Access to Isolable Azomethine Ylides by Photochemical Transformation of 2,3-Dihydroisoxazoles

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Dedicated to Professor Howard E. Zimmerman

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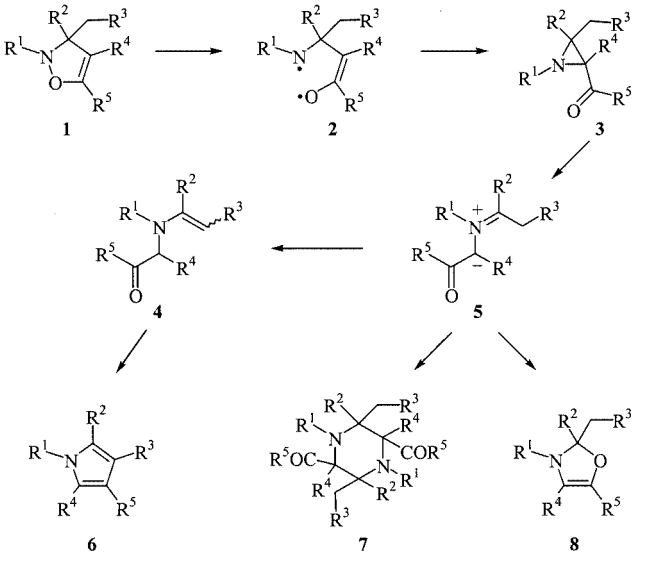
Photochemical excitation of the 2,3-dihydroisoxazoles **19**–**21** resulted in the formation of the stable azomethine ylides **22**, **25**, and **28**, representing the first isolable examples of such species bearing stabilizing groups only at one end of the 1,3-dipole. The UV and NMR spectroscopic data of the photoproducts clearly indicate that the iminium and the anionic parts of the azomethine ylide systems are not planar. This conclusion is unambiguously confirmed by crystal structure analysis of **25b**, in which a twist angle of 73° was determined between the two polar moieties. In the case of **25d** the rotation barrier around the central CN bond amounts to 16 kcal/mol at 333 K. In line with the unusual stability of the ylides is their low reactivity against dipolarophiles. Only the highly reactive *N*-methyltriazolidinedione gives formation of the products **33a**, **35a**–**c**, and **41**, but these are the result not of an initial 1,3-dipolar cycloaddition but rather of a formal [4+2] addition with involvement of **34a**, **36a**–**c**, and **41** as unstable primary products. On heating in refluxing toluene the azomethine ylides are transformed into annulated pyrrole systems (**42/43**, **46/47**, **48/49**). In contrast to other examples, the direct thermal transformation of the annulated 2,3-dihydroisoxazoles into pyrroles is not successful, but the reaction can be achieved by simultaneous thermal and photochemical activation, as shown for the conversion of **19** into the pyrroles **42/43**.

Introduction

Azomethine ylides are important building blocks, mostly used in situ as reactive intermediates, for the construction of N-heterocyclic compounds.[1] Among their most successful preparations are: (i) the thermal or photochemical CC-cleavage of aziridines,[2,3] (ii) the prototropic rearrangements of imines,[4] (iii) the decarboxylative route from amino acids and aldehydes,[5] and (iv) the widely variable desilylation methods of iminium precursors.[6,7] In connection with our ongoing work on novel applications of 1,3-dipoles in heterocyclic synthesis[8] we have explored the potential of 2,3-dihydroisoxazoles (type **1**) as precursors of stabilized and possibly isolable azomethine ylides **5**. The isolation of 2,3-dihydroisoxazoles is difficult in many cases because of their lability, and secondary reactions often afford a number of products.[9] The most frequently observed transformations are shown in Scheme 1 and include the formation of pyrroles **6**,[10] 2,3-dihydrooxazoles **8**,[9,11] and piperazines **7**.[9,12] The isolation of acyl aziridines **3** has been described for a few compounds formed under mild conditions and possessing sufficiently high barriers against further transformations.[13,14] We have recently shown that 2π- and 4π-substituted 2,3-dihydroisoxazoles can be used as masked azomethine ylides for subsequent 1,5- and 1,7-dipolar cyclization reactions.[15]



