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Heterocyclic β-Enamino Esters, 32[1]

Reactions of Aliphatic Diamines and Methylamine with 2-Amino-4,5-dihydro-3-furancarboxylic Esters. Revised Constitutions by ^{13}C NMR Studies

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^{13}C NMR spectra of the reaction products of ethyl 2-amino-4,5-dihydro-3-furancarboxylates **3a – e** with ethylenediamine and 1,3-diaminopropane, respectively, were measured, and the constitutions were confirmed with the aid of gated decoupling technique to be 3-(2-imidazolidinylidene)- and 3-(hexahydro-2-pyrimidinylidene)dihydro-2(3*H*)-furanones **1a – i**, instead of furo[2,3-*e*]-1,4-diazepinones and furo[2,3-*b*][1,5]diazocinones **2a – i**, respectively. – The reaction of **3b – e** with methylamine has been studied, and a mixture of *E*- and *Z*-isomers of 3-[amino(methylamino)methylene]-4,5-dihydro-2(3*H*)-furanones **6b – e** and **6'b – e** has been obtained. The ratios of *E*- and *Z*-isomers are approximately 40:60, irrespective of the different substituents.

Heterocyclische β-Enaminoester, 32[1]

Zur Reaktion aliphatischer Diamine und von Methylamin mit 2-Amino-4,5-dihydro-3-furancarbonsäureestern. Revidierte Konstitutionsvorschläge durch ^{13}C-NMR-Analyse

Die ^{13}C-NMR-Spektren der Reaktionsprodukte von 2-Amino-4,5-dihydro-3-furancarbonsäureethylestern **3a – e** mit Ethylendiamin und 1,3-Diaminopropan wurden vermessen und die Konstitutionen mit Hilfe der Gated Decoupling Technik als 3-(2-Imidazolidinyliden)- bzw. 3-(Hexahydro-2-pyrimidinyliden)dihydro-2(3*H*)-furanone **1a – i** und nicht als Furo[2,3-*e*]-1,4-diazepinone bzw. Furo[2,3-*b*][1,5]diazocinone **2a – i** gesichert. – **3b – e** reagieren mit Methylamin zu einem Gemisch aus *E*- und *Z*-Isomeren der 3-[Amino(methylamino)methylen]-4,5-dihydro-2(3*H*)-furanone **6b – e** und **6'b – e**. Unabhängig von der Substitution beträgt das *E*-/*Z*-Verhältnis ungefähr 40:60.

A. Reaction with Aliphatic Diamines

Pacini and *Ghirardelli*[3] have reported the reaction product of *cis*-tetrahydro-4,5-dimethyl-2-oxo-3-furonitrile with ethylenediamine to be *cis*-hexahydro-6,7-dimethylfuro[2,3-*e*]-1,4-diazepin-5-one. This prompted extensive investigations of this reaction employing 2-amino-4,5-dihydro-3-furancarboxylic esters and several amino derivatives[4].

Among the other examples of 2-amino-4,5-dihydro-3-furancarboxylates we have treated also ethyl *cis*-2-amino-4,5-dihydro-4,5-dimethyl-3-furoate[3] with ethylenediamine and obtained the identical reaction product as reported by *Pacini* and *Ghirardelli*[3]. And consequently, all other

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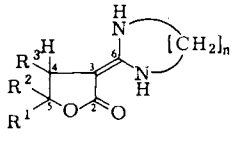
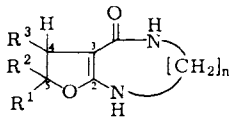
analogs obtained were assigned to the same constitutions of furo[2,3-*e*]-1,4-diazepinones **2a – d**; similarly, a furo[2,3-*b*][1,5]diazocinone constitution **2f – h** seemed to follow for the reaction products of 2-amino-4,5-dihydro-3-furancarboxylic esters with 1,3-diaminopropane[4c].

In fact, for a long time detailed UV-, IR-, and ^{1}H NMR investigations of these two series of compounds **2a – d** and **2f – h** caused no doubt on these constitutions of furo[2,3-*e*]-1,4-diazepinones and furo[2,3-*b*][1,5]diazocinones, respectively. Exceptionally the $-N-CH_2-CH_2-N-$ moiety of the "diazepine ring" in the ^{1}H NMR spectra showed remarkably a singlet[4], which was explained with a pseudoisochronism or fast inversion, although low temperature ^{1}H NMR measurements did not show any coalescence phenomenon.

