Synthesis and Structure of Enaminecarbaldehydes and Enamino Ketones

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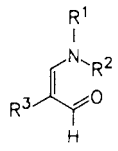
The synthesis of enaminecarbaldehydes **1a–s** and **17a–c** as well as enamino ketones **2a–k**, and their *N*-acyl derivatives **19a–k** and **21–t** with electron accepting substituents at C-2 and at the CO group, respectively, is described. Condensation of methyl 2-formyl-3-oxopropanoate (**13**) with ammonia and the amines **14b–s** gave the enaminecarbaldehydes **1a** and **1b–s**, respectively, in 72–93% yield. The enaminecarbaldehydes **17** were obtained by formylation of **15** with acetic formic anhydride. The synthesis of the enamino ketones **2a–k** was accomplished in 61–97% yield by reaction of ammonia and amines with the enol ethers **24a–f**, which were formed by treatment of reactive acyl chlorides **23** with ethyl vinyl ether. The enaminecarbaldehyde **1a** as well as the enamino ketones **2a–k** could be acylated to give **19a–k** and **21–t**, respectively, which can be used in the *hetero* Diels-Alder reaction.

Synthese- und Struktur von Enamincarbaldehyden und Enamino-Ketonen

Die Synthese der Enamincarbaldehyde **1a–s** und **17a–c** sowie der Enamino-Ketone **2a–k** und deren *N*-Acyl-Derivate **19a–k** und **21–t** mit Elektronenacceptor-Substituenten an C-2 bzw. an der CO-Gruppe wird beschrieben. Kondensation von 2-Formyl-3-oxopropansäure-methylester (**13**) mit Ammoniak und den Aminen **14b–s** ergab die Enamincarbaldehyde **1a** bzw. **1b–s** in einer Ausbeute von 72–93%. Die Enamincarbaldehyde **17** konnten durch Formylierung von **15** mit dem gemischten Ameisensäure-essigsäureanhydrid erhalten werden. Die Synthese der Enamino-Ketone **2a–k** erfolgte mit einer Ausbeute von 61–97% durch Kondensation von Ammoniak und Aminen mit den Enolethern **24a–f**, die durch Umsetzung reaktiver Acylchloride **23** mit Ethylvinyl-ether dargestellt wurden. Die für *hetero*-Diels-Alder-Reaktionen benötigten *N*-Acyl-Derivate **19a–k** und **21–t** wurden durch Acylierung des Enamincarbaldehyds **1a** und der Enamino-Ketone **2a–k** gebildet.

Simple enaminecarbaldehydes and enamino ketones are usefull starting compounds in the synthesis of heterocyclic compounds[1]. In contrast, enaminecarbaldehydes **1** and enamino ketones **2**, which bear an electron acceptor substituent at C-2 and at the CO-group, respectively, have so far hardly been investigated, and their synthetic value has not been completely evaluated.



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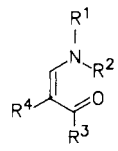
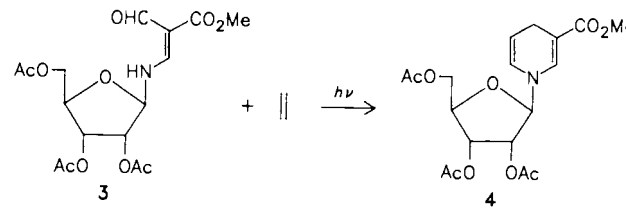
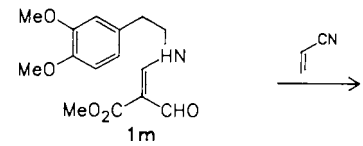


2

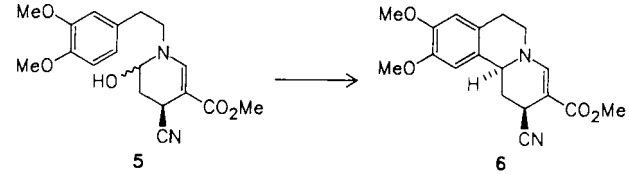
These compounds are of great utility, since they show ambident behavior in cycloaddition reactions; thus, as found by us, they can undergo a novel type of photochemical [2+2] as well as a thermal [4+2] cycloaddition. The photochemical cycloaddition of these enaminecarbaldehydes or enamino ketones lead via several intermediates to 2-hydroxytetrahydropyridines and 1,4-dihydropyridines[2]. Using this procedure, NADH analogues **4** can be obtained by reaction of *N*-glycosyl enaminecarbaldehydes such as **3** and alkenes, e.g. ethene[3]. This is at present one of the best methods for the synthesis of these biologically relevant substances[4]. In addition, 1,4-dihydropyridines have great importance as calcium antagonists[5] and the 2-hydroxytetrahydropyridines can be used as intermediates for the synthesis of ipecacuanha alkoloids by an iminium ion cyclization. Thus, photochemical reaction of the enaminecarbaldehyde **1m** and acrylonitrile gives the 2-hydroxytetrahydropyridine **5**, which cyclizes on treatment with boron trifluoride etherate on aluminum oxide to provide **6** in 80% yield[6].



3 **4**

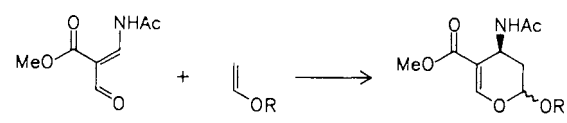


1m



5 **6**

On the other hand, the *hetero* Diels-Alder reactions of 7 and enol ethers **8** afford dihydropyrans **9**, which can be used for the synthesis of branched 3-amino sugars of the garosamine type[7]. In addition,



7 **8** **9**

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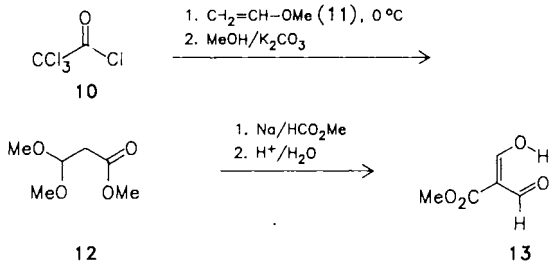
the *hetero* Diels-Alder reaction of the enamino ketones **2** is a key step in the preparation of 3-amino sugars of the daunosamine type[8].

It is essential that the enaminecarbaldehydes **1** and enamino ketones **2** used for the photochemical cycloaddition bear a hydrogen atom at the nitrogen to stabilize a cyclic form by intramolecular hydrogen bonding. This prevents a fast deactivation of the excited state by *E/Z* isomerization. Instead of *N*-alkyl, also *N*-acyl enaminecarbaldehydes **19** can be applied in the photochemical cycloaddition; however, in the latter case a loss of regioselectivity is observed. For the *hetero* Diels-Alder reaction only *N*-acyl enaminecarbaldehydes **19** and *N*-acyl enamino ketones **2l–t** can be used, since for the *N*-alkyl compounds **1** and **2a–k** the energy of the LUMO is too high to allow a thermal cycloaddition at a resonable reaction temperature.

In this paper we describe the synthesis of several enaminecarbaldehydes and enamino ketones, which have been used for photochemical cycloadditions and *hetero* Diels-Alder reactions.

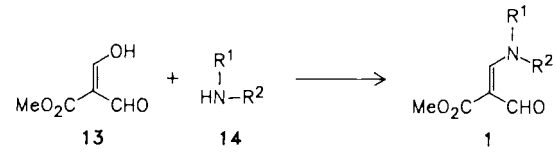
Synthesis of the Enaminecarbaldehydes

For the synthesis of the enaminecarbaldehydes **1a–s** methyl 2-formyl-3-oxopropanoate (diformylacetate, **13**) was used as educt. **13** can easily be obtained by a novel and highly efficient method appyling the reaction of trichloroacetyl chloride (**10**) with methyl vinyl ether (**11**), which gives 3,3-dimethoxypropanoate (**12**) after workup with methanol in the presence of potassium carbonate[9]; **12** was then formylated with methyl formate to give **13**[10].

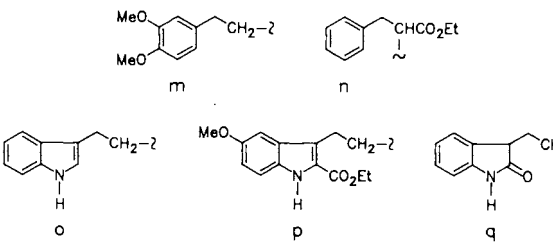


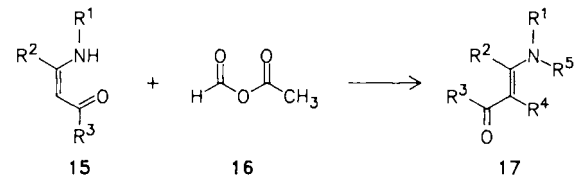
Condensation of **13** with primary or secondary amines **14b–s** in anhydrous toluene[11] in the presence of freshly calcined sodium sulfate at room temperature afforded the *N*-alkylated enamines **1b–s** in 72–93% yield. The reaction conditions are less suitable for gaseous amines and ammonia; here the condensation should be performed in anhydrous tetrahydrofuran at 50–60°C. Instead of the free amines their hydrochlorides can also be used; in this case an appropriate amount of sodium methanolate or better of a strongly basic ion exchange resin has to be added. Most of the applied amines could be purchased or are described in the literature. **14p** was obtained from diethyl 3-chloropropylmalonate and *p*-methoxyaniline according to a method by Szántay[12]. **14q** could be synthesized in a 5-step sequence from isatin by Knoevenagel reaction with cyanoacetic ester, catalytic hydrogenation of the double bond, hydrolysis, decarboxylation, and catalytic hydrogenation of the nitrile group to the amino function[13].

In cases, where the appropriate vinylogous acids or esters are not available, the formylation of enamino ketones such as **15a–c**[14] with acetic formic anhydride[15] (**16**) can be used for the synthesis of enaminecarbaldehydes. Thus, **17a** and **17b** were prepared from **15a** and **15b** applying this procedure in 77% yield. As a side reaction acylation at the nitrogen can occur; this was particularly pronounced with unsubstituted enaminecarbaldehyde **15c** (R^2 = H). Reaction of **15c** with **16** gave 38% of the desired product **17c** and 49% of the *N*-formyl derivative **17d**.

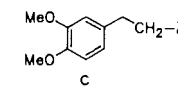


14, 1	R^1	R^2	14, 1	R^1	R^2
a	H	H	k	$C_6H_5CH_2$	H
b	CH_3	H	l	$C_6H_5CH(CH_3)$	H
c	$C(CH_3)_3$	H	m	m	H
d	n-C_4H_9	H	n	n	H
e	$CH_3CH_2O(CH_2)_3$	H	o	o	H
f	H_2C=$CHCH_2$	H	p	p	H
g	$MeO_2C(CH_2)_4$	H	q	q	H
h	C_6H_5	H	r	C_2H_5	C_2H_5
i	p-$O_2NC_6H_4$	H	s	$C_6H_5CH_2$	C_6H_5–CH_2
j	p-$MeOC_6H_4$	H			



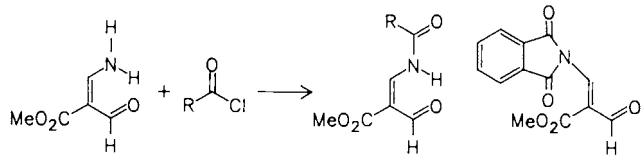


15, 17	R^1	R^2	R^3	R^4	R^5
a	CH_3	CH_3	OCH_3	CHO	H
b	CH_3	C_2H_5	OCH_3	CHO	H
c	c	H	CH_3	CHO	H
d	c	H	CH_3	H	CHO



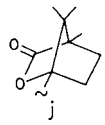
The vinylogous amide **1a** can easily be acylated to **19a–k** by reaction with acyl chlorides **18** in dichloromethane/ether/pyridine in 54–87% yield. **19a** could also be obtained in 60% yield by condensation of diformylacetate **13** with acetamide. The urea derivative **19k** was synthesized by addition of **1a** to phenyl isocyanate. Monoalkylated enaminecarbaldehydes, e.g. **1b–q**, can also be acylated, however, the *N*-acyl derivatives are quite unstable, and a deacylation occurs

during workup. In contrast, the *N*-acyl derivaties with hydrogen at the nitrogen are stable except for **19b**, and some of them (**19a, c, d, f, g**) could be obtained in a crystalline form. Also, the phthalimide derivative **20**, formed by reaction of **1a** and phthalic chloride can be stored without decomposition.

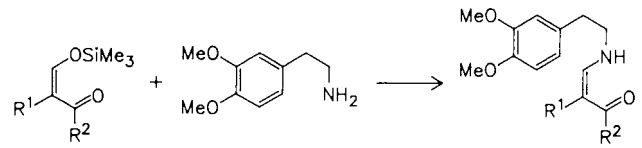


1a 18 19 20

18, 19	R
a	H_3C
b	$(H_3C)_3C$
c	C_6H_5
d	p-$O_2NC_6H_4$
e	3-indolyl-CH_2
f	H_3CO

18, 19	R
g	$C_6H_5CH_2OCHCH_3$
h	$CH_3COOCHC_6H_5$
i	$C_6H_5C(OCH_3)(CF_3)$
j	
k	C_6H_5NH

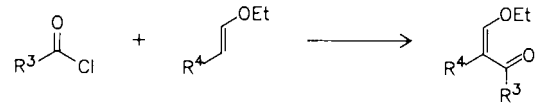
For the synthesis of enaminecarbaldehydes derived from less stable β-dicarbonyl compounds such as malonic aldehydes[16] or formyl acetone[17], the direct condensation method cannot be used. However, they are easily prepared by reaction of the trimethylsilyl enol ethers **21** with primary amines. Thus, amination of **21a** with homoveratrylamine **14m** afforded **22a** in excellent yield. In the same way the enamino ketone **22b** was obtained starting with **21b**.