Scheme 1

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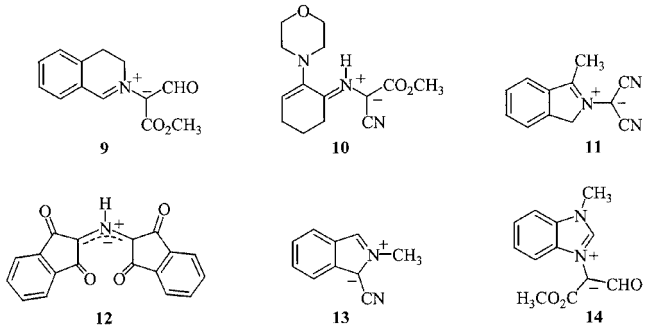
Generally, azomethine ylides are only isolable under ambient conditions if particular electronic requirements are met, as shown with the efficiently stabilized dipoles **9**,[16] **10**,[17] **11**,[18] **12**,[19] **13**,[20] and **14**[21] as representative examples (Scheme 2).[22,23]



Scheme 2

In order to avoid thermally provoked secondary reactions of the azomethine ylides, the intention in this work was to induce the transformation **1→5** by electronic excitation. Although the photochemical behavior of five-membered heteroaromatic systems and their dihydro analogues − including isoxazoles and 4,5-dihydroisoxazoles − has been extensively studied, photochemical experiments with the respective 2,3-dihydro isomers are still lacking.[24,25] We now describe the photochemical transformation of a series of differently annulated dihydroisoxazoles **19−21**[26] into the isolable azomethine ylides **22**, **25**, and **29**, discussion of their structures, and some investigations of the chemical reactivity of the dipolar systems.[27]

Results and Discussion

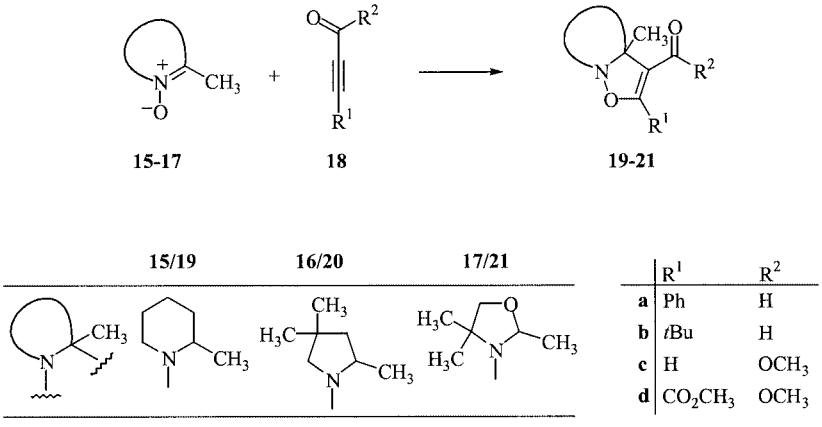
The well established 1,3-dipolar cycloaddition methodology was employed for the preparation of the required 2,3-dihydroisoxazoles **19−21**.[28] Treatment of the known nitrones **15−17** with the alkynes **18a−d** afforded the cycloadducts **19a−d**, **20a−d**, and **21a**, **21b**, and **21d** in good yields and with perfect regioselectivities (Scheme 3, Table 1). Only the reaction between methyl propiolate and **17** was unsuccessful, affording an unspecific mixture with only traces of **21c**. As can be seen from the reaction conditions, the cycloaddition reactivity of the piperidino nitrone **15** is significantly lower than those of **16** and **17**.

Table 1. Reaction conditions, yields, and UV data for the 2,3-dihydroisoxazoles **19a−d**, **20a−d**, and **21a**, **21b**, and **21d**

	Reaction conditions	Yield [%]	λ_{max} (ε)[a]
19a	EtOH, 30 min, rfx	80	302 (8800)
19b	EtOH, 30 min, rfx	83	282 (7500)
19c	EtOH, 10 h, rfx	59	269 (5300)
19d	EtOH, 2 h, rfx	77	268 (2900)
20a	Et_2O, 17 h, room temp.	85	303 (8000)
20b	Et_2O, 17 h, room temp.	83	285 (8800)
20c	Et_2O, 20 h, room temp.	85	261 (6100)
20d	Et_2O, 3 h, room temp.	92	269 (3800)
21a[b]	CH_2Cl_2, 24 h, room temp.	85	289 (8700)
21b[b]	CH_2Cl_2, 24 h, room temp.	69	278 (10800)
21d[b]	CH_2Cl_2, 26 h, room temp.	69	265 (4400)

[a] In CH_3CN. [b] Treatment of **18a**, **18b**, and **18d** with nitrone **17** prepared in situ.