Scheme 1



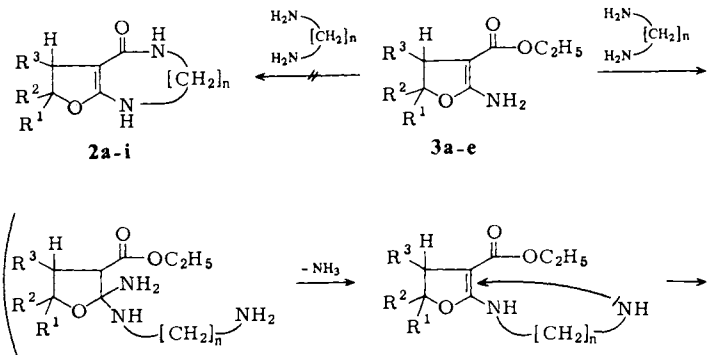
1a-i



2a-i

1,2	n	R^1	R^2	R^3
a	2	H	H	H
b	2	CH_3	H	H
c	2	CH_3	CH_3	H
d	2	CH_3	H	CH_3
e	2	C_2H_5	H	H
f	3	H	H	H
g	3	CH_3	CH_3	H
h	3	CH_3	H	CH_3
i	3	C_2H_5	H	H

Scheme 2



2a-i **3a-e** **1a-i**

3	R^1	R^2	R^3
a	H	H	H
b	CH_3	H	H
c	CH_3	CH_3	H
d	CH_3	H	CH_3
e	C_2H_5	H	H

Further experimental results with these "heteroannelated" compounds like addition and cyclization reactions with halogens and methyl propiolate, respectively, which will be published elsewhere[5], suggested a reinvestigation of their constitutional formulae.

Thus, our interest was guided to an unusual high absorption band in the region of 1760 cm^{-1}, which was always observed in the IR spectra of the reaction products being only compatible with a γ-lactone moiety.

And indeed, these products turned out to be 3-(2-imidazolidinylidene)- and 3-(hexahydro-2-pyrimidinylidene)-4,5-dihydro-2(3*H*)-furanones **1a – i**, and not the heteroannelated systems **2a – i**; **1e, i** represent additional examples prepared from **3e** (R^1 = C_2H_5; R^2, R^3 = H) and the appropriate diamines.

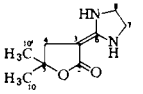
As a consequence, ethylenediamine and 1,3-diaminopropane attack the heterocyclic β-enamino esters **3a – e** in a similar way as *o*-phenylenediamine, 2-aminoethanol, 2-aminophenol, and 1,8-diaminonaphthalene[4], as follows (Scheme 2):

In a stepwise addition-elimination sequence finally the furan ring is cleaved to give – *via* a γ-hydroxyester intermediate – a γ-lactone derivative, particularly **1a – i**.

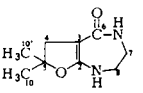
While UV-, IR-, and ^1H NMR data do not allow to differentiate unequivocally between the alternative constitutions **1** and **2**, detailed ^{13}C NMR investigations turned out to be the crucial method for distinguishing between both formulae, as C-2 and C-6 in **1a – i**, as well as C-2 in **2a – i** should exhibit quite different chemical shifts due to their unlike constitutions.

For the example of **1c, g** (or: **2c, g**) obtained from **3c** and ethylenediamine or 1,3-diaminopropane, respectively, the ^{13}C NMR spectra were measured employing the gated decoupling technique and Gauss resolution enhancement. The resulting spectroscopic data are listed in Tables 1 and 2.

Tab. 1. ^{13}C Chemical Shifts and Coupling Constants of **1c** (or: **2c**) [62.9 MHz (^{13}C), 250 MHz (^1H); [D_6]DMSO; δ-values Relative to TMS]



1c

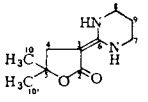


(2c)

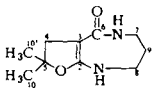
δ [ppm]	Multiplicity	$J_{C,H}$ [Hz]	$^2J_{C,H}/^3J_{C,Ha)}$ [Hz]	Coupled Protons	C-Atom 1c	C-Atom (2c)
171.6	long-range triplet		2.9	4-H_2	C-2	C-6
159.7	long-range nonet		2.6	4-H_2	C-6	C-2
				7-H_2		
				8-H_2, NH, NH		
78.0	long-range nonet		3.9	4-H_2	C-5	C-5
				10,10′-H_6		
64.4	long-range triplet		4.8	4-H_2	C-3	C-3
43.5	triplet of long-range quartets	144.0	4.3	8-H_2	C-7	C-7 or C-8
				NH		
42.4	triplet of long-range quartets	144.0		7-H_2	C-8	C-7 or C-8
			2.8	NH		
38.9	triplet of long-range septets	132.0		10,10′-H_6	C-4	C-4
			3.9			
28.9	quartet of long-range sextets	126.0		10 or 10′-H_3	C-10	C-10
			3.9	4-H_2	C-10′	C-10′

a) Obtained after Gauss resolution enhancement.