21 14m 22

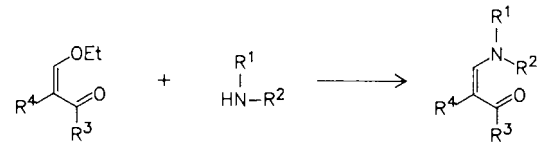
21, 22	R^1	R^2
a	C_2H_5	H
b	H	CH_3

The enamino ketones **2a–k** were prepared in 61–97% yield analogously to the enaminecarbaldehydes **1** by condensation of ammonia and amines **25** with the enol ethers **24a–k**, which can easily be synthesized by reaction of activated acyl chlorides **23a–k** and ethyl vinyl ether according to Effenberger[9,18]. Acylation of the non- or monoalkylated enamino ketones **2** with acyl chlorides in the presence of 4-dimethylaminopyridine/triethylamine afforded the *N*-acyl derivatives **2l–r**, mostly in excellent yield; the use of pyridine as base was not suitable in this reaction. In the same way as described for **21** also chiral enamino ketones can be obtained starting from monoesters of oxalyl chloride with chiral alcohols. Reaction of an excess of oxalyl dichloride with (+)-menthol gave (+)-menthyl oxalyl chloride **23k**, which was treated with ethyl vinyl ether to afford the enol ether **24k**. Condensation of **24k** with ammonia at 50–60°C in tetrahydrofuran followed by acylation with phthaloyl dichloride gave the chiral enamino ketone **2t** in a total yield of 60%.



23 24

24	R^3	R^4
a	CO_2Me	H
b	CCl_3	H
c	$CHCl_2$	H
d	CCl_3	Br
j	CO_2Et	Br
k	CO_2-menthyl	H



24 25 2

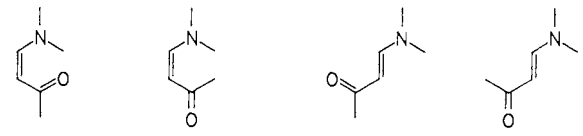
2, 24, 25	R^1	R^2	R^3	R^4
a	H	H	CO_2Me	H
b	H	H	CCl_3	H
c	H	H	$CHCl_2$	H
d	H	H	CCl_3	Br
e	Bzl	H	CO_2Me	H
f	CH_3	H	CCl_3	H
g	$CH(CH_3)Ph$	H	CCl_3	H
h	CH_3	CH_3	CCl_3	H
i	$C_6H_5CH(OH)CHCH_3$	CH_3	CCl_3	H
j	H	H	CO_2Et	Br
k	H	H	CO_2-menthyl	H
l	C_6H_5CO	H	CO_2Me	H
m	MeO_2CCO	H	CO_2Me	H
n	C_6H_5CO	$C_6H_5CH_2$	CO_2Me	H
o	EtO_2CCO	CH_3	CCl_3	H
p	p-$O_2NC_6H_4CO$	C_6H_5–$CH(CH_3)$	CCl_3	H
q	–phthaloyl–		CO_2Me	H
r	–phthaloyl–		CCl_3	H
s	C_6H_5CO	H	CO_2Et	Br
t	–phthaloyl–		CO_2-menthyl	H

Structure of the Enaminecarbaldehydes and Enamino Ketones

Simple enaminecarbaldehydes or enamino ketones with the general structure O=C–C=C–N can exist in the four different configurations/conformations **A–D**[19].

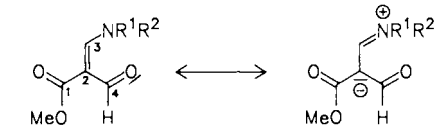
The enaminecarbaldehydes **1**, **17** and **19**, however, bear an additional carbonyl group, which can also display two different ori-

entations. Thus, for **1**, **17** and **19** eight possible conformations have to be discussed. The rules for the nomenclature of the simple compounds are not sufficient for these substances, since they do not allow to determine the conformation of both carbonyl groups.



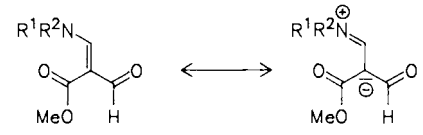
Z, s–Z **A** *Z, s–E* **B** *E, s–Z* **C** *E, s–E* **D**

Therefore we suggest, to extend the normal rules by addition of the conformation of the second carbonyl group with lower priority, e.g. as in **E** and **F**.



E, s–Z, s–Z = apapap

E



Z, s–Z, s–Z = apspap

F

A second possibility, however, would be a nomenclature based on the conformations obtained by rotation about the three bonds C-1–C-2, C-2–C-3, and C-2–C-4, e.g. as in **E** and **F**.

According to the torsion angles, the C=O and C=N groups can have a synperiplanar (sp) arrangement with $30° > \Theta > 330°$ and an antiperiplanar (ap) arrangement with $150° < \Theta < 210°$.

The *E,s-Z,s-Z* arrangement **E** would be named an apapap and the *Z,s-Z,s-Z* arrangement **F** an apspap conformation.

The existence of the different configurations/conformations is due to partial double bonds between C-1–C-2, C-2–C-3, and C-2–C-4. The strength of the bonds is mainly influenced by substituents at C-2 and the N atom. Thus, electron-withdrawing groups at the *N* atom enhance the character of the double bond between C-2 and C-3, and reduce the barrier of rotation about the single bonds between the CO groups and C-2[20]. On the other hand, electron-withdrawing substituents at C-2 reduce the character of the double bond between C-2 and C-3[21].

Most of the prepared enaminecarbaldehydes **1** exist as a mixture of the two isomeric forms **E** and **F**. For the determination of the structure, spectroscopic methods such as UV[22], IR[23], and NMR spectroscopy have been used. The relationship between the configuration of enamino ketones and the wave length as well as the intensity of their UV absorption has already been discussed in several papers, and general rules for the calculation of λ_{max} based on increments have been published[22]. Since the λ_{max} values for the parent enaminecarbaldehyd and the enamino ester are different and the increment for the second CO group is zero, the rules can be used for the determination of the configuration of enaminecarbaldehydes of type **1**.

The results (Table 1) show that for enaminecarbaldehydes **1a–q** with an –NHR group the configuration/conformation **E** is more populated, whereas in compounds **1r–s** with an $-NR_2$ group ($R \neq H$) the confirguration/conformation **F** should dominate.

Table 1. Calculated and measured λ_{max} [nm] for different enaminecarbaldehydes **1**

1	R^1	R^2	Calculated for isomer **E**	Calculated for isomer **F**	Measured
a	H	H	287	268	287[a]
d	H	*n*-C_4H_9	306	287	299[b]
h	H	C_6H_5	339	330	337[b]
r	C_2H_5	C_2H_5	275	297	310[c]

[a] In CH_3CN. – [b] In ether. – [c] In CH_3OH.

In contrast to UV measurements, ^{1}H-NMR spectroscopy allows a rather exact determination of the ratio of isomers **E** and **F** using the absorption of the aldehydic proton (4-H) and the methoxycarbonyl moiety. Thus, in the dominating *E,s-Z,s-Z* isomer **E**, 4-H absorbs at lower (0.03–0.20 ppm) and the CH_3O groups at higher field compared to isomer **F**. The coupling constants for the aldehydic proton are found to be $J = 3.6$ Hz for isomer **E** and $J = 0–1$ Hz for isomer **F**.

Table 2. Selected ^{1}H-NMR data [δ(4-H)] of enaminecarbaldehydes **1** in $CDCl_3$

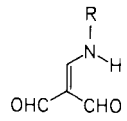
	Conformation *E,s-Z,s-Z*	*Z,s-Z,s-Z*		Conformation *E,s-Z,s-Z*	*Z,s-Z,s-Z*
1a	9.80	9.62	**j**	9.93	–
b	9.83	9.63	**k**	9.77	9.69
c	9.63	9.57	**l**	9.80	–
d	9.80	9.72	**m**	9.75	9.61
d	9.66[a]	9.48[a]	**n**	9.84	–
d	9.68[b]	9.58[b]	**o**	9.97	9.83
e	9.73	9.70	**p**	9.62	9.43
f	9.70	–	**q**	9.70	9.57
g	9.80	9.75	**r**	–	9.68
h	9.95	–	**s**	–	9.77
i	9.98	9.90			

[a] In CD_3OD. – [b] In [D_6]DMSO.

According to the Sternhell[24] equation for a planar system, a coupling constant of $J = 2$ Hz should be found for the aldehydic proton in isomer **E**. The higher value observed may be explained by the partial double bond character of the bond C-4–C-2. However, the measured coupling constants only fit with an *E.s-Z,s-Z* orientation **E**. Similar results were obtained by Breitmeier[25] with related systems.

Calculations for configuration/conformation **F** give a coupling constant for the aldehydic proton of $J = 0.1–1.6$ Hz. Although this correlates well with the observed value, the difference to the coupling constant of 4-H in isomer **E** is too small to be an exact proof. However, we were able to

confirm the results of the calculations by experimental evidence using enaminecarbaldehyde **26**. In this compound two formyl groups exist, which have either the *Z,s-Z* or the *E,s-Z* configuration/conformation. In agreement with our considerations we found two signals for the aldehydic protons, one at $\delta = 9.73$ with $J = 3.6$ Hz and one at $\delta = 9.53$ with $J < 0.5$ Hz.



26

Although there is no clear-cut proof for the *s-Z* conformation of the ester CO and aldehyde CO group, respectively, in the isomers **E** and **F**, we assume this preference from the chemical shift of the vinylic proton[22c]. Also, it has been shown that the *s-Z* conformer of α,β-unsaturated carbonyl compounds is stabilized by about 8 kJ/mole compared to the *s-E* conformer.

The ratio of the isomers **E** and **F** in solution depends on the solvent, the temperature, and the character of the substituents at C-2 and the nitrogen.

It has been found that for the enaminecarbaldehydes **1a–q** with an NH group the amount of the less populated configuration/conformation **F** increases with growing polarity of the solvent and rising temperature. **1d** shows a ratio of isomer **E** and **F** at 25°C of 91:9 in $CDCl_3$, 78:22 in [D_6]DMSO, and 75:25 in [D_4]MeOH. At lower temperatures only isomer **E** is found. The *N*-aryl enaminecarbaldehydes **1h** and **1j** exist in $CDCl_3$ at 25°C as isomer **E** only, whereas for the *N*-aryl enaminecarbaldehyde **1i** and for the *N*-acyl compounds **19** a ratio of **E** and **F** of about 80:20 is found at room temperature. In contrast to these results, *N,N*-dialkyl enaminecarbaldehydes **1r** and **1s** exclusively exist in the configuration/conformation **F**. In the latter compounds hydrogen bonding is not possible and resonance stabilization would be larger in the *Z,s-Z,s-Z* orientation **F**. We assume that in these compounds the ester moiety is not in plane with the enamine any more. This has been confirmed for the phthalimide derivative **20** by crystal structure analysis and also deduced from the low reactivity of **20** in *hetero* Diels-Alder reactions[7].

Table 3. Selected ^{13}C-NMR data (δ) of enaminecarbaldehydes **1** in $CDCl_3$

Carbon	Conformation	1a[a]	b	f	h	j	m	o
C-1	*E,s-Z,s-Z*	169.82	167.78	167.70	167.32	167.38	167.68	167.87
C-1	*Z,s-Z,s-Z*	169.69	169.36	169.33	–	169.28	169.28	169.35
C-4	*E,s-Z,s-Z*	191.58	189.96	190.25	191.10	190.57	190.06	190.07
C-4	*Z,s-Z,s-Z*	189.87	187.12	187.31	187.59	187.31	187.22	187.42

[a] In CD_3OD.

^{13}C-NMR spectroscopy has so far only rarely been used for the determination of the configuration/conformation of enamino ketones[21a,26]. No systematic investigations are known for diacyl enamines. In contrast to the monoacyl enamines, the difference of the chemical shift values for C-2 and C-3 of isomers **E** and **F** is small. However, a pronounced difference is found for the aldehyde CO group (C-4). C-4 absorbs at $\delta = 189-192$ in the *E,s-Z,s-Z* (**E**) and at $\delta = 186-189$ in the *Z,s-Z,s-Z* (**F**) isomer (Table 3).

For **1r** only one set of signals is found with an absorption for C-4 at $\delta = 187.2$, indicating that this compound has a *Z,s-Z,s-Z* configuration/conformation. This is in agreement with the results obtained from UV and ^{1}H-NMR spectroscopy.

The chemical shift values in ^{13}C-NMR spectra correlate quite well with the electron density at the carbons. A comparison of chemical shift values for C-2, C-3 and C-1/C-4 of **1a** and **29**[25] clearly shows that for the enaminecarbaldehyde **1a** the iminium enolate resonance structure **28** in **27**↔**28** has more importance than for the simple enaminecarbaldehydes **29** (Fig. 1). Of great interest is also a comparison of the ^{13}C-NMR data of **30** and **31** (Fig. 1). **30** is much more polarized; this can be explained by a deviation of the enamino ketone system from planarity due to a steric interaction of the methyl groups at C-3 and the nitrogen.

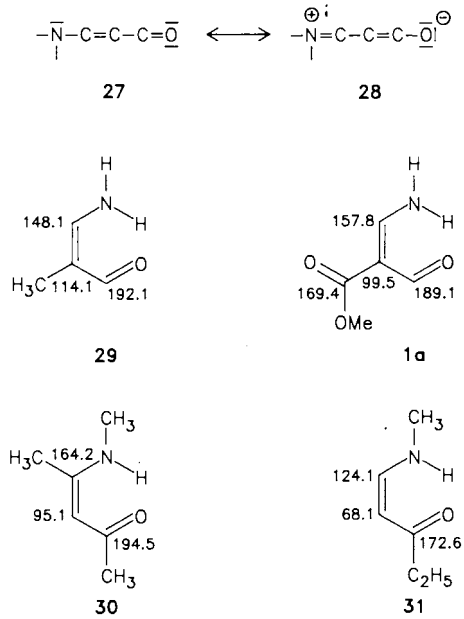


Figure 1. Comparison of ^{13}C-NMR data of enaminecarbaldehydes **1a** and **29** as well as of enamino ketones **30** and **31**

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*.