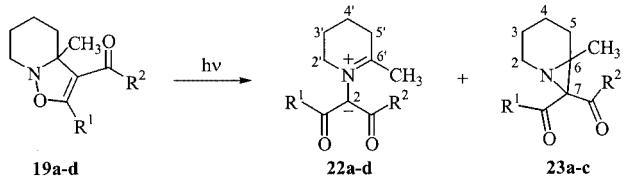
The wavelengths of the **c** and **d** series are slightly red-shifted (261−278 nm, see Table 1) relative to the UV absorption maxima of the dihydroisoxazoles **a** and **b** (278−302 nm), thus allowing excitation through the use of a Vycor filter (λ > ca. 230 nm) for the **c** and **d** compounds and of a Jenaglass filter (λ > ca. 280 nm) in the latter case. Irradiation of a ca. 10^{-3} molar solution of **19a** in benzene with a high-pressure mercury lamp (Hanua 150 W) afforded a main product, identified as the azomethine ylide **22a**, in 88% yield (m.p. 133 °C) after complete conversion (36 min) and subsequent chromatographic purification. Under similar conditions, the *tert*-butyl derivative **19b** is likewise transformed into **22b** (75%, m.p. 104 °C). In the cases of **19c** and **19d** the photolysis was performed in diethyl ether, and compounds of the dipolar structure **22** were again isolated as the major products (**c**: 25%, **d**: 58%). The low yields, especially of **22c**, are mainly due to product loss during the chromatographic workup; according to ^1H NMR analysis carried out prior to purification, both **22c** and **22d** had been



	R^1	R^2
a	Ph	H
b	*t*Bu	H
c	H	OCH_3
d	CO_2CH_3	OCH_3

Scheme 3

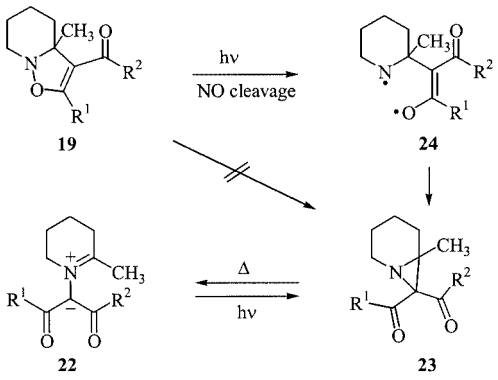
formed in about 70−80% yields. Furthermore, careful inspection of the ^{1}H NMR spectra of the **a-c** series (but not **d**) revealed additional signals compatible with the azabicyclo[4.1.0]heptene structure **23**, the ratios of **22**:**23** amounting to approximately 10:1 (**a**), 60:1 (**b**), and 6:1 (**c**). Unfortunately, all attempts to isolate the bicyclic isomers have so far failed. The dipolar compounds **22a**−**d** are the first representatives of isolable azomethine ylides bearing stabilizing groups only at one terminus of the 1,3-dipolar system. The few examples with π-substituents on both sides are mostly derived from conjugated iminium compounds such as isoquinolinium or dihydroisoquinolinium ylides.[16,29,30]