Table 2. ^{13}C Chemical Shifts and Coupling Constants of **1g** (or: **2g**) [22.6 MHz (^{13}C), 90 MHz (^{1}H); [D_6]DMSO; δ-values Relative to TMS]



1g

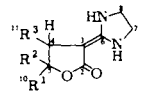


(2g)

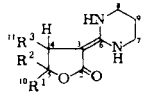
δ [ppm]	Multiplicity	J_{C-H} [Hz]	$^2J_{C-H}/^3J_{C-Ha)}$ [Hz]	Coupled Protons	C-Atom **1g**	C-Atom **(2g)**
171.1	long-range triplet		2.9	4-H_2	C-2	C-6
154.6	broad, not resolved				C-6	C-2
77.1	long-range nonet		3.7	10,10′-H_6 4-H_2	C-5	C-5
63.8	long-range triplet		2.2	4-H_2	C-3	C-3
38.9	triplet of long-range septets	131.1	4.2	10,10′-H_6	C-4	C-4
38.1	triplet, weakly resolved, long-range multiplet	146.5			C-7	C-7 or C-8
37.7	triplet, weakly resolved, long-range multiplet	146.5			C-8	C-7 or C-8
29.0	quartet of long-range sextets	126.0	4.4	10 or 10′-H_3 4-H_2	C-10 C-10′	C-10 C-10′
20.8	triplet of long-range quintets	131.0	3.7	7-H_2 8-H_2	C-9	C-9

a) Obtained after Gauss resolution enhancement.

Table 3. ^{13}C NMR Data of **1a–i** in [D_6]DMSO (TMS δ = 0 ppm)



1a–e

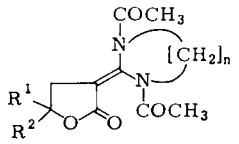


1f–i

Compd.	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11
1a	173.2	63.0	25.4	64.0	159.9	43.6	42.5			
1b	172.3	63.6	33.0	71.5	159.6	43.5	42.3		22.5	
1c	171.6	64.4	38.9	78.0	159.7	43.5	42.4		28.9	
1d	172.3	72.4	35.1	75.0	159.4	43.2	42.5		15.4	14.5
1e	172.3	63.6	30.8	76.4	159.6	43.5	42.4		29.2 9.2	
1f	172.7	62.4	25.4	63.2	154.7	38.1	37.7	20.8		
1g	171.1	63.8	38.9	77.1	154.6	38.1	37.7	20.8	29.0	
1h	171.9	72.1	34.7	74.4	154.4	38.1	37.7	20.7	15.3	14.4
1i	172.0	63.1	30.8	75.6	154.6	38.1	37.7	20.8	29.3 9.2	

As we have found, it is even difficult to distinguish between both structural types **1** and **2** only from their ^{13}C chemical shifts. But from the long-range coupling constants, especially from the long-range coupling constants of the carbonyl-C, C-2 in **1c, g** and C-6 in **2c, g**, respectively, an easy distinction can be made. In the case of **1c** and **1g** this carbon should show a long-range triplet; otherwise, the signal of the appropriate carbon in **2c** and **2g** will be splitted into a complex pattern. And in fact, the experimental results indicated triplet signals. In the 22.6 MHz ^{13}C NMR spectrum the signal at $\delta = 154-160$ showed only an unresolved broad multiplet, but at 62.9 MHz this signal resulted in a nonet, which again is in accordance with the constitutions of **1c, g**.

Scheme 3

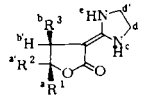


4	n	R^1	R^2
a	2	H	H
g	3	CH_3	CH_3

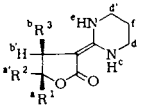
4a, g

Inspecting now again carefully the IR- and ^1H NMR spectra reported[4] for "**2a – i**" the lactone C = O-absorption in the range of 1650 – 1690 cm^{-1} is due to the conjugation

Tab. 4. ^1H NMR Data of **1a – i** in $CDCl_3$ (TMS $\delta = 0$ ppm) (J in Hz)