Experimental

IR: Perkin-Elmer 297. – UV: Varian-Cary 219. – ^{1}H NMR: Varian EM-360A, XL-100, XL-200, FT-80A. The assignment of the chemical shifts to the two isomers is indicated by "-*E*" for the *E,s-Z,s-Z* (**E**) and "-*Z*" for the *Z,s-Z,s-Z* isomer (**F**). – Melting points: Kofler melting point apparatus (corrected values). – Elemental analyses were carried out at the analytical laboratory of the university.

Methyl 3-Amino-2-formyl-2-propenoate (**1a**): A suspension of freshly calcined Na_2SO_4 (15.0 g) and **13** (2.60 g, 20.0 mmol) in anhydrous tetrahydrofuran (100 ml) is heated to reflux. Dry ammonia is passed through the solution with vigorous stirring, whereby a colorless precipiate is formed. The addition of ammonia is continued until the primarily formed precipitate has dissolved and **13** cannot be detected any more by TLC. Na_2SO_4 is filtered off and washed twice with warm acetone. The combined extracts are dried with Na_2SO_4, and the solvent is removed in vacuo to afford the crude product, which is purified by recrystallization; yield 2.18 g (84%), m.p. 115°C (CH_3CN). IR (KBr): ν = 3370 cm^{-1}, 3240 (N–H), 1680, 1645 (C=O), 1510 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 227 nm (4.201), 287 (4.167). – ^{1}H NMR (CD_3CN): δ = 3.69 (s, 2.3 H, OCH_3-*E*), 3.72 (s, 0.7 H, OCH_3-*Z*), 6.6–8.0 (br., 1 H, NH), 7.91 (dd, *J* = 16.0, 8.2 Hz, 0.2 H, 3-H-*Z*), 7.96 (ddd, *J* = 16.0, 8.2, 3.5 Hz, 1 H, 3-H-*E*), 9.62 (s, 0.2 H, CHO-*Z*), 9.80 (d, *J* = 3.5 Hz, 0.8 H, CHO-*E*), 9.2–10.6 (br., 1 H, NH).

$C_5H_7NO_3$ (129.1) Calcd. C 46.51 H 5.46 N 10.85
Found C 46.50 H 5.51 N 10.93

Synthesis of the Enaminecarbaldehydes **1b–s**. – *General Procedure I. – Reaction of Methyl 2-Formyl-3-oxopropenoate* (**13**) *with Primary or Secondary Amines* **14b–s**: To a solution of **13** (2.60 g, 20.0 mmol) in anhydrous toluene (100 ml) are added freshly calcined Na_2SO_4 (15 g) and an equimolar amount of a primary or secondary amine **14b–s**, dissolved in 30 ml of anhydrous toluene. The reaction mixture is stirred at room temp. for 1–3 h (TLC control on silica gel with mixtures of ethyl acetate and petroleum ether), Na_2SO_4 is filtered off, and the combined solvents are evaporated under reduced pressure to afford the crude product. Purification was accomplished by recrystallization from ether, ethyl acetate, or acetonitrile.

Methyl 2-Formyl-3-methylamino-2-propenoate (**1b**): Methylamine was condensed with **13** according to procedure I. Recrystallization gave 2.66 g (93%) of **1b**, m.p. 69°C. – IR (KBr): ν = 3210 cm^{-1} (N–H), 1685, 1625 (C=O), 1595 (C=C). – UV (ether): λ_{max} (lg ε) = 231 nm (4.182), 298 (4.174). – ^{1}H NMR ($CDCl_3$): δ = 3.17 (d, *J* = 4.5 Hz, 3 H, NCH_3), 3.77 (s, 3 H, OCH_3) 7.93 (m, 1 H, 3-H), 9.63 (s, 0.1 H, CHO-*Z*), 9.83 (d, *J* = 3.6 Hz, 0.9 H, CHO-*E*), 10.70 (br., 1 H, NH).

$C_6H_9NO_3$ (143.1) Calcd. C 50.35 H 6.34 N 9.79
Found C 50.34 H 6.41 N 9.86

Methyl 3-tert-Butylamino-2-formyl-2-propenoate (**1c**): *tert*-Butylamine was condensed with **13** according to procedure I. Recrystallization gave 3.68 g (81%) of **1c**, m.p. 55°C. – IR (KBr): ν = 3200 cm^{-1} (N–H), 1690, 1650 (C=O), 1595 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 235 nm (4.209), 300 (4.218). – ^{1}H NMR ($CDCl_3$): δ = 1.35 [s, 9 H, $C(CH_3)_3$], 3.74 (s, 2.4 H, OCH_3-*E*), 3.77 (s, 0.6 H, OCH_3-*Z*), 7.98 (dd, *J* = 14, 4 Hz, 0.8 H, 3-H-*E*), 8.05 (d, *J* = 14 Hz, 0.2 H, 3-H-*Z*), 9.57 (s, 0.2 H, CHO-*Z*), 9.63 (d, *J* = 4 Hz, 0.8 H, CHO-*E*), 10.95 (br., 1 H, NH).

$C_9H_{15}NO_3$ (185.2) Calcd. C 58.36 H 8.16 N 7.56
Found C 58.56 H 8.14 N 7.47

Methyl 3-Butylamino-2-formyl-2-propenoate (**1d**): *n*-Butylamine was condensed with **13** according to procedure I; yield 3.24 g (88%) of **1d**, n_D^{20} = 1.5228. – IR (film): ν = 3210 cm^{-1} (N–H), 1700, 1650 (C=O), 1595 (C=C). – UV (ether): λ_{max} (lg ε) = 231 nm (4.070), 299 (4.190). – ^{1}H NMR ($CDCl_3$): δ = 0.93 (t, *J* = 6 Hz, 3 H, CH_3), 1.13–1.92 (m, 4 H, 2 CH_2), 3.40 (q, *J* = 7 Hz, 2 H, NCH_2), 3.56 (s, 2.7 H, OCH_3-*E*), 3.60 (s, 0.3 H, OCH_3-*Z*), 7.97 (dd, *J* = 14, = 4 Hz, 1 H, 3-H), 9.72 (s, 0.1 H, CHO-*Z*), 9.80 (d, *J* = 4 Hz, 0.9 H, CHO-*E*), 10.70 (br., 1 H, NH).

$C_9H_{15}NO_3$ (185.2) Calcd. C 58.36 H 8.16 N 7.56
Found C 58.83 H 7.86 N 7.53

Methyl 3-(3-Ethoxypropylamino)-2-formyl-2-propenoate (**1e**): 3-Ethoxypropylamine was condensed with **13** according to procedure I. Recrystallization gave 3.96 g (92%) of **1e**, m.p. 53°C. – IR (KBr): ν = 3200 cm^{-1}, 3140 (N–H), 1690, 1645 (C=O), 1580 (C=C). – UV (ether): λ_{max} (lg ε) = 232 nm (4.211), 299 (4.212). – ^{1}H-NMR ($CDCl_3$): δ = 1.25 (t, *J* = 9 Hz, 3 H, CH_2CH_3), 1.88 (quint, *J* = 9 Hz, 2 H, $CH_2CH_2CH_2$), 3.34–3.64 (m, 6 H, NCH_2, CH_2OCH_2), 3.70 (s, 2.7 H, OCH_3-*E*), 3.73 (s, 0.3 H, OCH_3-*Z*), 7.90 (m, 1 H, 3-H), 9.70 (s, 0.1 H, CHO-*Z*), 9.73 (d, *J* = 4 Hz, 0.9 H, CHO-*E*), 10.66 (br., 1 H, NH).

$C_{10}H_{17}NO_4$ (215.2) Calcd. C 55.80 H 7.96 N 6.51
Found C 55.90 H 7.92 N 6.49

Methyl 2-Formyl-3-(2-propen-1-ylamino)-2-propenoate (**1f**): Allylamine was condensed with **13** according to procedure I. Recrystallization gave 2.84 g (84%) of **1f**, m.p. 42°C. – IR (KBr): ν = 3320 cm^{-1} (N–H), 3040 (C=C–H), 1710, 1675, 1640 (C=O), 1600, 1580 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 233 nm (4.203), 300 (4.213). – ^{1}H NMR ($CDCl_3$): δ = 3.70 (s, 3 H, OCH_3), 3.91 (m_c, 2 H, NCH_2), 5.00–6.20 (m, 3 H, $CH=CH_2$), 7.85 (dd, *J* = 14.0, 3.5 Hz, 1 H, 3-H), 9.70 (d, *J* = 3.5 Hz, 1 H, CHO), 10.50 (br., 1 H, NH).

$C_8H_{11}NO_3$ (169.2) Calcd. C 56.80 H 6.55 N 8.28
Found C 56.82 H 6.52 N 8.33

Dimethyl 2-Formyl-4-azanon-2-ene-1,9-dioate (**1g**): To a solution of **13** (2.60 g, 20.0 mmol) and methyl 5-aminopentanoate hydrochloride (2.64 g, 20.0 mmol) in anhydrous toluene (60 ml) was added dropwise a solution of sodium methanolate (1.19 g, 22.0 mmol) in methanol (20 ml) at 20°C. The mixture was stirred for 15 h at room temp. and worked up according to procedure I. Recrystallization gave 3.60 g (74%) of **1g**, m.p. 60°C. – IR (KBr): ν = 3220 cm^{-1} (N–H), 1735, 1695, 1630 (C=O), 1590 (C=C). – UV (CH_3OH): λ_{max} (lg ε) = 236 nm (4.201), 2.99 (4.228). – ^{1}H NMR ($CDCl_3$): δ = 1.68 (m, 4 H, CH_2CH_2), 2.35 (t, *J* = 6 Hz, 2 H, $CH_2CO_2CH_3$), 3.38 (m, 2 H, NCH_2), 3.70, 3.80 (2s, 6 H, 2 OCH_3), 7.90 (m, 1 H, 3-H), 9.75 (s, 0.1 H, CHO-*Z*), 9.80 (d, *J* = 3.5 Hz, 0.9 H, CHO-*E*), 10.73 (br., 1 H, NH).

$C_{11}H_{17}NO_5$ (243.3) Calcd. C 54.31 H 7.04 N 5.76
Found C 54.36 H 6.86 N 5.80

Methyl 2-Formyl-3-phenylamino-2-propenoate (**1h**): Aniline was condensed with **13** according to procedure I. Recrystallization gave 3.57 g (87%) of **1h**, m.p. 73°C. – IR (KBr): ν = 3080 cm^{-1} (N–H), 1695, 1655 (C=O), 1600, 1580 (C=C). – UV (ether): λ_{max} (lg ε) = 232 nm (4.213), 337 (4.316). – ^{1}H NMR ($CDCl_3$): δ = 3.83 (s, 3 H, OCH_3), 7.30 (m, 5 H, PhH), 8.43 (dd, *J* = 14.0, 3.5 Hz, 1 H, 3-H), 9.95 (d, *J* = 3.5 Hz, 1 H, CHO), 12.35 (br., 1 H, NH).

$C_{11}H_{11}NO_3$ (205.2) Calcd. C 64.38 H 5.40 N 6.83
Found C 64.58 H 5.54 N 6.84

Methyl 2-Formyl-3-(4-nitrophenylamino)-2-propenoate (**1i**): 4-Nitroaniline was condensed with **13** according to procedure I. Recrystallization gave 4.45 g (89%) of **1i**, m.p. 172°C. – IR (KBr): ν = 3080 cm^{-1} (N–H), 1705, 1630 (C=O), 1590, 1570 (C=C), 1500 (NO_2). – UV (ether): λ_{max} (lg ε) = 225 nm (3.964), 361 (4.253). – ^{1}H NMR ($CDCl_3$): δ = 3.85 (s, 2.5 H, OCH_3-*E*), 3.86 (s, 0.5 H, OCH_3-*Z*), AA'BB' system, δ_a = 7.33, δ_b = 8.30 (4 H, PhH), 8.37 (m, 1 H, 3-H), 9.90 (s, 0.2 H, CHO-*Z*), 9.98 (d, *J* = 3.5 Hz, 0.8 H, CHO-*E*), 12.50 (br., 1 H, NH).

$C_{11}H_{10}N_2O_5$ (250.2) Calcd. C 52.80 H 4.03 N 11.20
Found C 52.81 H 4.09 N 11.20

Methyl 2-Formyl-3-(4-methoxyphenylamino)-2-propenoate (**1j**): 4-Methoxyanilin was condensed with **13** according to procedure I. Recrystallization gave 3.38 g (72%) of **1j**, m.p. 100°C. – IR (KBr): ν = 3060 cm^{-1} (N–H), 1690, 1645 (C=O), 1595, 1565 (C=C). – UV (ether): λ_{max} (lg ε) = 239 nm (4.145), 348 (4.328). – ^1H NMR ($CDCl_3$): δ = 3.81 (s, 6H, $2OCH_3$), AA'BB' system, δ_a = 6.92, δ_b = 7.15 (4H, PhH), 8.32 (dd, *J* = 14.0, 3.5 Hz, 1H, 3-H), 9.93 (d, *J* = 3.5 Hz, 1H, CHO), 12.55 (br., 1H, NH).

$C_{12}H_{13}NO_4$ (235.2) Calcd. C 61.27 H 5.57 N 5.95
Found C 61.37 H 5.65 N 6.08

Methyl 3-Benzylamino-2-formyl-2-propenoate (**1k**): Benzylamine was condensed with **13** according to procedure I. Recrystallization gave 4.03 g (92%) of **1k**, m.p. 84°C. – IR (KBr): ν = 3200 cm^{-1}, 3140 (N–H), 1690, 1645 (C=O), 1590, 1580 (C=C). – UV (ether): λ_{max} (lg ε) = 236 nm (4.201), 299 (4.209). – ^1H NMR ($CDCl_3$): δ = 3.70 (s, 3H, OCH_3), 4.53 (d, *J* = 6 Hz, 2H, NCH_2), 7.23 (m, 5H, PhH), 7.90 (m, 1H, 3-H), 9.69 (s, 0.1H CHO-*Z*), 9.77 (d, *J* = 3.5 Hz, 0.9H, CHO-*E*), 10.93 (br., 1H, NH).