Scheme 4

The structures of the azomethine ylides **22** were determined by spectroscopic/analytical investigations (see Exp. Section) as well as from some chemical transformations (vide infra). In addition to the elemental analyses and/or MS and HRMS data, through which the isomeric natures of the photoproducts and their starting compounds were established, the IR, UV, and NMR spectroscopic data unambiguously support the proposed structures. For **22a**, characteristic NMR absorptions are: δ_H = 8.91 (CHO), 3.90 (2′-H), 2.91 (5′-H), 2.34 (6′-CH_3); δ_C = 33.4 (C-5′), 53.7 (C-2′), 123.0 (C-2), 140.3 (C-6′). Interestingly, the UV absorption bands are at relatively short wavelengths, with maxima at 333 (ε = 3500) and 280 nm (ε = 13500), which is probably due to reduced conjugation between the twisted cyclic and the acyclic parts of the dipole system.[31] Because all attempts to isolate the bicyclic aziridines **23a**−**c** were unsuccessful, their identification had to be performed on the basis of their ^{1}H NMR spectra: the following signals are indicative for **23a/b/c**: 2.58/2.41/2.47 (6-CH_3), 3.55/3.57 (**a**, **c**: 5′-H), 3.79/3.90 (**a**, **c**: 2′-H), 9.29/9.70/9.53 (CHO).

The proposed pathway of the transformation **19**→**22/23** is outlined in Scheme 5. It includes the photochemically induced NO-cleavage to the diradical **24** as first step, followed by bond reorganization to the bicyclic aziridine **23**, which undergoes CC-cleavage to afford the final product **22**. To examine the multiplicity of the excited state, the irradiation of **19a** was also performed in acetone, both as solvent and as triplet sensitizer (E_T = 80 kcal/mol). Under conditions otherwise analogous to those described for the direct excitation, a reaction mixture giving an 85% yield of **22a** and **23a** in a 10:1 ratio was obtained after chromatography purification. The almost identical results strengthen the supposition that the reacting species is triplet in nature. In this case a two-step mechanism with an intermediate such as **24** should be operative, thus excluding an alternative symmetry-allowed 1,3-N shift **19a**→**23a**, which would be conceivable from the excited singlet state of **19**.



Scheme 5

Further evidence for the intermediacy of aziridines **23** was obtained from independent photolysis experiments. After irradiation of ca. 10^{-3} molar solutions of **22a** in benzene for 10 min, the ^{1}H NMR spectrum of the photolysate indicated the presence of a ca. 10:1 mixture of **22a** and bicyclic aziridine **23a**, the isomer ratio being the same as obtained from the photoreaction of **19a**. This therefore indicates that the electronically excited ylide **22a** is transformed into the aziridine **23a**. In order to slow down or suppress thermal reactions, the irradiation of a sample of **19a** in CD_3CN was performed in a NMR tube at −30 °C until complete conversion. Analysis of the ^{1}H NMR spectrum revealed the appearance of two products, **22a** and **23a**, but now in a 2:1 ratio. After the mixture had warmed to room temperature, however, the ratio had again changed to 10:1. From the above results it is concluded that **23a** is thermally converted into the azomethine ylide **22a**, whereas the reverse reaction takes place on electronic excitation.

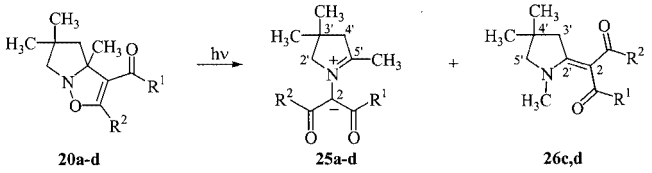
The photolysis experiments with the pyrrolo isoxazolines **20a**−**d** (see Table 1 for the UV data) were performed under the conditions described for the piperidino derivatives **19**. Despite the use of light of higher energy (λ > 230 nm) the consumption of **20c** and **20d** is considerably slower than for **20a** and **20b** (λ > 280 nm). According to the product analyses, one compound − namely the corresponding azomethine ylide (**25a**−**d**) − was formed exclusively or predominately in each case (60−91% yield, see Table 2). There were no indications of the presence of aziridines of type **23**, but further products were isolated in 8 and 17% yields, respectively, in the cases of **20c** and **20d**. These similarly turned out to be isomeric with the starting dihydrooxazolines and were identified as the pyrrolidinylidenemalonates **26c** and **26d** (Scheme 6).