1a-e



1g-i

Compd.	H^a	$H^{a'}$	H^b	$H^{b'}$	H^c	$H^{d+d'}$	H^e	H^f
1a	4.28t (7.9)		2.72t (7.9)		6.91	3.60s	4.47	
1b	1.36d (6.2)	4.59 ($J_{aa'} = 6.2$, $J_{a'b} = 6.0$, $J_{a'b'} = 8.4$, $J_{bb'} = 12.0$)	2.31	2.85	6.93	3.60s	4.45	
1c	1.38s		2.53s		6.95	3.60s	4.38	
1d	1.29d (6.6)	4.53 quint (6.8)	0.99d (6.6)	2.91 quint (6.9)	7.00	3.59s	4.48	
1e	0.95t (7.4) 1.63m	4.37 ($J_{aa'} = 6.2$, $J_{a'b} = 6.2$, $J_{a'b'} = 8.8$, $J_{bb'} = 12.2$)	2.37	2.81	6.86	3.58s	5.01	
1g	1.38s		2.47s		8.13	3.34t (6.0)	4.32	1.94 quint (6.0)
1h	1.28d (6.6)	4.46 quint (6.8)	0.95d (6.6)	2.77 quint (6.8)	8.17	3.34t (5.9)	4.40	1.95 quint (5.8)
1i	0.95t (7.4) 1.62m	4.33 ($J_{aa'} = 6.2$, $J_{a'b} = 6.4$, $J_{a'b'} = 9.2$ $J_{bb'} = 11.4$)	2.30	2.73	8.04	3.34t (5.8)	4.52	1.94 quint (5.8)

with the enamine group[6]. The singlet of the $-\underset{|}{N}-CH_2-CH_2-\underset{|}{N}-$ moiety in its ^1H NMR spectrum is also in best agreement with **1a–i**. Similarly, the easy formation of the diacetyl derivatives **4a, g** by the reaction with acetic anhydride[4b,c] is consistent with the constitutional formulae **1a–i** and must be revised to 3-(1,3-diacetyl-2-imidazolidinylidene)- and 3-(1,3-diacetylhexahydro-2-pyrimidinylidene)-4,5-dihydro-2(3*H*)-furanones **4a** and **4g**, respectively.

Furthermore, the shift dependence of the proton signal versa the concentration of the chemical shift reagent[4b] is much better explained with the constitutions **1a–i**. Due to the shift reagent placed near to the carbonyl group, the shift of the neighboring protons is definitely more influenced.

The ^{13}C NMR data are listed in Table 3. From these results follows for the lactone C-2 the value δ = 171.1–173.2. This certain upfield shift in comparison to the value of 178.4 reported in the literature[7] can be explained in terms of a conjugation with the *exo*-3-double bond. The C-6 in the 5-membered imidazolidine ring occurs at ca. 5 ppm lower field than the same C-6 in the hexahydropyrimidine ring. It seems worthwhile to notice also the smaller value of C-3 (δ = 62.4–72.4); this indicates that the electrophilic attack can be expected to happen to this carbon atom, which was actually found in our further investigations[5].

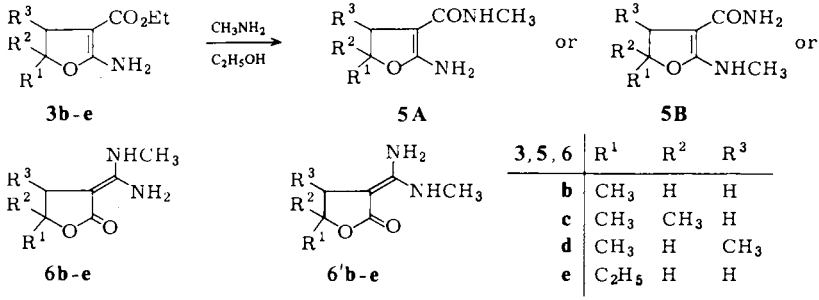
The ^1H NMR spectra of **1a–i** were measured or remeasured. The data are listed in Table 4. In **1g–i** the H^c occurs at lower field than in **1a–e**, as this proton in **1g–i** is more coordinated with the adjacent carbonyl group. In **1b, e, i** $H^{b,b'}$ and $H^{a'}$ form an ABX-system, while $H^{a'}$ is further splitted by the vicinal protons of the alkyl group.

B. Reaction with Methylamine

For better understanding of the reaction mechanism described above and the constitution of the reaction products applying amines, we have now studied the reaction with methylamine.

Reacting the ethyl 2-amino-4,5-dihydro-3-furancarboxylates **3b–e** with methylamine in ethanolic solution we obtained a good-to-fair yield of crystalline products. According to the elemental analyses and the mass spectra, the formation of the tentative structures **5, 6** and their tautomers can be discussed (Scheme 4).