$C_{12}H_{13}NO_3$ (219.2) Calcd. C 65.74 H 5.98 N 6.39
Found C 65.63 H 5.99 N 6.39

Methyl (S)-2-Formyl-3-(1-phenylethylamino)-2-propenoate (**1l**): (*S*)-1-Phenylethylamine was condensed with **13** according to procedure I. Recrystallization gave 4.43 g (95%) of **1l**, m.p. 68°C, $[\alpha]_D^{20}$ = –162.3 (*c* = 0.67 in $CHCl_3$). – IR (KBr): ν = 3450 cm^{-1} (N–H), 1695, 1640 (C=O), 1590, 1580 (C=C). – UV (ether): λ_{max} (lg ε) = 236 nm (4.279), 302 (4.272). – ^1H NMR ($CDCl_3$): δ = 1.60 (d, *J* = 7 Hz, 3H, CH_3), 3.70 (s, 3H, OCH_3), 4.60 (m, 1H, NCH), 7.28 (m, 5H, PhH), 7.93 (dd, *J* = 14.0, 3.5 Hz, 1H, 3-H), 9.80 (d, *J* = 3.5 Hz, 1H, CHO), 11.06 (br., 1H, NH).

$C_{13}H_{15}NO_3$ (233.3) Calcd. C 66.94 H 6.48 N 6.00
Found C 67.02 H 6.48 N 5.99

Methyl 3-[2-(3,4-Dimethoxyphenyl)ethylamino]-2-formyl-2-propenoate (**1m**): 2-(3,4-Dimethoxyphenyl)ethylamine was condensed with **13** according to procedure I. Recrystallization gave 5.40 g (92%) of **1m** m.p. 91°C. – IR (KBr): ν = 3200 cm^{-1} (N–H), 1695, 1645 (C=O), 1595 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 233 nm (4.354), 301 (4.230). – ^1H NMR ($CDCl_3$): δ = 2.82 (t, *J* = 7 Hz, 2H, $PhCH_2$), 3.56 (q, *J* = 7 Hz, 2H, NCH_2), 3.68 (s, 3H, OCH_3), 3.82 (s, 6H, $2OCH_3$), 6.64 (d, *J* = 2 Hz, 1H, ar-2-H), 6.68 (dd, *J* = 8, 2 Hz, 1H, ar-6-H), 6.80 (d, *J* = 8 Hz, 1H, ar-5-H), 7.77 (dd, *J* = 14.0, 3.5 Hz, 0.9H, 3-H-*E*), 7.85 (d, *J* = 14 Hz, 0.1H, 3-H-*Z*), 9.61 (s, 0.1H, CHO-*Z*), 9.75 (d, *J* = 3.5 Hz, 0.9H, CHO-*E*), 10.70 (br., 1H, NH).

$C_{15}H_{19}NO_5$ (293.3) Calcd. C 61.42 H 6.53 N 4.78
Found C 61.25 H 6.55 N 4.83

Methyl (S)-3-(1-Ethoxycarbonyl-2-phenylethylamino)-2-formyl-2-propenoate (**1n**): (*S*)-1-Ethoxycarbonyl-2-phenylethylamine was condensed with **13** according to procedure I. Recrystallization gave 5.40 g (88%) of **1n**, m.p. 59°C, $[\alpha]_D^{20}$ = –166.8 (*c* = 1.0 in $CHCl_3$). – IR (KBr): ν = 3400 cm^{-1} (N–H), 1740, 1705, 1655 (C=O), 1585, 1500 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 232 nm (4.137), 300 (4.210). – ^1H NMR ($CDCl_3$): δ = 1.25 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 3.05 (dd, *J* = 14.1, 8.8 Hz, 1H, $PhCH_aH_b$), 3.27 (dd, *J* = 14.1, 5.0 Hz, 1H, $PhCH_aH_b$), 3.70 (s, 3H, OCH_3), 4.13 (ddd, *J* = 9.0, 8.8, 5.0 Hz, 1H, O_2CCH), 4.23 (q, *J* = 7.2 Hz, 2H, CH_2CH_3), 7.16 (dd, *J* = 7.5, 2.0 Hz, 2H, ar-2-H, ar-6-H), 7.26–7.38 (m, 3H, ar-3-H, ar-4-H, ar-5-H), 7.57 (dd, *J* = 13.7, 3.5 Hz, 1H, 3-H), 9.84 (d, *J* = 3.5 Hz, 1H, CHO), 10.96 (br., 1H, NH).

$C_{16}H_{19}NO_5$ (305.3) Calcd. C 62.94 H 6.27 N 4.59
Found C 62.73 H 6.14 N 4.64

Methyl 3-[2-(3-Indolyl)ethylamino]-2-formyl-2-propenoate (**1o**): Tryptamine was condensed with **13** according to procedure I. Recrystallization gave 4.41 g (81%) of **1o**, m.p. 128°C. – IR (KBr): ν = 3400 cm^{-1}, 3200 (N–H), 1680, 1640 (C=O), 1600 (C=C). – UV (CH_3OH): λ_{max} (lg ε) = 222 nm (4.524), 291 (4.154). – ^1H NMR ($CDCl_3$): δ = 3.05 (t, *J* = 6 Hz, 2H, CH_2), 3.57 (m, 2H, NCH_2), 3.75 (s, 3H, OCH_3), 6.80–7.73 (m, 5H, indole-CH), 7.88 (m, 1H, 3-H), 8.80 (s, 1H, indole-NH), 9.83 (s, 0.1H, CHO-*Z*), 9.97 (d, *J* = 3.5 Hz, 0.9H, CHO-*E*), 10.95 (br., 1H, NH).

$C_{15}H_{16}N_2O_3$ (272.3) Calcd. C 66.16 H 5.92 N 10.29
Found C 66.30 H 5.77 N 10.30

Methyl 3-[2-(2-Ethoxycarbonyl-5-methoxy-3-indolyl)ethylamino]-2-formyl-2-propenoate (**1p**): 2-Ethoxycarbonyl-5-methoxytryptamine was condensed with **13** according to procedure I. Recrystallization gave 6.51 g (87%) of **1p**, m.p. 201°C. – IR (KBr): ν = 3340 cm^{-1}, 3240 (N–H), 1710, 1685, 1650 (C=O), 1500 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 226 nm (4.226), 300 (4.219). – ^1H NMR ([D_6]DMSO): δ = 1.35 (t, *J* = 7 Hz, 3H, CH_2CH_3), 3.30–3.70 (m, 4H, NCH_2CH_2), 3.58 (s, 2.3H, CO_2CH_3-*E*), 3.63 (s, 0.7H, CO_2CH_3-*Z*), 3.78 (s, 3H, OCH_3), 4.30 (q, *J* = 7 Hz, 2H, CH_2CH_3), 6.77–7.43 (m, 3H, indole-CH), 7.63 (d, *J* = 14 Hz, 0.3H, 3-H-*Z*), 7.70 (dd, *J* = 14.0, 3.5 Hz, 0.7 H, 3-H-*E*), 9.43 (s, 0.3H, CHO-*Z*), 9.62 (d, *J* = 3.5 Hz, 0.7H, CHO-*E*), 10.65 (br., 1H, NH), 11.52 (s, 1H, indole-NH).

$C_{19}H_{22}N_2O_6$ (374.4) Calcd. C 60.95 H 5.92 N 7.48
Found C 61.13 H 5.97 N 7.61

Methyl 3-[2-(2,3-Dihydro-2-oxo-3-indolyl)-ethylamino]-2-formyl-2-propenoate (**1q**): 2-(2,3-Dihydro-2-oxo-3-indolyl)ethylamine was condensed with **13** according to procedure I. Recrystallization gave 4.32 g (75%) of **1q**, m.p. 153°C. – IR (KBr): ν = 3300 cm^{-1}, 3220 (N–H), 1735, 1720, 1650 (C=O), 1595 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 235 nm (4.241), 299 (4.160). – ^1H NMR ($CDCl_3$): δ = 2.30 (m, 2H, CH_2), 3.20–3.70 (m, 3H, NCH_2, indole-3-H), 3.70 (s, 3H, OCH_3), 6.77–7.33 (m, 4H, indole-CH), 7.78 (m, 1H, 3-H), 9.10 (br., 1H, indole-NH), 9.57 (s, 0.1H, CHO-*Z*), 9.70 (d, *J* = 3.5 Hz, 0.9H, CHO-*E*), 10.67 (br., 1H, NH).

$C_{15}H_{16}N_2O_4$ (288.3) Calcd. C 62.49 H 5.59 N 9.72
Found C 62.52 H 5.42 N 9.69

Methyl 3-Diethylamino-2-formyl-2-propenoate (**1r**): Diethylamine was condensed with **13** according to procedure I. Recrystallization gave 2.81 g (76%) of **1r**, m.p. 55°C. – IR (KBr): ν = 1690 cm^{-1}, 1640 (C=O), 1575 (C=C). – UV (CH_3OH): λ_{max} (lg ε) = 245 nm (4.003), 310 (4.135). – ^1H NMR ($CDCl_3$): δ = 1.14 (t, *J* = 7 Hz, 3H, CH_2CH_3), 1.30 (t, *J* = 7 Hz, 3H, CH_2CH_3), 3.70 (s, 3H, OCH_3), 3.32–3.95 (m, 4H, $2CH_2$), 7.72 (d, *J* = 1.1 Hz, 1H, 3-H), 9.68 (d, *J* = 1.1 Hz, 1H, CHO).

$C_9H_{15}NO_3$ (185.2) Calcd. C 58.36 H 8.16 N 7.56
Found C 58.60 H 8.00 N 7.58

Methyl 3-Dibenzylamino-2-formyl-2-propenoate (**1s**): Dibenzylamine was condensed with **13** according to procedure I. Recrystallization gave 4.26 g (69%) of **1s**, m.p. 69°C. – IR (KBr): ν = 1690 cm^{-1}, 1645 (C=O), 1590, 1560 (C=C). – UV (ether): λ_{max} (lg ε) = 303 nm (4.011). – ^1H NMR ($CDCl_3$): δ = 3.70 (s, 3H, OCH_3), 4.40 (s, 2H, CH_2), 4.82 (s, 2H, CH_2), 7.23 (m, 10H, PhH), 7.90 (d, *J* = 1 Hz, 1H, 3-H), 9.77 (d, *J* = 1 Hz, CHO).

$C_{19}H_{19}NO_3$ (309.4) Calcd. C 73.77 H 6.19 N 4.53
Found C 73.85 H 6.29 N 4.72

Synthesis of the Enaminecarbaldehydes **17a–d**. – *General Procedure II. – Formylation of the Enamino Ketones* **15a–c** *with Acetic Formic Anhydrid* (**16**): To a stirred solution of **15a–c** (20.0 mmol) in anhydrous CH_2Cl_2 (20 ml) a solution of **16**[15] (2 ml, 23

mmol) in anhydrous CH_2Cl_2 (5 ml) is added dropwise. After stirring for 4 h at room temp. a saturated aqueous solution of sodium hydrogen carbonate is added slowly, stirring is continued for 30 min, then the layers are seperated and the aqueous layer is extracted (CH_2Cl_2, 2 × 30 ml). The combined organic extracts are washed (brine) and dried (Na_2SO_4). The solvent is removed unter reduced pressure, and the residue purified by recrystallization or chromatography.

Methyl 2-Formyl-3-methyl-3-methylamino-2-propenoate (**17a**): Formylation of **15a** according to procedure II yielded after recrystallization (toluene/hexane) 2.42 g (77%) of **17a**, m.p. 74°C. – IR (KBr): ν = 3400 cm^{-1}, 3200 (N–H), 1690 (C=O), 1610 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 237 nm (4.101), 297 (4.112). – ^1H NMR ($CDCl_3$): δ = 2.40 (s, 3H, CH_3), 3.00 (d, *J* = 5 Hz, 3H, NCH_3), 3.62 (s, 3H, OCH_3), 9.60 (s, 1H, CHO), 12.56 (br. m, 1H, NH).

$C_7H_{11}NO_3$ (157.2) Calcd. C 53.49 H 7.05 N 8.91
Found C 53.39 H 7.14 N 8.96

Methyl 3-Ethyl-2-formyl-3-methylamino-2-propenoate (**17b**): Formylation of **15b** according to procedure II (addition of **16** at 0°C) yielded after chromatography [ethyl acetate/petroleum ether (1:5)] 2.64 g (77%) of **17b**. – IR (KBr): ν = 3460 cm^{-1} (N–H), 1700 (C=O), 1610 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 238 nm (4.114), 298 (4.143). – ^1H NMR ($CDCl_3$): δ = 1.22 (t, *J* = 7 Hz, 3H, CH_2CH_3), 2.95 (q, *J* = 7 Hz, 2H, CH_2CH_3), 3.08 (d, *J* = 5 Hz, 3H, NCH_3), 3.72 (s, 3H, OCH_3), 9.81 (s, 1H, CHO), 12.60 (br. m, 1H, NH).

$C_8H_{13}NO_3$ (171.2) Calcd. C 56.13 H 7.65 N 8.18
Found C 56.02 H 7.65 N 8.23

Formylation of **15c**: Reaction of **15c** (400 mg, 1.61 mmol) with 2 ml of **16** for 1 h afforded 2 products, which were separated by chromatography [ethyl acetate/petroleum ether (4:1)].

Fraction 1: *2-Acetyl-3-[2-(3,4-dimethoxyphenyl)ethylamino]propenal* (**17c**): Yield 169 mg (38%) of **17c**, R_f = 0.33 [ethyl acetate/petroleum ether (4:1)], m.p. 93°C (ether/petroleum ether). – IR (KBr): ν = 3220 cm^{-1} (N–H), 3000 (C=C–H), 1680, 1645 (C=O), 1600, 1520 (C=C). – UV (CH_3CN) λ_{max} (lg ε) = 252 nm (4.591), 298 (4.190). – ^1H NMR ($CDCl_3$): δ = 2.27 (s, 1.35 H, $COCH_3$-*E*), 2.42 (s, 1.65H, $COCH_3$-*Z*), 2.87 (t, *J* = 7 Hz, 2H, ar-CH_2), 3.60 (q, *J* = 7 Hz, 2H, NCH_2), 3.82 (s, 6H, $2OCH_3$), 6.60–6.80 (m, 3H, PhH), 7.46 (d, *J* = 14 Hz, 0.55H, 3-H-*Z*), 7.83 (dd, *J* = 14, *J* = 3.5 Hz, 0.54H, 3-H-*E*), 9.40 (s, 0.55H, CHO-*Z*), 9.82 (d, *J* = 3.5 Hz, 0.45H, CHO-*E*), 10.95 (br., 1H, NH).