The NMR spectra of the dipoles **25** agree well with the data for the corresponding piperidino derivatives **22** (Table 3), and the UV absorptions are again, as would be expected, at shorter wavelengths (Table 2). As already discussed for the azomethine ylides **22**, the non-planarity of the ylide system might be the reason for this. This explanation is supported in the case of **25** by the observation that

Table 2. Photolysis of **20a−d**

	Conditions[a]	Products[b] **25** [UV data][c]	**26**
20a	benzene, λ > 280 nm, 1.5 h	88 [330 (3600), 278 (13400)]	−
20b	benzene, λ > 280 nm, 1.7 h	91 [331 (1600), 274 (16600)]	−
20c	acetonitrile, λ > 230 nm, 3.7 h	60 [335 (2100), 256 (13700)]	8
20d	acetonitrile, λ > 230 nm, 4.5 h	75 [326 (1700), 261 (11800)]	17

[a] 1.0 mmol of **20** in 250 mL of solvent. [b] Yields in %, after purification. [c] λ_{max} [nm] (ε), in CH_3CN.



Scheme 6

the methylene protons at C-2′ and C-4′ give rise to broadened AB signals in the ^{1}H NMR spectra, thus indicating their non-equivalence. Because of the bulky substituents at the azomethine moiety there is obviously no free rotation around the central CN bond and hence no planarity of the molecules. A strong indication of a barrier to the geometrical change of the dipole system was provided by dynamic NMR experiments with **25d**. When a sample of **25d** was heated in pentadeuteriobromobenzene, the 19.5 Hz splitting of the methylene protons at C-4′ disappeared and the coalescence temperature was reached at 333 K, corresponding to a $\Delta G^{\#}$ value of 16 kcal/mol (δ_A = 2.51, δ_B = 2.30, in C_6D_5Br).

Table 3. Selected NMR spectroscopic data (δ-values, in $CDCl_3$) of the azomethine ylides **25a**, **25b**, and **25d**

	^{1}H-shift				^{13}C-shift				
	2′-H	3′-CH_3	4′-H	5′-CH_3	C-2	C-2′	C-3′	C-4′	C-5′
25a	4.10	1.32	2.98	2.30	116.8	71.7	35.7	52.7	184.9
	4.22	1.35							
25b	3.84	1.29	2.82	2.17	115.2	71.5	35.4	52.4	186.4
	4.05	1.30	2.98						
25c	3.85	1.25	2.80	2.28	101.8	72.1	35.3	50.1	185.4
	4.28		3.00						
25d	4.89	1.29	2.86	2.33	97.7	72.3	35.5	52.6	171.0
	4.20		3.04						

Final confirmation of the non-planarity of **25b** was obtained by crystallographic analysis[32] (Figure 1). Among the various parameters, it is of particular interest that the N−C6 bond is significantly longer (1.445 Å) than the N−C2 bond of the azomethine ylide system (1.292 Å), indicating little or no π-conjugation between the ring nitrogen and C6. The former bond length is only slightly shorter than the average length of a $^{(sp3)}N-C^{(sp3)}$ bond (1.48 Å), compared to 1.35 Å for a $^{(sp2)}N-C^{(sp2)}$ bond. On the other hand, the second N−C bond of the ylide is even shorter than a pure C=N bond.

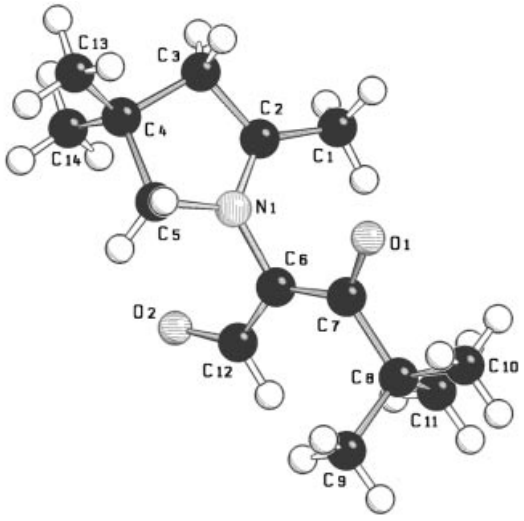


Figure 1. Crystal structure of the azomethine ylide **25b** (SCHAKAL drawing, hydrogen atoms omitted; the numbering does not correspond with the correct nomenclature); selected bond lengths [Å] and angles [°]: C2−N 1.292, N−C5 1.467, N−C6 1.445, C2−C3 1.491, C3−C4 1.531, C4−C5 1.541, C6−C7 1.429, C6−C12 1.395; C2−N−C5 112.7, C2−N−C6 126.2, C7−C6−N 116.1, C2−N−C5 112.7, C7−C6−C12 130.5; angle between the planes C5−N−C2 and C7−C6−C12 72.7