Scheme 4



3b-e **5A** **5B**

6b-e **6'b-e**

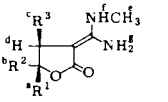
3,5,6	R^1	R^2	R^3
b	CH_3	H	H
c	CH_3	CH_3	H
d	CH_3	H	CH_3
e	C_2H_5	H	H

The ^1H NMR spectra reveal three singlets at δ = 5.60–8.00, which all undergo deuterium exchange. The protons of the 2-amino group in 2-amino-4,5-dihydro-3-

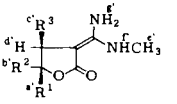
furamide[3] and in 2-amino-4,5-dihydro-3-furancarboxylic esters[6] are reported to display only one singlet; therefore the structure **5A** can be ruled out. As there is no 3-H signal present and consequently no coupling of the 4-H by neighboring protons was detected, also a tautomeric mixture of **5A** could be neglected.

Attempts to dehydrate the reaction products by treatment with the system triphenylphosphane/hexachloroethane/triethylamine[8], or e. g. with dicyclohexylcarbodiimide, did not lead to the detection of any nitrile function. Under normal conditions the two amide protons only scarcely display two separated signals in ^{1}H NMR. Therefore, also structure **5B** was excluded, and on the basis of the fore-mentioned reason, the tautomeric mixture of **5B** was not considered.

Table 5. ^{1}H NMR Data of **6b–e/6'b–e** in [D$_6$]DMSO; TMS as Internal Standard; δ[ppm] (*J* in Hz)



6b-e



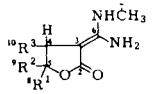
6'b-e

Compd.	$H^{aa'}$	$H^{bb'}$	$H^{cc'}$	$H^{dd'}$	$H^{ee'}$	$H^{fg'}$	H^{g}	$H^{f'}$
6b					2.79d			
	1.24d	4.39	2.22	2.80	(5.0)	5.98s	6.87s	7.82s
6'b	(6.0)	(J_{ab} = 6.0, J_{bc} = 6.2, J_{bd} = 8.2, J_{cd} = 12.2)			2.84d (5.0)			
6c			2.38s		2.68d (5.2)			
	1.23s					6.09s	6.86s	7.69s
6'c			2.43s		2.74d (5.2)			
6d			0.89d		2.82d			
	1.20d	4.32 quint	(6.6)		(4.8)	5.95s	6.90s	7.97s
6'd	(6.6)	(6.6)	0.91d (6.6)		2.85d (5.2)			
6e					2.87d			
	0.92t	1.55m 4.20	2.29	2.75	(4.8)	5.67s	6.76s	7.87s
6'e	(7.4)	7.4(J_{ab} = 6.2, J_{bc} = 6.4, J_{bd} = 8.8, J_{cd} = 12.2)			2.88d (5.2)			

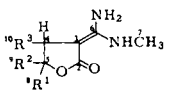
Now, after all only the constitutions of **6b – e** can be discussed or mixtures with their geometrical isomers **6'b – e**. As the integration of the three signal groups reveals, the reaction products consist most probably of a mixture of *trans*- and *cis*-isomers (*E*- and *Z*-forms) **6b – e** and **6'b – e**. The signal assignment can be reasonably explained as follows: The signal at δ = 7.69 – 7.97 is assigned to CH_3NH in **6'b – e**. Furthermore, the methyl group favours an NH-chelate bridge to the lactone carbonyl, therefore this signal is found at lower field. The signal at δ = 6.76 – 6.90 is assigned to the NH_2-protons in **6b – e**, and the signal at δ = 5.67 – 6.09 to CH_3NH and NH_2 in **6'b – e**. The ^{1}H NMR data are listed in Table 5. And in fact, a pair of methyl signals CH_3NH indicates that the reaction product is indeed a *E*-/*Z*-mixture of **6b – e** and

6'b – e. In compounds **6b** and **6e** H^b, H^c, and H^d form an ABX-system, while in **6e** the H^b is additionally splitted by the vicinal alkyl group. In **6e** the 5-ethyl protons and H^b form an A_2B_3X-system. **6'b** and **6'e** behave similar to **6b** and **6e**.