$C_{15}H_{19}NO_4$ (277.3) Calcd. C 64.97 H 6.91 N 5.05
Found C 64.97 H 6.88 N 4.96

Fraction 2: *N-Formyl-4-[2-(3,4-dimethoxyphenyl)ethylamino]-3-buten-2-one* (**17d**): Yield 218 mg (49%) of **17d** as a colorless oil, R_f = 0.56 [ethyl acetate/petroleum ether (4:1)]. – IR (film): ν = 3010 cm^{-1} (C=C–H), 1695, 1630 (C=O), 1600, 1520 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 232 nm (4.014), 274 (4.282). – ^1H NMR ($CDCl_3$): δ = 2.28 (s, 2.3H, $COCH_3$), 2.36 (s, 0.7H, $COCH_3$), 2.76–2.92 (m, 2H, ar-CH_2), 3.70–3.90 (m, 2H, NCH_2), 3.88 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 5.85 (d, *J* = 15 Hz, 0.77 H, 3-H), 5.88 (d, *J* = 15 Hz, 0.23H, 3-H), 6.60–6.90 (m, 3H, PhH), 7.67 (d, *J* = 15 Hz, 0.77H, 4-H), 7.86 (s, 0.23H, CHO), 8.18 (d, *J* = 15 Hz, 0.23H, 4-H), 8.50 (s, 0.77H, CHO).

$C_{15}H_{19}NO_4$ Calcd. 277.3241 Found 277.3241 (MS)

Synthesis of the Enaminecarbaldehydes **19a–k** *and* **20**. – *General Procedure III.* – *Acylation of Methyl 3-Amino-2-formyl-2-propenoate* (**1a**): To a stirred solution of **1a** (1.50 g, 11.6 mmol) and pyridine (1.37 g, 17.4 mmol) in 30 ml of anhydrous CH_2Cl_2 and 15 ml anhydrous ether is added dropwise at 0°C 17.4 mmol of the freshly distilled acyl chloride. The mixture is allowed to warm up to room temp. and stirring is continued for several hours (TLC control). The precipitate is filtered off, washed with ether, and the combined organic solvents are evaporated in vacuo. The residue is purified by chromatography or recrystallization.

Methyl 3-Acetylamino-2-formyl-2-propenoate (**19a**). – *Variant A:* Reaction of **1a** with acetyl chloride according to procedure III yielded after chromatography [ethyl acetate/petroleum ether (1:1)] 1.28 g (64%) of **19a**, m.p. 69–71°C (*tert*-butyl methyl ether).

Variant B: To a stirred solution of diformylacetate **13** (1.50 g, 11.6 mmol) in 50 ml of anhydrous toluene were added freshly calcinated Na_2SO_4 (12 g) and acetamide (0.75 g, 12.7 mmol).The mixture was heated for 48 h to 70°C. Workup according to variant A yielded 1.20 g (60%) of **19a**. – IR (KBr): ν = 3280 cm^{-1} (N–H), 1725, 1670 (C=O), 1590 (C=C). – UV (CH_3OH): λ_{max} (lg ε) = 220 nm (3.962), 294 (4.230). – ^1H NMR ($CDCl_3$): δ = 3.82 (s, 2.85H, OCH_3-*E*), 3.87 (s, 0.15H, OCH_3-*Z*), 8.45 (m, 1H, 3-H), 9.81 (s, 0.05H, CHO-*Z*), 9.94 (d, *J* = 3.5 Hz, 0.95H, CHO-*E*), 11.70 (br., 1H, NH).

$C_7H_9NO_4$ (171.2) Calcd. C 49.12 H 5.30 N 8.18
Found C 49.14 H 5.34 N 8.06

Methyl 3-(tert-Butylcarbonylamino)-2-formyl-2-propenoate (**19b**): Reaction of **1a** with pivaloyl chloride according to procedure III yielded after chromatography [ethyl acetate/petroleum ether (1:1)] 1.85 g (75%) of **19b** as a colorless oil. – IR (KBr): ν = 3250 cm^{-1} (N–H), 1715, 1665 (C=O), 1570 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 216 nm (3.901), 302 (4.178). – ^1H NMR ($CDCl_3$): δ = 1.18 [s, 1.8H, $C(CH_3)_3$-*Z*], 1.29 [s, 7.2H, $C(CH_3)_3$-*E*], 3.79 (s, 2.4H, OCH_3-*E*), 3.85 (s, 0.6, OCH_3-*Z*), 8.46 (m, 1H, 3-H), 9.77 (s, 0.2H, CHO-*Z*), 9.93 (d, *J* = 3.6 Hz, 0.8H, CHO-*E*), 12.18 (br., 1H, NH).

$C_{10}H_{15}NO_4$ (213.2) Calcd. C 56.33 H 7.09
Found C 56.44 H 6.98

Methyl 3-Benzoylamino-2-formyl-2-propenoate (**19c**): Reaction of **1a** with benzoyl chloride according to procedure III yielded after chromatography [ethyl acetate/petroleum ether (1:1)] 2.30 g (85%) of **19c** m.p. 99°C (ether). – IR (KBr): ν = 3240 cm^{-1} (N–H), 1725, 1705, 1660 (C=O), 1580 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 244 nm (3.931), 313 (4.340). – ^1H NMR ($CDCl_3$): δ = 3.88 (s, 2.7H, OCH_3-*E*), 3.92 (s, 0.3H, OCH_3-*Z*), 7.25–8.00 (m, 5H, PhH), 8.70 (d, *J* = 11.6 Hz, 0.1H, 3-H-*Z*), 8.72 (dd, *J* = 11.6, 3.6 Hz, 0.9H, 3-H-*E*), 9.88 (s, 0.1H, CHO-*Z*), 10.06 (d, *J* = 3.6 Hz, 0.9H, CHO-*E*), 12.88 (br. d, *J* = 12 Hz, 1H, NH).

$C_{12}H_{11}NO_4$ (233.2) Calcd. C 61.80 H 4.75 N 6.01
Found C 62.04 H 4.88 N 6.01

Methyl 2-Formyl-3-(4-nitrobenzoylamino)-2-propenoate (**19d**): Reaction of **1a** with 4-nitrobenzyl chloride according to procedure III yielded after chromatography (ethyl acetate) 2.61 g (81%) of **19d**, m.p. 195°C ($CHCl_3$). – IR (KBr): ν = 3260 cm^{-1} (N–H), 3055 (C=C–H), 1700, 1640 (C=O), 1565 (C=C), 1525 (NO_2). – UV (CH_3CN): λ_{max} (lg ε) = 259 nm (4.123), 315 (4.301). – ^1H NMR ($CDCl_3$): δ = 3.88 (s, 2.85H, OCH_3-*E*), 3.95 (s, 0.15H, OCH_3-*Z*), 8.25 (m, 4H, PhH), 8.69 (m, 1H, 3-H), 9.90 (s, 0.05H, CHO-*Z*), 10.06 (d, *J* = 3.5 Hz, 0.95H, CHO-*E*), 12.94 (br. d, *J* = 11 Hz, 1H, NH).

$C_{12}H_{10}N_2O_6$ (278.2) Calcd. C 51.80 H 3.62 N 10.07
Found C 51.62 H 3.66 N 10.17

Methyl 3-[2-(3-Indolyl)-acetylamino]-2-formyl-2-propenoate (**19e**): Reaction of **1a** with indolyl acetyl chloride according to procedure III yielded after recrystallization (CH_3CN) 2.06 g (62%) of **19e**, m.p. 146°C. – IR (KBr): ν = 3400 cm^{-1}, 3360, 3240 (N–H), 1745, 1705, 1665 (C=O), 1585 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 218 nm (4.272), 283 (4.131), 289 (4.170), 300 (4.093). – ^1H NMR ($CDCl_3$): δ = 3.69 (s, 0.9H, OCH_3-*Z*), 3.84 (s, 2.1H, OCH_3-*E*), 4.02 (s, 2H,

$OCCH_2$), 7.14–7.66 (m, 5H, indole-H), 8.44 (br., 1H, indole-NH), 8.44 (d, J = 12 Hz, 0.3H, 3-H-*Z*), 8.50 (dd, J = 12.0, 3.5 Hz, 0.7H, 3-H-*E*), 9.85 (s, 0.3H, CHO-*Z*), 9.89 (d, J = 3.5 Hz, 0.7H, CHO-*E*), 10.69 (br., 0.3H, NH-*Z*), 11.83 (br., 0.7H, NH-*E*).

$C_{15}H_{14}N_2O_4$ (286.3) Calcd. C 62.93 H 4.93 N 9.79
Found C 63.10 H 5.04 N 9.66

Methyl 2-Formyl-3-methoxycarbonylamino-2-propenoate (**19f**): Reaction of **1a** with methyl chloroformate according to procedure III yielded after chromatography [ethyl acetate/hexane (1:2)] 1.69 g (78%) of **19f**, m.p. 66°C (ethyl acetate/hexane). – IR (KBr): ν = 3280 cm^{-1} (N–H), 3020 (C=C–H), 1750, 1730, 1710, 1660 (C=O), 1590 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 213 nm (4.070), 291 (4.282). – ^1H NMR ($CDCl_3$): δ = 3.85 (s, 2.2H, CO_2CH_3-*E*), 3.89 (s, 0.8H, CO_2CH_3-*Z*), 3.92 (s, 3H, $NHCO_2CH_3$), 8.38 (br. m, 1H, 3-H), 9.86 (s, 0.3, CHO-*Z*), 10.01 (d, J = 3.5 Hz, 0.7H, CHO-*E*), 10.30 (br., 0.3H, NH-*Z*), 11.30 (br., 0.7H, NH-*E*).

$C_7H_9NO_5$ (187.2) Calcd. C 44.92 H 4.85 N 7.48
Found C 44.83 H 4.87 N 7.49

Methyl (S)-3-(2-Benzyloxypropionylamino)-2-formyl-2-propenoate (**19g**): Reaction of **1a** with (*S*)-*O*-benzyllactoyl chloride [prepared from (*S*)-*O*-benzyllactic acid and oxalyl dichloride] according to procedure III yielded after chromatography [ether/*tert*-butyl methyl ether/hexane (1:1:4)] 2.50 g (74%) of **19g**, m.p. 73°C (ethyl acetate/hexane), $[\alpha]_D^{20}$ = −2.8 (c = 1.0 in $CHCl_3$). – IR (KBr): ν = 3230 cm^{-1} (N–H), 3060, 3030 (C=C–H), 1730, 1710, 1660 (C=O), 1560 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 209 nm (4.253), 301 (4.276). – ^1H NMR ($CDCl_3$): δ 1.48 (d, J = 7 Hz, 3H, CH_3), 3.84 (s, 3H, OCH_3), 4.14 (q, J = 7 Hz, 1H, 1′-H), 4.65 (s, 2H, $PhCH_2$), 7.28–7.50 (m, 5H, PhH), 8.44 (d, J = 12.5 Hz, 0.1H, 3-H-*Z*), 8.46 (dd, J = 12.5, 3.5 Hz, 0.9H, 3-H-*E*), 9.91 (s, 0.1H, CHO-*Z*), 10.08 (d, J = 3.5 Hz, 0.9H, CHO-*E*), 11.56 (br., 0.1H, NH-*Z*), 12.48 (br., 0.9H, NH-*E*).

$C_{15}H_{17}NO_5$ (291.3) Calcd. C 61.85 H 5.88 N 4.81
Found C 61.73 H 5.79 N 4.75

Methyl (R)-3-(2-Acetyloxy-2-phenylacetylamino)-2-formyl-2-propenoate (**19h**): Reaction of **1a** with (*R*)-*O*-acetylmandeloyl chloride [prepared from (*R*)-*O*-acetylmandelic acid and oxalyl dichloride] according to procedure III yielded after chromatography [ethyl acetate/hexane (1:2)] 2.30 g (65%) of **19h** as a colorless oil, $[\alpha]_D^{20}$ = −5.8 (c = 1.0 in $CHCl_3$). – IR (film): ν = 3240 cm^{-1} (N–H), 3060, 3030 (C=C–H), 1740, 1710, 1660 (C=O), 1580 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 206 nm (4.240), 300 (4.264). – ^1H NMR ($CDCl_3$): δ = 3.29 (s, 0.6H, $OCCH_3$-*Z*), 3.33 (s, 2.4H, $OCCH_3$-*E*), 3.84 (s, 2.4H, CO_2CH_3-*E*), 3.90 (s, 0.6H, CO_2CH_3-*Z*), 6.21 (s, 1H, 1′-H), 7.32–7.56 (m, 5H, PhH), 8.42 (d, J = 12 Hz, 0.2H, 3-H-*Z*), 8.46 (dd, J = 12, 3.5 Hz, 0.8H, 3-H-*E*), 9.88 (s, 0.2H, CHO-*Z*), 10.05 (d, J = 3.5 Hz, 0.8H, CHO-*E*), 11.55 (br., 0.2H, NH-**Z**), 12.43 (br., 0.8H, NH-*E*).