The structural data are in agreement with the other known X-ray data relating to the isolable azomethine ylides **10**,[17b] **11**,[18] **12**,[19] and **13**[20] (Table 4). With the exceptions of the symmetric bis-indanedione derivative **12** and the endocyclic system **13**, there are significant differences between the C−N bond lengths, indicating strong bond localization with high double bond and single bond character, respectively. Whereas the C−N−C bond angle in **13** (110°) is consistent with the value for five-membered rings, the corresponding angles in **10−12** and **25b** are in the 121−134° range. An important feature of the structures is the geometry of the dipole unit. The expected planarity of the 1,3-dipole is seen only in **10** (the arrangement is obviously assisted by a hydrogen bond between the N−H and the carbonyl oxygen of the ester function) and in **13** (due to the endocyclic structure). In contrast, compounds **11** and **12** have twist angles of 30° and 20°, respectively. However, most striking is the fact that the cyclic immonium and the anionic parts of **25b** are twisted around the N−C6 bond with an angle of 73°, the two components being arranged in an almost orthogonal manner, resulting in significant charge separation. With this observation in mind, the relatively short-wavelength UV absorptions of the azomethine ylides and the signal doubling of the methylene protons of **25a−d** find a convincing explanation.

In view of the non-planarity of the dipolar system, the unexpected stability of the compounds **25** (the same should apply for **22**) must be due to a particular electronic stabilization of the ionic centers, and possibly steric effects. This is a further example of thermodynamic and/or kinetic stabilization of not usually isolable intermediates, such as the Ard-

Table 4. C−N distances, C−N−C angles, and twist angles in the dipoles **25b** and **10**−**13**

	C−N [Å]	C−N−C [°]	twist [°]
25b	1.30/1.44	121	73
10[17]	1.30/1.43	134	
11[18]	1.32/1.40	127	30
12[19]	1.34/1.35	128	20
13[20]	1.35/1.37	110	

uengo carbenes[33] or particularly substituted carbocations, carbanions, or radicals.[34] However, it has to be emphasized that the electronic nature of the original species has significantly changed in all those cases. The question therefore arises of whether the compounds still belong to the respective parent class of compounds. With regard to the above discussion, as well as to the chemical experiments with several derivatives of the azomethine ylides **22** and **25** (vide infra), there are at least doubts.

The structure determination of the minor photoproducts of **20c** and **20d**, confirmed as isomers by elemental analyses and MS, raised some problems. Comparison of the NMR spectra with the data for the dipoles **25c** and **25d** showed that there were two main differences: the low-field absorption of one methyl group (3.06/301 ppm compared to 2.28/2.33 ppm) and the appearance of the ring methylene protons as sharp singlets at δ = 3.12/3.4 and 3.09/3.85, respectively. The assignment of the pyrrolidinylidenemalonate structures **26c** and **26d** was supported by an X-ray analysis of **26d**[32] (Figure 2). The relatively short N−C4 bond (1.309 Å) and the unusually long C4−C5 bond (1.427 Å) are indications that the dipolar resonance structure of **26d** represents an important contribution to the carbonyl-substituted enamine system. The exocyclic double bond is not planar, the twist angle amounting to 36°.

The formation of the enamines **26c** and **26d** can be explained by the assumption of an excited state cleavage of the NO bond as first step, producing the diradical **27** (see Scheme 7), followed by a 1,2-migration of the methyl group to afford **26**. Although the mechanism seems quite plausible, we are aware of only one analogous methyl shift, which is involved, however, during a thermal reaction between bis(trifluoroacetylene) and an aromatic nitrone.[35]

The photolysis of the oxazolo-dihydroisoxazole derivatives **21a**, **21b**, and **21d** in each case gave only one photoisomer, with the structure of the corresponding azomethine ylide (**28a**, **28b**, and **28d**; Scheme 8). As judged from the NMR spectra of the raw photolysates, the yields of the products were almost quantitative, the given yields of 89, 60, and 90%, respectively, being due to their partial decomposition during workup and showing rather the lower limit. The hindered rotation around the central CN bonds in compounds **28** is nicely reflected by the appearance of two NMR singlets for the C-4′ methyl groups and the AB patterns for the C−5′ methylene protons in **28b** and **28d** (Table 5).