Table 6. ^{13}C NMR Data of **6b – e/6'b – e** in [D_6]DMSO; TMS as Internal Standard; δ[ppm]



6b-e



6'b-e

Compd.	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
6b		64.8	33.0	70.7	158.3	27.5			
	172.4						22.6		
6'b		64.6	33.4	70.9	158.5	27.6			
6c		65.6		77.1	158.3	27.5			
	171.6		38.8				28.9	28.9	
6'c		65.4		77.3	158.5	27.6			
6d		73.9	34.7	74.4	158.1				
	172.5					27.5	15.3		14.2
6'd		73.6	35.1	74.6	158.3				
6e		64.9	30.9	75.6	158.3	27.5			
	172.5						29.3, 9.2		
6'e		64.7	31.3	75.8	158.5	27.7			

Table 7. The Ratio [%] of *E*- and *Z*-Isomers **6b – e/6'b – e**
a) Estimated from ^{13}C NMR data, measured with inverse gated decoupling technique

	6b/6'b	**6c/6'c**	**6d/6'd**	**6e/6'e**	
C-3	39/61	40/60	43/57	39/61	
C-4	39/61		43/57	39/61	
C-5	39/61	43/57	45/55	42/58	
C-6	39/61	39/61	42/58	35/65	
C-7	39/61	41/59		47/53	
	39/61	41/59	43/57	41/59	Average

b) Estimated from ^1H NMR data

	39/61	43/57	44/56	40/60	Average

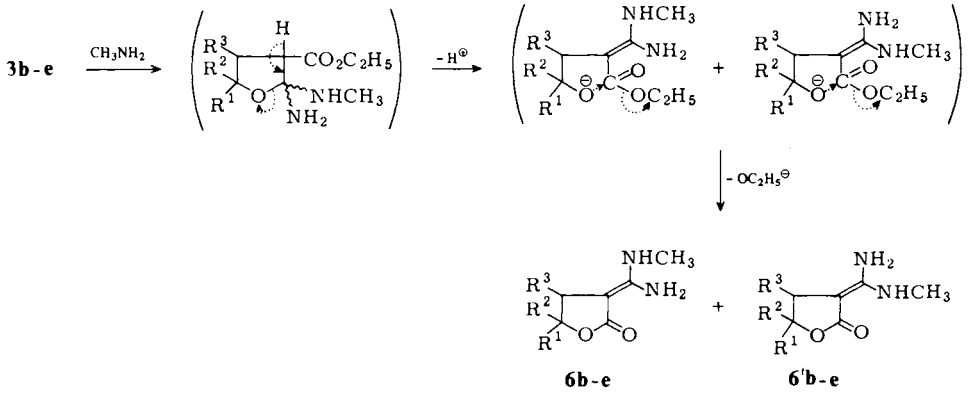
Pairs of signals appear also in the ^{13}C NMR spectra, which confirms furthermore that the reaction products consist of a mixture of **6b – e** and **6'b – e**. The spectra were measured by inverse gated decoupling technique, which allows an approximative estimation of the relative rations **6b – e/6'b – e**. Chemical shifts as well as *E*- and *Z*-isomer ratios are listed in Tables 6 and 7, respectively. Additionally Table 7 contains the ratios estimated from the integral of the three NH signals, but these results seem to be less precise and are shown only for comparison. The ^{13}C chemical shifts of the

lactone carbonyl appear between δ = 171.6 – 172.5 and of C-3 between δ = 64.6 – 73.9; both values are in good agreement with the data reported for **1a – i**[1].

Summing up the values given in Table 7, the ratios of *E*- and *Z*-isomers are approximately 40:60, irrespective of the different substituents.

The formation of the *E*- and *Z*-isomers **6b – e** and **6'b – e** is depicted in Scheme 5.

Scheme 5



According to this scheme, we conclude that the reaction of **3b – e** both with aliphatic diamines and methylamine proceeds on the same pathway leading to the same type of reaction products, namely 3-ylidene-4,5-dihydro-2(3*H*)-furanones, and, thus, can be explained in terms of the analogous mechanism.

The authors are grateful to Prof. Dr. *E. Breitmaier,* University of Bonn, for helpful discussions, to Dr. *G.-J. Wolff,* Bruker Analytik, Karlsruhe, for measuring the 62.9 MHz ^{13}C NMR spectra with Gauss resolution enhancement, and to Mr. *C. Schmidt* for measuring the other NMR spectra. This work was further supported by the *Fonds der Chemischen Industrie,* the *Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen,* and the *Bayer AG.* – Z.-T. H. thanks the *Max-Planck-Gesellschaft* for granting a fellowship.

Experimental Part

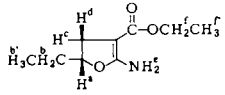
IR spectra: Perkin-Elmer 157-G. – ^1H- and ^{13}C NMR spectra: Bruker WH-90 and WM-250. – MS: MS-30 of the AEI. – Melting points: not corrected. – Elemental analyses: Analytical Laboratory of the Institute.