$C_{15}H_{15}NO_6$ (305.3) Cacld. C 59.02 H 4.95 N 4.59
Found C 59.19 H 5.01 N 4.71

Methyl (S)-2-Formyl-3-(2-methoxy-2-phenyl-2-trifluoromethylacetylamino)-2-propenoate (**19i**): Reaction of **1a** with (*R*)-2-methoxy-2-phenyl-2-trifluoromethylacetyl chloride [prepared from (*S*)-2-methoxy-2-phenyl-2-trifluoromethylacetic acid and oxalyl dichloride] according to procedure III yielded after chromatography [ethyl acetate/hexane (1:5)] 2.80 g (70%) of **19i** as a colorless oil, $[\alpha]_D^{20}$ = +113.0 (c = 1.0 in $CHCl_3$). – IR (film): ν = 3260 cm^{-1} (N–H), 3060 (C=C–H), 1740, 1710, 1670 (C=O), 1580 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 204 nm (sh, 4.211), 301 (4.224). – ^1H NMR ($CDCl_3$): δ 3.57 (q, J = 1.7 Hz, 3H, OCH_3), 3.87 (s, 2.3H, CO_2CH_3-*E*), 3.91 (s, 0.7H, CO_2CH_3-*Z*), 7.34–7.64 (m, 5H, PhH). 8.46 (d, J = 12.5 Hz, 0.2H, 3-H-*Z*), 8.48 (dd, J = 12.5, 3.5 Hz, 0.8H, 3-H-*E*), 9.92 (s, 0.2H, CHO-*Z*), 10.06 (d, J = 3.5 Hz, CHO-*E*), 11.81 (br., 0.2H, NH-*Z*), 12.58 (br. d, J = 12.5 Hz, 0.8H, NH-*E*).

$C_{15}H_{14}F_3NO_5$ (345.3) Calcd. C 52.18 H 4.09 F 16.51 N 4.06
Found C 52.11 H 4.24 F 16.80 N 4.00

Methyl (S)-3-Camphanoylamino-2-formyl-2-propenoate (**19j**): Reaction of **1a** with (*S*)-camphanoyl chloride according to procedure III yielded after chromatography [ether/hexane (5:3)] 3.12 g (87%) of **19j** as a colorless oil, $[\alpha]_D^{20}$ = +49.8 (c = 1.0 in $CHCl_3$). – IR (film): ν = 3260 cm^{-1} (N–H), 1800, 1725, 1675 (C=O), 1580 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 302 nm (4.221). – ^1H NMR ($CDCl_3$): δ = 0.96 (s, 3H, CH_3), 1.11 (s, 1.0H, CH_3-*Z*), 1.12 (s, 2.0H, CH_3-*E*), 1.16 (s, 3H, CH_3), 1.68–1.84 (m, 1H, CH_2), 1.93–2.14 (m, 2H, CH_2), 2.47–2.64 (m, 1H, CH_2), 3.88 (s, 2.0H, CO_2CH_3-*E*), 3.94 (s, 1.0H, CO_2CH_3-*Z*), 8.50 (d, J = 12.5 Hz, 0.3H, 3-H-*Z*), 8.53 (dd, J = 12.0, 3.5 Hz, 0.7H, CHO-*E*), 11.60 (br. d, J = 12 Hz, 0.3H, NH-*Z*), 12.39 (br. d, J = 12 Hz, 0.7H, NH-*E*).

$C_{15}H_{19}NO_6$ (309.3) Calcd. C 58.25 H 6.19 N 4.53
Found C 58.45 H 6.13 N 4.45

Methyl 2-Formyl-3-phenylaminocarbonylamino-2-propenoate (**19k**): To a suspension of diformylacetate **13** (387 mg, 3.00 mmol) in $CHCl_3$ (10 ml) was added phenyl isocyanate (375 mg, 3.15 mmol), and the mixture was heated 3 h to reflux. After cooling in an icebath the precipitated crystals were filtered off; yield after recrystallization ($CHCl_3$) 436 mg (59%) of **19k** as yellowish crystals, m.p. 157°C. – IR (KBr): ν = 3280 cm^{-1} (N–H), 1740, 1705, 1660 (C=O), 1545 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 222 nm (4.253), 311 (4.410). – ^1H NMR ($CDCl_3$): δ = 3.75 (s, 3H, CH_3), 6.90–7.60 (m, 5H, PhH), 8.38 (br., 1H, 3-H), 9.74 (br., 1H, CHO), 10.83 (br., 2H, NH).

$C_{12}H_{12}N_2O_4$ (248.2) Calcd. C 58.06 H 4.87
Found C 57.96 H 4.79

Methyl 2-Formyl-3-phthalimido-2-propenoate (**20**): Reaction of **1a** with phthaloyl dichloride according to procedure III using two equivalents of pyridine yielded after chromatography (ethyl acetate) 1.62 g (54%) of **20**, m.p. 192°C (CH_3CN). – IR (KBr): ν = 1740 cm^{-1}, 1675 (C=O), 1650 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 221 nm (4.365), 252 (sh, 4.343), 272 (4.496). – ^1H NMR ($CDCl_3$): δ = 3.74 (s, 2.7H, OCH_3-*E*), 3.80 (s, 0.3H, OCH_3-*Z*), 7.78 (s, 0.9H, 3-H-*E*), 7.84 (s, 0.1H, 3-H-*Z*), 8.02 (m_c, 4H, PhH), 9.64 (s, 0.9H, CHO-*E*), 9.81 (s, 0.1H, CHO-*Z*).

$C_{13}H_9NO_5$ (259.2) Calcd. C 60.24 H 3.50 N 5.40
Found C 60.33 H 3.60 N 5.37

2-Ethyl-3-trimethylsiloxyacrolein (**21a**): To a suspension of the sodium salt of 2-ethylmalonaldehyde[16] (2.24 g, 20.0 mmol) in anhydrous ether (40 ml) were added at 0°C 5 ml (40 mmol) of chlorotrimethylsilane, dissolved in 8 ml of anhydrous ether. The reaction mixture was stirred for 2 h at 0°C and allowed to stay for 12 h at room temp. NaCl was filtered off unter N_2, the solvent was removed and the crude product was distilled under vacuum to afford 2.60 g (82%) of **21a** as a colorless liquid, b.p. 50°C/0.3 Torr. – IR (film): ν = 1640 cm^{-1} (C=O), 1605 (C=C). – ^1H NMR ($CDCl_3$): δ = 0.30 [s, 9H, $Si(CH_3)_3$], 0.95 (t, J = 7 Hz, 3H, CH_2CH_3), 2.29 (q, J = 7 Hz, 2H, CH_2CH_3), 7.10 (s, 1H, 3-H), 9.27 (s, 1H, CHO).

4-Trimethylsiloxy-3-butene-2-one (**21b**): To a suspension of sodium hydride (2.4 g, 0.1 mol) in anhydrous cyclohexane (100 ml) was added a mixture of acetone (5.8 g, 0.1 mol) and methyl formate (12.0 g, 0.2 mol; both freshly distilled from P_4O_{10}) under N_2. The reaction mixture was refluxed for 3 h, and after cooling to room

temp. 3 ml of methanol was added to destroy excess of sodium hydride. The solvent was removed in vacuo to afford 12.5 g of the crude sodium salt of formyl acetone. To a mixture of the crude product in anhydrous ether (150 ml) was added a solution of chlorotrimethylsilane (30 ml) in anhydrous ether (45 ml) at 0°C. After stirring for 3 h the reaction mixture was allowed to stay for 12 h at room temp. The formed NaCl was filtered off under N_2, the solvent was removed, and the crude product was distilled under vaccum to afford 8.85 g (56%) of **21b** as a slightly yellow liquid, b.p. 85°C/2.2 Torr. – IR (film): ν = 1635 cm^{-1} (C=O), 1610 (C=C). – ^1H NMR ($CDCl_3$): δ = 0.30 [s, 9H, $Si(CH_3)_3$], 2.12 (s, 2.7H, CH_3-*E*), 2.33 (s, 0.3H, CH_3-*Z*), 5.50 (d, *J* = 4.2 Hz, 0.1H, 3-H-*Z*), 5.69 (d, *J* = 12 Hz, 1H, 3-H-*E*), 7.52 (d, *J* = 12 Hz, 0.9H, 4-H-*E*), 7.87 (d, *J* = 4.2 Hz, 0.1H, 4-H-*Z*).

Synthesis of the Enamincarbaldehyde **22a** *and the Enamino Ketone* **22b**. – *General Procedure IV. – Amination of Trimethylsilylenolethers* **21a, b** *with Homoveratrylamine* (**14m**): To a stirred solution of **21a, b** (10.0 mmol) in anhydrous CH_2Cl_2 (20 ml) was added dropwise at 0°C an equimolar amount of homoveratrylamine (1.81 g), dissolved in anhydrous CH_2Cl_2 (5 ml). After stirring for 1 h the solvent was evaporated in vacuo and the solid residue purified by recrystallization.

3-[2-(3,4-Dimethoxyphenyl)ethylamino-2-ethylacrolein (**22a**): Reaction of **21a** with **14m** according to procedure IV afforded after recrystallization (ether) 2.18 g (83%) of **22a**, m.p. 115°C. – IR (KBr): ν = 3235 cm^{-1}, 3150 (N–H), 1660 (C=O), 1625 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 230 nm (3.490), 286 (4.211). – ^1H NMR ($CDCl_3$): δ = 0.91 (t, *J* = 6.6 Hz, 3H, CH_2CH_3), 2.13 (q, *J* = 6.6 Hz, 2H, CH_2CH_3), 2.80 (t, *J* = 6.2 Hz, 2H, ar-CH_2), 3.46 (q, *J* = 6.2 Hz, 2H, NCH_2), 3.82 (s, 6H, $2OCH_3$), 5.60 (br. s, 1H, NH), 6.62 (d, *J* = 11.6 Hz, 1H, 3-H), 6.60–6.80 (m, 3H, PhH), 8.76 (s, 0.9H, CHO-*E*), 9.06 (d, *J* = 3.6 Hz, 0.1H, CHO-Z).

$C_{15}H_{21}NO_3$ (263.3) Calcd. C 68.42 H 8.04 N 5.32
Found C 68.37 H 8.07 N 5.46

3-[2-(3,4-Dimethoxyphenyl)ethylamino]-3-butene-2-one (**22b**): Reaction of **21b** with **14m** according to procedure IV afforded after recrystallization (CH_3CN) 2.20 g (88%) of **22b**, m.p. 128°C. – IR (KBr): ν = 3250 cm^{-1} (N–H), 1660 (C=O), 1625, 1520 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 230 nm (3.509), 284 (4.132). – ^1H NMR ($CDCl_3$): δ 1.98 (s, 3H, CH_3), 2.74 (t, *J* = 7 Hz, 2H, ar-CH_2), 3.35 (q, *J* = 7 Hz, 2H, NCH_2), 3.82 (s, 6H, $2OCH_3$), 4.88 (d, *J* = 7.6 Hz, 1H, 3-H), 6.41 (dd, *J* = 12.4, 7.6 Hz, 1H, 4-H), 6.60–6.80 (m, 3H, PhH), 9.80 (br. s, 1H, NH).

$C_{14}H_{19}NO_3$ (249.3) Calcd. C 67.45 H 7.68 N 5.62
Found C 67.41 H 7.65 N 5.55

Synthesis of the Enamino Ketones **2a–i**. – *General Procedure V. – Amination of the Enones* (**24a–d**): To a solution of 15.0 mmol of the enone **24a–d**[9,18] in 20 ml of anhydrous tetrahydrofuran is added at 20–60°C an excess of ammonia or an equimolar amount of a primary or secondary amine. The reaction mixture is stirred at 20–60°C for several hours (TLC control on silica gel with mixtures of *tert*-butyl methyl ether and petroleum ether). After the reaction is completed the solvent is evaporated and the residue purified by chromatography or recrystallization.

Methyl 4-Amino-2-oxo-3-butenoate (**2a**): Reaction of **24a** with ammonia at 50°C according to procedure V yielded after chromatography (ethyl acetate) 1.84 g (95%) of **2a**, m.p. 98°C (ethyl acetate/*tert*-butyl methyl ether). – IR (KBr): ν = 3320 cm^{-1}, 3180 (N–H), 1730, 1660 (C=O). – UV (CH_3CN): λ_{max} (lg ε) = 326 nm (4.108). – ^1H NMR ($CDCl_3$): δ = 3.78 (s, 3H, OCH_3), 5.65 (dd, *J* = 7.5, 0.5 Hz, 1H, 3-H), 6.80 (br., 1H, NH), 7.25 (dt, *J* = 15.0, 7.5 Hz, 1H, 4-H), 9.41 (br., 1H, NH).

$C_5H_7NO_3$ (129.1) Calcd. C 46.51 H 5.46 N 10.85
Found C 46.68 H 5.50 N 10.78

4-Amino-1,1,1-trichloro-3-butene-2-one (**2b**): Reaction of **24b** with ammonia at 55°C according to procedure V yielded after recrystallization (*tert*-butyl methyl ether) 2.60 g (92%) of **2b**, m.p. 88°C. – IR (KBr): ν = 3310 cm^{-1}, 3220 (N–H), 1650 (C=O), 820 (C–Cl). – UV (CH_3CN): λ_{max} (lg ε) = 311 nm (4.161). – ^1H NMR ($CDCl_3$): δ = 5.74 (dd, *J* = 7.5, 1.2 Hz, 1H, 3-H), 5.96 (br., 1H, NH), 7.22 [dt, *J* = 15.0, 7.5(t) Hz, 1H, 4-H], 8.95 (br., 1H, NH).

$C_4H_4Cl_3NO$ (188.4) Calcd. C 25.50 H 2.14 N 7.43
Found C 25.68 H 2.17 N 7.44

4-Amino-1,1-dichloro-3-buten-2-one (**2c**): Reaction of **24c** with ammonia at 60°C according to procedure V yielded after recrystallization (*tert*-butyl methyl ether/petroleum ether) 1.92 g (83%) of **2c**, m.p. 30°C. – IR (KBr): ν = 3490 cm^{-1}, 3310 (N–H), 1650 (C=O), 1520 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 307 nm (4.131). – ^1H NMR (CD_3CN): δ = 5.20 (d, *J* = 5 Hz, 1H, 3-H), 5.96 (s, 1H, CCl_2H), 6.50 (br., 1H, NH), 7.10 [dt, *J* = 10, 5(t) Hz, 1H, 4-H], 8.80 (br., 1H, NH).