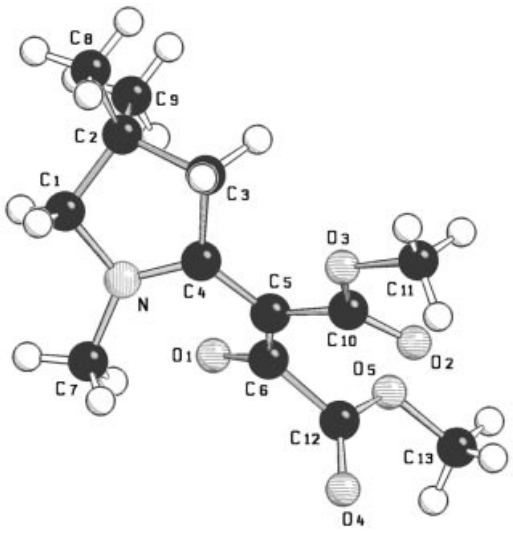
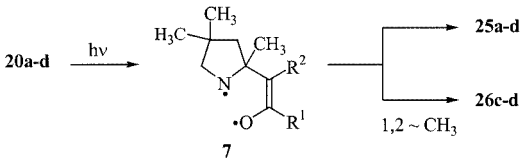
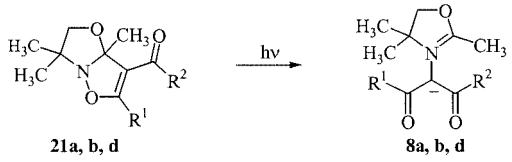


Figure 2. Crystal structure of the pyrrolidinylidenemalonate **26d** (SCHAKAL drawing, hydrogen atoms omitted; the numbering does not correspond with the correct nomenclature); selected bond lengths [Å] and angles [°]:C1−C2 1.533, C2−C3 1.544, C3−C4 1.504, N−C1 1.474, N−C4 1.314, C4−C5 1.436; N−C4−C3 108.9, N−C4−C5 124.1, C3−C4−C5 126.9; angle between the planes N−C4−C3 and C6−C5−C10 36.0



Scheme 7



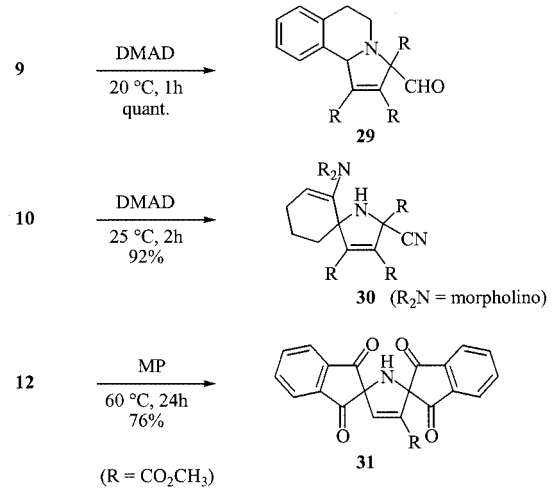
Scheme 8

Table 5. Selected NMR spectroscopic data (δ-values in $CDCl_3$) for the azomethine ylides **28a**, **28b**, and **28d**

	^{1}H-shift			^{13}C-shift			
	5′−H	2′−CH_3	4′-CH_3	C−2	C−2′	C−4′	C−5′
28a	4.70	2.28	1.53 1.57	108.8	176.8	69.9	82.1
28b	4.64 4.62	2.15	1.36 1.48	110.3	176.6	69.6	82.0
28d	4.63 4.72	2.33	1.52 1.53	89.1	178.1	70.1	82.4

With regard to the chemical reactivity of isolable azomethine ylides, there are reports of cycloaddition reactions with appropriate dipolarophiles under mild conditions,

such as the formation of **29**–**31** from the respective compounds **9**,[16] **10**,[17] and **12**[19] (Scheme 9).