The synthesis of the heterocyclic β-enamino esters **3a – d** is described in loc. cit.[9,10].

Ethyl 2-Amino-5-ethyl-4,5-dihydro-3-furancarboxylate (**3e**): In the first step *5-ethyltetrahydro-2-oxo-3-furonitrile* was prepared from equimolar amounts of ethyl cyanoacetate and 1,2-epoxybutane in the presence of a molar equivalent of sodium ethoxide according to the procedure described in loc. cit.[9]; yield 63%, b.p. 152 – 155°C/2 torr; n_D^{25} = 1.4560.

This intermediary lactone was subsequently converted into **3e** as follows: 41.7 g (300 mmol) of the fore-mentioned α-cyanolactone and 0.69 g (30 mmol) of sodium gave in 115 ml absol. ethanol according to the procedure described in loc. cit.[10] **3e** in a yield of 38.7 g (70%); b.p.

130–132°C/1.5 torr. – IR (KBr): 3425, 3300 (NH), 1670, 1615, 1530 cm^{-1} (EI, EII, EIII bands[6]). – ^1H NMR ($CDCl_3$): δ = 4.59 (m, H^a), 1.69 (m, H^b), 0.97 (t, $H^{b'}$), 2.52 (m, H^c), 2.94 (m, H^d), J_{ab} = 6.4, J_{ad} = 9.3, J_{ac} = 7.4, J_{cd} = 12.4, $J_{bb'}$ = 7.3 Hz; 5.58 (s, H^e), 4.17 (q, H^f, J = 7 Hz), 1.27 (t, $H^{f'}$, J = 7 Hz).



$C_9H_{15}NO_3$ (185.2) Calcd. C 58.36 H 8.16 N 7.56 Found C 58.38 H 8.13 N 7.74

The following compounds, **1a–d,f–h**, **4a**, **g** have to be renamed as follows:

compound	name	described in loc. cit.	as number
	-2(3*H*)-furanone		
1a	4,5-Dihydro-3-(2-imidazolidinylidene)-	[4b]	**2a**
1b	4,5-Dihydro-3-(2-imidazolidinylidene)-5-methyl-	[4b]	**2b**
1c	4,5-Dihydro-3-(2-imidazolidinylidene)-5,5-dimethyl-	[4b]	**2c**
1d	4,5-Dihydro-3-(2-imidazolidinylidene)-4,5-dimethyl-	[4b]	**2d**
1f	3-(Hexahydro-2-pyrimidinylidene)-4,5-dihydro-	[4c]	**3a**
1g	3-(Hexahydro-2-pyrimidinylidene)-4,5-dihydro-5,5-dimethyl-	[4c]	**3b**
1h	3-(Hexahydro-2-pyrimidinylidene)-4,5-dihydro-4,5-dimethyl-	[4c]	**3c**
4a	3-(1,3-Diacetyl-2-imidazolidinylidene)-4,5-dihydro-	[4b]	**3**
4g	3-(1,3-Diacetylhexahydro-2-pyrimidinylidene)-4,5-dihydro-5,5-dimethyl-	[4c]	**4**

5-Ethyl-4,5-dihydro-3-(2-imidazolidinylidene)-2(3H)-furanone (**1e**): 0.93 g (5.0 mmol) of **3e**, 0.30 g (5.0 mmol) of ethylenediamine, and 8 ml of ethanol were stirred at ca. 40°C for 6 h. After removal of the solvent, the crude product was recrystallized from ethanol, 0.64 g (70%) of **1e** were obtained, m. p. 116–120°C. – IR (KBr): 3385, 3160 (NH), 1667 (C=O), 1606 cm^{-1} (C=C).

$C_9H_{14}N_2O_2$ (182.2) Calcd. C 59.32 H 7.74 N 15.38
Found C 58.83 H 7.93 N 15.15 M.W. 182 (MS)

5-Ethyl-3-(hexahydro-2-pyrimidinylidene)-4,5-dihydro-2(3H)-furanone (**1i**): 0.93 g (5.0 mmol) of **3e**, 0.37 g (5.0 mmol) of 1,3-diaminopropane, and 8 ml of toluene were refluxed for 6 h. After removal of the solvent, the crude product was recrystallized from ethanol, 0.29 g (30%) of **1i** were obtained, m.p. 138–140°C. – IR (KBr): 3320, 3272 (NH), 1655 (C=O), 1580 cm^{-1} (C=C).