$C_4H_5Cl_2NO$ (154.0) Calcd. C 31.20 H 3.27 N 9.10
Found C 30.94 H 3.35 N 9.10

4-Amino-3-bromo-1,1,1-trichloro-3-buten-2-one (**2d**): Reaction of **24d** with ammonia at 60°C according to procedure V yielded after chromatography [ethyl acetate/petroleum ether (1:1] 2.45 g (61%) of **2d**, m.p. 134°C (*tert*-butyl methyl ether/petroleum ether). – IR (KBr): ν = 3420 cm^{-1}, 3330 (N–H), 1625 (C=O), 1540 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 310 nm (4.121). – ^1H NMR (CD_3CN): δ = 6.40 (br., 2H, NH_2), 8.30 (m, 1H, 4-H).

$C_4H_3BrCl_3NO$ (267.3)
Calcd. C 17.97 H 1.13 Br 29.89 Cl 39.78 N 5.24
Found C 18.09 H 1.22 Br 29.98 Cl 39.72 N 5.26

Methyl 4-Benzylamino-2-oxo-3-butenoate (**2e**): Reaction of **24a** with benzylamine at 20°C according to procedure V yielded after chromatography (*tert*-butyl methyl ether) 2.86 g (87%) of **2e**, m.p. 95–97°C (ethyl acetate). – IR (KBr): ν = 3230 cm^{-1} (N–H), 1740 (C=O), 1555 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 337 nm (4.176). – ^1H NMR (CD_3CN): δ = 3.73 (s, 3H, OCH_3), 4.48 (d, *J* = 6.3 Hz, 2H, NCH_2), 6.18 (d, *J* = 7 Hz, 1H, 3-H), 7.29 (dd, *J* = 12.5, 17 Hz, 1H, 4-H), 7.30 (s, 5H, PhH), 7.70 (br., 1H, NH).

$C_{12}H_{13}NO_3$ (219.2) Calcd. C 65.74 H 5.98 N 6.39
Found C 65.94 H 6.10 N 6.48

1,1,1-Trichloro-4-methylamino-3-buten-2-one (**2f**): Reaction of **24b** with methylamine at 60°C according to procedure V yielded after chromatography (*tert*-butyl methyl ether) 2.67 (88%) of **2f** as a colorless oil. – IR (film): ν = 3310 cm^{-1} (N–H), 1650 (C=O), 1590 (C=C), 810 (C–Cl). – UV (CH_3CN): λ_{max} (lg ε) = 322 nm (4.234). – ^1H NMR ($CDCl_3$): δ = 3.13 (d, *J* = 5 Hz, 3H, CH_3), 5.65 (d, *J* = 7 Hz, 1H, 3-H), 7.04 (dd, *J* = 13.5, 7.0 Hz, 1H, 4-H), 9.00 (br., 1H, NH).

$C_5H_6Cl_3NO$ (202.5) Cacld. C 29.66 H 2.99 N 6.92
Found C 29.62 H 2.92 N 6.87

1,1,1-Trichloro-4-[(S)-1-phenylethylamino]-3-buten-2-one (**2g**): Reaction of **24b** with (*S*)-1-phenylethylamine at 20°C according to procedure V yielded after chromatography (ether) 4.08 g (93%) of **2g** as a yellowish oil, $[\alpha]_D^{20}$ = 58.9 (*c* = 1.0 in CH_3OH). – IR (film): ν = 3300 cm^{-1} (N–H), 1645 (C=O), 1585 (C=C), 830 (C–Cl). – UV (CH_3CN): λ_{max} (lg ε) = 327 nm (4.277). – ^1H NMR

($CDCl_3$): δ = 1.62 (d, *J* = 6.6 Hz, 3H, CH_3), 4.54 (quint, *J* = 6.6 Hz, 1H, NCH), 5.64 (d, *J* = 7.5 Hz, 1H, 3-H), 7.00 (dd, *J* = 13.5, 7.5 Hz, 1H, 4-H), 7.00–7.60 (m, 5H, PhH), 10.00 (br., 1H, NH).

$C_{12}H_{12}Cl_3NO$ (292.6) Calcd. C 49.26 H 4.13 N 4.79
Found C 49.30 H 4.05 N 4.85

1,1,1-Trichloro-4-dimethylamino-3-buten-2-one (**2h**): Reaction of **24b** with dimethylamine at 50°C according to procedure V yielded after recrystallization (*tert*-butyl methyl ether) 3.15 g (97%) of **2h**, m.p. 72°C (*tert*-butyl methyl ether/petroleum ether). – IR (KBr): ν = 1665 cm^{-1} (C=O), 1590 (C=C), 830 (C–Cl). – UV (CH_3CN): λ_{max} (lg ε) = 328 nm (4.487). – ^1H NMR ($CDCl_3$): δ = 2.95 (s, 3H, CH_3), 3.18 (s, 3H, CH_3), 5.55 (d, *J* = 12 Hz, 1H, 3-H), 7.75 (d, *J* = 12 Hz, 1H, 4-H).

$C_6H_8Cl_3NO$ (216.5) Calcd. C 33.29 H 3.72 N 6.47
Found C 33.39 H 3.67 N 6.48

1,1,1-Trichloro-4-⟨N-[(1S),(2R)-2-hydroxy-1-methyl-2-phenylethyl]-N-methylamino⟩-3-buten-2-one (**2i**): Reaction of **24b** with (–)-ephedrine at 40°C according to procedure V yielded after recrystallization (ether) 4.80 g (95%) of **2i**, m.p. 143°C, $[\alpha]_D^{20}$ = +52.8 (*c* = 1.0 in $CHCl_3$). – IR (KBr): ν = 3430 cm^{-1} (N–H), 1645 (C=O), 1550 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 329 nm (4.353). – ^1H NMR ($CDCl_3$): δ = 1.35 (d, *J* = 7 Hz, 3H, CH_3), 2.45 (br., 1H, OH), 2.80 (s, 3H, NCH_3), 3.60 (dq, *J* = 7.0, 5.3 Hz, 1H, 1'-H), 4.75 (d, *J* = 5.3 Hz, 1H, 2'-H), 5.48 (d, *J* = 12 Hz, 1H, 3-H), 7.29 (s, 5H, PhH), 7.78 (d, *J* = 12 Hz, 1H, 4-H).

$C_{14}H_{16}Cl_3NO_2$ (336.6) Calcd. C 49.95 H 4.79 N 4.16
Found C 49.94 H 4.95 N 4.17

Synthesis of the Acylated Enamino Ketones **2l–t**. – *General Procedure VI. – Acylation of the Enamino Ketones* (**2a, b, e–g**): To a solution of 10.0 mmol of the enamino ketone **2a, b, e–g**, *p*-dimethylamino pyridine (366 mg, 3.00 mmol), and triethylamine (2.02 g, 20.0 mmol) in 40 ml of anhydrous tetrahydrofuran/*tert*-butyl methyl ether (1:1) under N_2 is added at 0°C 20.0 mmol of the acyl chloride. The reaction mixture is warmed to room temp. and stirred for 1–12 h. After addition of ether (50 ml) the precipitated ammonium salt is filtered off, washed twice with ether (20 ml), and the combined organic layers are evaporated in vacuo. The residue is purified by chromatography or recrystallization.

Methyl 4-Benzoylamino-2-oxo-3-butenoate (**2l**): Reaction of **2a** with benzoyl chloride according to procedure VI; the reaction mixture was stirred for 1 h at room temp. Yield after chromatography [ethyl acetate/petroleum ether (1:1)] 1.63 g (70%) of **2l**, m.p. 90–92°C (*tert*-butyl methyl ether). – IR (KBr): ν = 3410 cm^{-1} (N–H), 1730, 1700 (C=O). – UV (CH_3CN): λ_{max} (lg ε) = 329 nm (4.228). – ^1H NMR ($CDCl_3$): δ = 3.88 (s, 3H, OCH_3), 6.35 (d, *J* = 8 Hz, 1H, 3-H), 7.90 (d, *J* = 8 Hz, 1H, 4-H), 7.40–8.00 (m, 5H, PhH), 12.30 (br., 1H, NH).

$C_{12}H_{11}NO_4$ (233.2) Calcd. C 61.80 H 4.75 N 6.01
Found C 61.96 H 4.84 N 6.01

Methyl 4-Methoxycarbonylcarbonylamino-2-oxo-3-butenoate (**2m**): Reaction of **2a** with methyl chloro oxalate according to procedure VI for 1 h at 60°C yielded after recrystallization (ethyl acetate) 1.22 g (57%) of **2m**, m.p. 160°C. – IR (KBr): ν = 3290 cm^{-1} (N–H), 1710 (C=O), 1610 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 309 nm (4.189). – ^1H NMR ([D_6]DMSO): δ = 3.75 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.63 (d, *J* = 13.4 Hz, 1H, 3-H), 7.80 (dd, *J* = 13.4, 10.5 Hz, 1H, 4-H), 11.40 (br. d, *J* = 10.5 Hz, 1H, NH).

$C_8H_9NO_6$ (215.2) Calcd. C 44.66 H 4.22 N 6.51
Found C 44.64 H 4.30 N 6.58

Methyl 4-(N-Benzoyl-N-benzylamino)-2-oxo-3-butenoate (**2n**): Reaction of **2e** with benzoyl chloride according to procedure VI for 1 h at 50°C yielded after chromatography [ethyl acetate/petroleum ether (1:2)] 3.14 g (97%) of **2n**, m.p. 106–110°C (*tert*-butyl methyl ether/petroleum ether). – IR (KBr): ν = 1730 cm^{-1}, 1690 (C=O), 1560 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 311 nm (4.206). – ^1H NMR ($CDCl_3$): δ = 3.75 (s, 3H, OCH_3), 5.08 (s, 2H, NCH_2), 6.25 (d, *J* = 13.8 Hz, 1H, 3-H), 7.20–7.50 (m, 10H, PhH), 8.23 (d, *J* = 13.8 Hz, 1H, 4-H).

$C_{19}H_{17}NO_4$ (323.3) Calcd. C 70.58 H 5.30 N 4.33
Found C 70.63 H 5.21 N 4.40

1,1,1-Trichloro-4-(N-ethoxycarbonyl-N-methylamino)-3-buten-2-one (**2o**): Reaction of **2f** with ethyl chloro oxalate according to procedure VI for 12 h at room temp. yielded after chromatography [ethyl acetate/petroleum ether (1:2)] 2.75 g (91%) of **2o**, m.p. 63°C (*tert*-butyl methyl ether/petroleum ether). – IR (KBr): ν = 1735 cm^{-1}, 1700 (C=O), 1580 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 297 nm (4.304). – ^1H NMR ($CDCl_3$): δ = 1.40 (t, *J* = 7 Hz, 3H, CH_3), 3.30 (s, 3H, NCH_3), 4.40 (q, *J* = 7 Hz, 2H, CH_2), 6.28 (d, *J* = 13.6 Hz, 1H, 3-H), 8.10 (br. d, *J* = 13.6 Hz, 1H, 4-H).

$C_9H_{10}Cl_3NO_4$ (302.5) Calcd. C 35.73 H 3.33 N 4.63
Found C 35.82 H 3.41 N 4.66

1,1,1-Trichloro-4-⟨N-(4-nitrobenzoyl)-N-[(S)-1-phenylethyl]-amino⟩-3-buten-2-one (**2p**): Reaction of **2g** with 4-nitrobenzoyl chloride according to procedure VI for 3 h at room temp. yielded after chromatography [ethyl acetate/petroleum ether (1:3)] 4.15 g (94%) of **2p**, m.p. 124–134°C (*tert*-butyl methyl ether), $[\alpha]_D^{20}$ = –58.9 (*c* = 1.0 in $CHCl_3$). – IR (KBr): ν = 1705 cm^{-1}, 1670 (C=O), 1590 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 265 nm (4.147), 308 (4.211). – ^1H NMR ($CDCl_3$): δ = 1.85 (d, *J* = 7 Hz, 3H, CH_3), 6.02 (d, *J* = 13.8 Hz, 1H, 3-H), 6.13 (q, *J* = 7 Hz, 1H, 1'-H), 7.33 (s, 5H, PhH), 7.75 (d, *J* = 13.8 Hz, 1H, 4-H), 8.00 (m_c, 4H, PhH).

$C_{19}H_{15}Cl_3N_2O_4$ (441.7) Calcd. C 51.67 H 3.42 N 6.34
Found C 51.88 H 3.54 N 6.28

Methyl 2-Oxo-4-phthalimido-3-butenoate (**2q**): Reaction of **2a** with phthaloyl dichloride in an anhydrous mixture of 40 ml of tetrahydrofuran/*tert*-butyl methyl ether (2:1) according to procedure VI using two equivalents of triethylamine for 1 h at room temp. yielded after chromatography (ethyl acetate) 1.97 g (76%) of **2q**, m.p. 151–154°C (ethyl acetate/*tert*-butyl methyl ether). – IR (KBr): ν = 1735 cm^{-1} (C=O), 1615 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 223 nm (4.461), 298 (4.379). – ^1H NMR ([D_6]DMSO): δ = 3.80 (s, 3H, OCH_3), 7.48 (d, *J* = 14.5 Hz, 1H, 3-H), 7.75 (d, *J* = 14.5 Hz, 1H, 4-H), 7.80–8.10 (m, 4H, PhH).

$C_{13}H_9NO_5$ (259.2) Calcd. C 60.24 H 3.50 N 5.40
Found C 60.15 H 3.65 N 5.42

1,1,1-Trichloro-4-phthalimido-3-buten-2-one (**2r**): Reaction of **2b** with phthaloyl dichloride in 40 ml of an anhydrous mixture of tetrahydrofuran/*tert*-butyl methyl ether (2:1) according to procedure VI using two equivalents of triethylamine for 12 h at room temp. yielded after chromatgraphy (ethyl acetate) 2.68 g (84%) of **2r**, m.p. 146°C (*tert*-butyl methyl ether). – IR (KBr): ν = 1740 cm^{-1} (C=O), 1625 (C=C), 845 (C–Cl). – UV (CH_3CN): λ_{max} (lg ε) = 223 nm (4.418), 285 (4.501). – ^1H NMR ([D_6]DMSO): δ = 7.75 (d, *J* = 14.5 Hz, 1H, 3-H), 7.90 (m_c, 4H, PhH), 8.04 (d, *J* = 14.5 Hz, 1H, 4-H).

