390 (NH), 1755 (lactone C=O), 1728 (ester C=O), 1640, 1610 cm^{-1} (C=C, C=N).

$C_{15}H_{20}N_2O_6$ (324.3)	Calcd.	C 55.55	H 6.22	N 8.64	
	Found	C 55.37	H 5.97	N 8.89	M.W. 324 (MS)

Methyl 2',3',4,5-Tetrahydro-4,5-dimethyl-2,5'-dioxospiro[furan-3(2H),8'(5'H)-imidazo[1,2-a]pyridine]-7'-carboxylate (**4a**): At 0 – 10 °C 0.14 g (1.0 mmol) of dimethyl acetylenedicarboxylate in 5 ml of benzene was added dropwise to the stirred mixture of 0.18 g (1.0 mmol) of **1c** in 20 ml of benzene. This needs about 1 h; then the mixture was stirred at 0 – 10 °C for additional 6 h. After removal of the solvent, the solid residue was recrystallized from methylene chloride. Yield 0.20 g (69%), m.p. 173 – 175 °C. – IR (KBr): 1765 (lactone C=O), 1728 (ester C=O), 1676 (amide C=O), 1655, 1650 cm^{-1} (C=C, C=N).

$C_{14}H_{16}N_2O_5$ (292.3)	Calcd.	C 57.53	H 5.52	N 9.59	
	Found	C 57.32	H 5.61	N 9.53	M.W. 292 (MS)

Methyl 3',4,4',5-Tetrahydro-5,5-dimethyl-2,6'-dioxospiro[furan-3(2H),9'(6'H)-[2H]pyrido[1,2-a]pyrimidine]-8'-carboxylate (**4b**): Using the same procedure as above, from 0.20 g (1.0 mmol) of **1d** and 0.14 g (1.0 mmol) of dimethyl acetylenedicarboxylate in benzene solution. Yield 0.25 g (81%), m.p. 193 – 195 °C. – IR (KBr): 1762 (lactone C=O), 1732 (ester C=O), 1680 (amide C=O), 1660, 1650 cm^{-1} (C=C, C=N).

$C_{15}H_{18}N_2O_5$ (306.3)	Calcd.	C 58.81	H 5.92	N 9.15	
4b:	Found	C 58.31	H 6.11	N 8.80	M.W. 306 (MS)
4c:	Found	C 58.47	H 6.05	N 8.92	M.W. 306 (MS)

Methyl 3',4,4',5-Tetrahydro-4,5-dimethyl-2,6'-dioxospiro[furan-3(2H),9'(6'H)-[2H]pyrido[1,2-a]pyrimidine]-8'-carboxylate (**4c**): Like **4a** from 0.20 g (1.0 mmol) of **1e** and 0.14 g (1.0 mmol) of dimethyl acetylenedicarboxylate in benzene solution. Yield 0.27 g (87%), m.p. 179 – 181 °C. – IR (KBr): 1766 (lactone C=O), 1734 (ester C=O), 1682 (amide C=O), 1657, 1650 cm^{-1} (C=C, C=N).

Methyl 2,5,7,9,10,10a-Hexahydro-9,9-dimethyl-5,7-dioxo-3H-imidazo[1,2-a]pyrano[4,3-c]pyridine-10a-carboxylate (**5**): The solution of 0.32 g (1.0 mmol) of **3b** in 5 ml of methanol was refluxed for 8 h. After removing most of the solvent, 0.11 g (40%) of **5** is obtained, m.p.

187 – 191 °C. – IR (KBr): 1760 (lactone C=O), 1735, 1715 (ester C=O), 1678 (amide C=O), 1650, 1645 cm^{-1} (C=C, C=N).

$C_{14}H_{16}N_2O_5$ (292.3) Calcd. C 57.53 H 5.52 N 9.59
Found C 57.71 H 5.90 N 9.35 M.W. 292 (MS)

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