$C_{10}H_{16}N_2O_2$ (196.3) Calcd. C 61.20 H 8.22 N 14.28
Found C 60.84 H 8.20 N 14.18 M.W. 196 (MS)

(E)- and (Z)-3-[Amino(methylamino)methylene]-4,5-dihydro-5-methyl-2(3H)-furanones (**6b** and **6'b**): 3.42 g (20 mmol) of enamino ester **3b**, 1.88 g (20 mmol) of 33% ethanolic methylamine solution, and 30 ml of ethanol were refluxed for 6 h. The solvent was then mostly removed, and 1.9 g (61%) of products **6b/6'b** were obtained, m.p. 162–165°C. – IR (KBr): 3380, 3320, 3216 (N–H), 1650 (C=O), 1560 cm^{-1} (C=C).

$C_7H_{12}N_2O_2$ (156.2) Calcd. C 53.83 H 7.75 N 17.94
Found C 53.41 H 7.90 N 17.48 M.W. 156 (MS)

(E)- and (Z)-3-[Amino(methylamino)methylene]-4,5-dihydro-5,5-dimethyl-2(3H)-furanones (**6c** and **6'c**): Using the same procedure as above, from 3.7 g (20 mmol) of **3c** and 20 mmol of ethanolic methylamine solution 2.4 g (71%) of **6c** and **6'c** were obtained, m.p. 199–203°C. – IR (KBr): 3360, 3310, 3190 (N–H), 1650 (C=O), 1575 cm^{-1} (C=C).

$C_8H_{14}N_2O_2$ (170.2) Calcd. C 56.45 H 8.29 N 16.46
Found C 56.05 H 8.44 N 16.31 M.W. 170 (MS)

(E)- and (Z)-3-[Amino(methylamino)methylene]-4,5-dihydro-4,5-dimethyl-2(3H)-furanones (**6d** and **6'd**): According to **6b/6'b** 3.7 g (20 mmol) of **3d** and 20 mmol of ethanolic methylamine solution afforded 1.7 g (50%) of **6d** and **6'd**, m.p. 179–182°C. – IR (KBr): 3352, 3300, 3190 (N–H), 1645 (C=O), 1558 cm^{-1} (C=C).

$C_8H_{14}N_2O_2$ (170.2) Calcd. C 56.45 H 8.29 N 16.46
Found C 56.35 H 8.49 N 16.08 M.W. 170 (MS)

(E)- and (Z)-3-[Amino(methylamino)methylene]-5-ethyl-4,5-dihydro-2(3H)-furanones (**6e** and **6'e**): According to **6b/6'b** 3.7 g (20 mmol) of **3e** and 20 mmol of ethanolic methylamine solution gave 1.09 g (32%) of **6e** and **6'e**, m.p. 121–123°C. – IR (KBr): 3355, 3300, 3190 (N–H), 1652 (C=O), 1560 cm^{-1} (C=C).

$C_8H_{14}N_2O_2$ (170.2) Calcd. C 56.45 H 8.29 N 16.46
Found C 56.23 H 8.51 N 16.48 M.W. 170 (MS)

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[1] Part 31: *H. Wamhoff* and *G. Haffmanns*, Chem. Ber. **117**, 585 (1984), preceding.
[2] Research Fellow of the Max-Planck-Gesellschaft; present address: Institute of Chemistry, Academia Sinica, Beijing, VR China.
[3] *P. L. Pacini* and *R. G. Ghirardelli*, J. Org. Chem. **31**, 4133 (1966).
[4] [4a] *H. Wamhoff* and *C. Materne*, Liebigs Ann. Chem. **754**, 113 (1971). – [4b] *H. Wamhoff, C. Materne*, and *F. Knoll*, Chem. Ber. **105**, 753 (1972). – [4c] *H. Wamhoff* and *C. Materne*, Chem. Ber. **107**, 1784 (1974).
[5] *Zhi-tang Huang* and *H. Wamhoff*, Chem. Ber., in press.
[6] *H. Wamhoff, H. W. Dürbeck*, and *P. Sohár*, Tetrahedron **27**, 5873 (1971).
[7] *J. B. Stothers*, Carbon-13 NMR Spectroscopy, p. 300, Academic Press, New York 1972.
[8] Cf. *R. Appel* and *M. Halstenberg*, in *J. I. G. Cadogan* (ed.), Organophosphorus Reagents in Organic Synthesis, p. 387ff., Academic Press Inc., London 1979.
[9] *S. A. Glickman* and *A. C. Cope*, J. Am. Chem. Soc. **67**, 1012 (1945).
[10] *F. Korte* and *K. Trautner*, Chem. Ber. **95**, 281 (1962).

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