$C_{12}H_6Cl_3NO_3$ (318.5) Calcd. C 45.25 H 1.90 N 4.40
Found C 45.38 H 2.02 N 4.42

Ethyl 4-Benzoylamino-3-bromo-2-oxo-3-butenoate (**2s**): Reaction of **24s** with ammonia at 50°C according to procedure V afforded crude **2j**, which was acylated with benzoyl chloride according to procedure VI for 1 h at room temp. Yield after chromatagraphy [ethyl acetate/petroleum ether (1:1)] 2.84 g (58%) of **2s**, m.p. 78°C

(*tert*-butyl methyl ether/petroleum ether). – IR (KBr): ν = 3390 cm^{-1} (N–H), 1730, 1710 (C=O). – UV (CH_2CN): λ_{max} (lg ε) = 241 nm (3.898), 310 (4.340). – ^1H NMR ($CDCl_3$): δ = 1.40 (t, *J* = 7 Hz, 3H, CH_3), 4.38 (q, *J* = 7 Hz, 2H, CH_2), 7.40–7.80 (m, 5H, PhH), 8.60 (br. d, *J* = 12 Hz, 1H, NH), 8.84 (d, *J* = 12 Hz, 1H, 4-H).

$C_{13}H_{12}BrNO_4$ (326.1) Calcd. C 47.88 H 3.71 N 4.29
Found C 47.89 H 3.77 N 4.40

(+)-Menthyl 2-Oxo-4-phthalimido-3-butenoate (**2t**): Reaction of **24t** with ammonia at 60°C according to procedure V afforded after filtration over silica gel [ethyl acetate/petroleum ether (1:1) crude **2k** as a brown oil, which was acylated with phthaloyl dichloride to procedure VI using two equivalents of triethylamine and 10 mol% of 4-pyrrolidinopyridine. The reaction mixture was stirred for 2 h at room temp. Yield after chromatography [ethyl acetate/petroleum ether (1:3)] 4.54 g (79%) of **2t**, m.p. 91–93°C (ether/petroleum ether), $[\alpha]_D^{20}$ = +49.6° (*c* = 1.0 in CH_3OH). – IR (KBr): ν = 1735 cm^{-1} (C=O), 1610 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 222 nm (4.441), 286 (4.388). – ^1H NMR ($CDCl_3$): δ = 0.60 to 2.20 (m, 18H, menthyl-H) 4.90 (dt, *J* = 10.5, 4.3 Hz, 1H, 1'-H), 7.80 (d, *J* = 15 Hz, 1H, 3-H), 7.70–8.10 (m, 4H, PhH), 8.10 (d, *J* = 15 Hz, 1H, 4-H).

$C_{22}H_{25}NO_5$ (383.4) Calcd. C 68.91 H 6.57 N 3.65
Found C 69.01 H 6.68 N 3.66

CAS Registry Numbers

(*E*)-**1a**: 116952-07-9 / (*E*)-**1b**: 116952-08-0 / (*E*)-**1c**: 93589-90-3 / (*E*)-**1d**: 116952-09-1 / (*E*)-**1e**: 116952-10-4 / (*E*)-**1f**: 116952-11-5 / (*E*)-**1g**: 116952-12-6 / (*E*)-**1h**: 116952-13-7 / (*E*)-**1i**: 116952-14-8 / (*E*)-**1j**: 116952-15-9 / (*E*)-**1k**: 116952-16-0 / (*E*)-**1l**: 116952-17-1 / (*E*)-**1m**: 116952-18-2 / (*E*)-**1n**: 116952-19-3 / (*E*)-**1o**: 116952-20-6 / (*E*)-**1p**: 116952-21-7 / (*E*)-**1q**: 116952-22-8 / (*Z*)-**1r**: 116952-23-9 / (*Z*)-**1s**: 116952-24-0 / (*Z*)-**2a**: 116952-40-0 / (*Z*)-**2b**: 116952-41-1 / (*Z*)-**2c**: 116952-42-2 / (*Z*)-**2d**: 116952-43-3 / (*Z*)-**2e**: 116952-44-4 / (*Z*)-**2f**: 116952-45-5 / (*Z*)-**2g**: 116952-46-6 / (*Z*)-**2h**: 116952-47-7 / (*Z*)-**2i**: 116952-48-8 / (*Z*)-**2k**: 116952-66-0 / (*Z*)-**2l**: 116952-49-9 / (*Z*)-**2m**: 116952-50-2 / (*Z*)-**2n**: 116952-51-3 / (*Z*)-**2o**: 116952-52-4 / (*Z*)-**2p**: 116952-53-5 / (*Z*)-**2q**: 116952-54-6 / (*Z*)-**2r**: 116952-55-7 / (*Z*)-**2s**: 116952-56-8 / (*Z*)-**2t**: 116952-57-9 / (*E*)-**13**: 64516-52-5 / **14b**: 74-89-5 / **14c**: 75-64-9 / **14d**: 109-73-9 / **14e**: 6291-85-6 / **14f**: 107-11-9 / **14g** · HCl: 29840-56-0 / **14h**: 62-53-3 / **14i**: 100-01-6 / **14j**: 104-94-9 / **14k**: 100-46-9 / **14l**: 98-84-0 / **14m**: 120-20-7 / **14n**: 3081-24-1 / **14o**: 61-54-1 / **14p**: 116952-58-0 / **14q**: 60716-71-4 / **14r**: 109-89-7 / **14s**: 103-49-1 / (*Z*)-**15a**: 21759-68-2 / (*Z*)-**15b**: 116952-59-1 / (*Z*)-**15c**: 16226-31-6 / **16**: 2258-42-6 / (*E*)-**17a**: 116952--25-1 / (*E*)-**17b**: 116952-26-2 / (*E*)-**17c**: 116952--27-3 / (*E*)-**17d**: 116952-28-4 / **18a**: 75-36-5 / **18b**: 3282-30-2 / **18c**: 98-88-4 / **18d**: 122-04-3/ **18e**: 50720-05-3 / **18f**: 79-22-1 / **18g**: 90192-47-5 / **18h**: 49845-69-4 / **18i**: 39637-99-5 / **18j**: 39637-74-6 / (*E*)-**19a**: 112112-54-6 / (*E*)-**19b**: 116952-29-5 / (*E*)-**19c**: 116952-30-8 / (*E*)-**19d**: 116952-31-9 / (*E*)-**19e**: 116952-32-0 / (*E*)-**19f**: 116952-33-1 / (*E*)-**19g**: 116952-34-2 / (*E*)-**19h**: 116952-35-3 / (*E*)-**19i**: 116952-36-4 / (*E*)-**19j**: 116970-19-5 / (*E*)-**19k**: 116952-37-5 / (*Z*)-**20**: 102794-85-4 / (*Z*)-**21a**: 116952-38-6 / (*Z*)-**21b**: 78124-56-8 / (*Z*)-**22a**: 116952-39-7 / (*Z*)-**22b**: 16226-31-6 / (*Z*)-**24a**: 116952-61-5 / (*Z*)-**24b**: 116952-62-6 / (*Z*)-**24c**: 116952-63-7 / (*E*)-**24d**: 116952-64-8 / (*E*)-**24s**: 116141-71-0 / (*Z*)-**24t**: 116952-65-9 / **25g**: 2627-86-3 / **25h**: 124-40-3 / **25i**: 299-42-3 / MeOCOCOCl: 5181-53-3 / EtCOCOCl: 4755-77-5 / PhNCO: 103-71-9 / $MeCONH_2$: 60-35-5 / $ClCOC_6H_4$-*o*-COCl: 88-95-9 / $HO_2CCHEtCHO$ · Na: 116952-60-4

[1] J. V. Greenhill, *Chem. Soc. Rev.* **6** (1977) 277; E. Breitmaier, F. W. Ullrich, B. Potthoff, R. Böhme, H. Bastian, *Synthesis* **1987**, 1 and cit. ref.; H. Mertens, R. Troschütz, *Arch. Pharm.* **320** (1987) 1143; M. N. Eberlin, C. Kascheres, *J. Org. Chem.* **53** (1988) 2084; G. Dannhardt, Y. Geyer, R. Obergrusberger, K. Ziereis, *Chem.-Ztg.* **111** (1987) 237; U. Kuckländer, K. Kuna, *Chem. Ber.* **120** (1987) 1601; M. C. Bellassoued- Fargeau, P. Maitte, *J. Heterocycl. Chem.* **23** (1986) 1753; M. Kussler, *Dyes Pigm.* **8** (1987) 179; M. M. Cooper, J. W., Huffman, *J. Chem. Soc., Chem. Commun.* **1987**, 348.

[2] L. F. Tietze, K. Brüggemann, *Angew. Chem.* **91** (1979) 575; *Angew. Chem., Int. Ed. Engl.* **18** (1979) 540; L. F. Tietze, A. Bergmann, K. Brüggemann, *Tetrahedron Lett.* **24** (1983) 3579; L. F. Tietze, A. Bergmann, K. Brüggemann, *Synthesis* (1986) 190.

[3] L. F. Tietze, A. Bergmann, *Angew. Chem.* **97** (1985) 135; *Angew. Chem. Int. Ed. Engl.* **24** (1985) 127.

[4] R. M. Kellogg, *Fortschr. Chem. Forsch.* **101** (1982) 140; J. Everse, B. Anderson, K. S. You, *The Pyridine Nucleotide Coenzymes*, Academic Press, New York 1982; D. M. Stout, A. I. Meyers, *Chem. Rev.* **82** (1982) 223.

[5] F. Bossert, H. Meyer, E. Wehinger, *Angew. Chem.* **93** (1981) 755; *Angew. Chem. Int. Ed. Engl.* **20** (1981) 762.

[6] L. F. Tietze, K. Brüggemann, *Angew. Chem.* **94** (1982) 550; *Angew. Chem. Int. Ed. Engl.* **21** (1982) 539.

[7] L. F. Tietze, E. Voß, K. Harms, G. M. Sheldrick, *Tetrahedron Lett.* **26** (1985) 5273.

[8] L. F. Tietze, E. Voß, *Tetrahedron Lett.* **27** (1986) 6181; L. F. Tietze, T. Hübsch, E. Voß, M. Buback, W. Tost, *J. Am. Chem. Soc.* **110**, in press; S. Apparao, M. E. Maier, R. R. Schmidt, *Synthesis* **1987**, 900.

[9] L. F. Tietze, H. Meier, E. Voß, *Synthesis* **1988**, 274.

[10] G. Büchi, J. A. Carlson, J. E. Powell, L. F. Tietze, *J. Am. Chem. Soc.* **95** (1973) 540.

[11] R. Nylander, *Dtsch. Apoth. Ztg.* **93** (1953) 678.

[12] C. Szántay, L. Szabó, G. Kalaus, *Synthesis* **1974**, 354.

[13] J. Harley-Mason, R. F. J. Ingleby, *J. Chem. Soc.* **1958**, 3639.

[14] A. Treibs, R. Schmidt, *Liebigs Ann. Chem.* **577** (1952) 105; A. Spassow, *Org. Synth.* Coll. Vol. III, 390; G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, R. Terrell, *J. Am. Chem. Soc.* **85** (1963) 207; L. Kozerski, *Tetrahedron* **32** (1976) 1299.

[15] L. I. Krimen, *Org. Synth.* **50** (1970) 1; W. Stevens, A, van Es, *Recl. Trav. Chim.Pays-Bas* **83** (1964) 863. – R. Schijf, J. W. Scheeren, A. van Es, W. Stevens, *Recl. Trav. Chim. Pays-Bas* **84** (1965) 594.

[16] Z. Arnold, F. Šorm, *Collect. Czech. Chem. Commun.* **23** (1958) 452; V. T. Klimko, A. P. Skoldinov, *Zh. Obshch. Khim.* **29** (1959) 3987.

[17] Autorenkollektiv, *Organikum*, 15. Auflage, S. 579, VEB Deutscher Verlag der Wissenschaften, Berlin 1977.

[18] F. Effenberger, R. Maier, K. H. Schönwälder, T. Ziegler, *Chem. Ber.* **115** (1982) 2766.

[19] J. Emsley, N. J. Freeman, R. J. Parker, R. Kuroda, R. E. Overill, *J. Mol. Struct.* **159** (1987) 173, cit. ref; K. Dixon, J. V. Greenhill, *J. Chem. Soc., Perkin Trans. 2*, **1974**, 164.

[20] W. E. Stewart, T. H. Siddall, *Chem. Rev.* **70** (1970) 517.

[21] [21a] J. Dabrowski, L. Kozerski, *Org. Magn. Reson.* **5** (1973) 469; [21b] H. Kessler, *Angew. Chem.* **82** (1970) 237, *Angew. Chem. Int. Ed. Engl.* **9** (1970) 219. – [21c] J. Sandström, I. Wennerbeck, *J. Chem. Soc., Chem. Commun.* **1971**, 1088.

[22] [22a] D. L. Ostercamp, *J. Org. Chem.* **35** (1970) 1632; C. Kashima, M. Yamamoto, N. Sugliyama, *J. Chem. Soc. C* **1970**, 111. – [22b] J. Dabrowski, K. Kamieńska-Trela, *J. Am. Chem. Soc.* **98** (1976) 2826. – [22c] G. Uray, O. S. Wolfbeis, H. Junek, *J. Mol. Struct.* **54** (1979) 77. – [22d] L. Kania, K. Kamieńska-Trela, M. Witanowski, *J. Mol. Struct.* **102** (1983) 1.

[23] D. Smith, P. J. Taylor, *Spectrochim, Acta, Part A*, **32** (1976) 1477.

[24] S. Sternhell, *Q. Revs., Chem. Soc.* **23** (1969) 236.

[25] C. Skötsch, E. Breitmaier, *Chem. Ber.* **113** (1980) 795.

[26] J. Dabrowski, K. Kamieńska-Trela, L. Kozerski, *Org. Magn. Reson.* **6** (1974) 499.

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