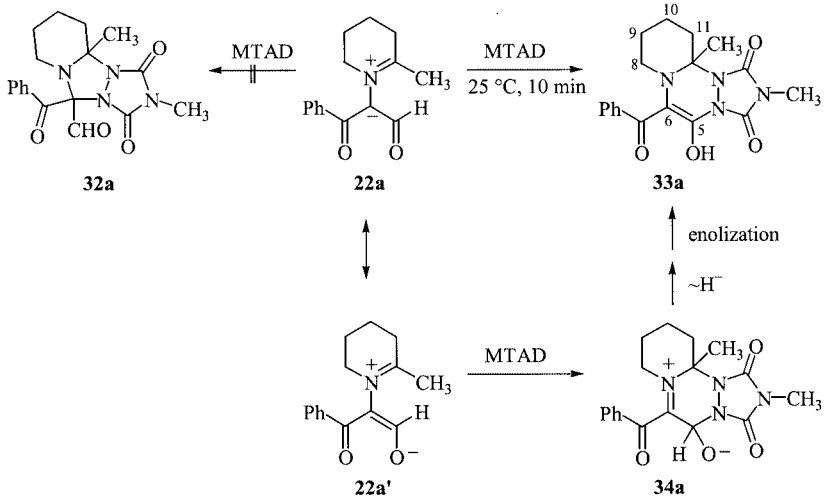
Scheme 9

In sharp contrast to the above results, all attempts to achieve such 1,3-dipolar cycloadditions between examples of the dipolar compounds **22**, **25**, and **28** and dimethyl acetylenedicarboxylate (DMAD), methyl propiolate (MP), or *N*-phenyl maleimide (NPMI) as dipolarophiles failed. At ambient temperatures there was no conversion, whereas only complex mixtures containing no separable products were obtained in boiling benzene solutions. Treatment of **22a** with methyltriazolinedione (MTAD) in dichloromethane, however, resulted in complete conversion after 10 min at 25 °C affording a single crystalline product in 78% yield (m.p. 155 °C). Although the elemental analysis and the MS supported the formation of a 1:1 adduct (*m*/*e* = 356), the expected structure **32a** was inconsistent with the NMR spectroscopic data. Most importantly, there was no aldehyde proton signal; instead a broad absorption at δ = 13.5 ppm, which disappeared on addition of D_2O, was a clear indication of a chelated OH group. Among the other data, the ^{13}C absorptions at δ = 162.4 and 110.8 ppm should be mentioned; these are caused by the two olefinic carbon atoms C-5/C-6 (Table 5) and support the proposed structure **33a**.

The formation of **33a** cannot be explained by a 1,3-dipolar cycloaddition, but must rather proceed through a formal [4+2] addition onto the enolate form **22a′** of the dipolar system to produce the betaine **34a**, which rearranges to the keto tautomer of **33a** by a 1,2-hydride shift (alternatively, a proton transfer to the oxygen to afford **33a** would also be conceivable). This unusual behavior of the azomethine ylide moiety must be due to the particular geometry discussed above, in which the interaction between the two parts of the molecule is significantly decreased. However, we have no obvious explanation for the fact that the attack of MTAD takes place at the carbonyl carbon of **22a**.

To the best of our knowledge there is only one previously described comparable reaction mode for the addition of dipolarophiles to 1,3-dipoles: the addition of electron-deficient alkynes to phosphanyldiazoalkanes. In this case the electrophilic attack of the diazaphosphanes produces 1,2,4-λ^5-diazophosphanes, probably through the intermediacy of 1,6-dipolar species.[36]

Under conditions similar to those described for **22a**, the reactions between the pyrrolidine derivatives **25a**–**c** and MTAD proceeded much more slowly and less cleanly. Because of the instabilities of the products and the increasing formation of polymeric material, the reactions were stopped after 30 min, a point at which less than 50% conversion had been reached. After chromatographic workup two monomeric products were isolated: the starting material **25** as the main component (ca. 40%) and a minor compound (10–14%) to which the structure of **35** was assigned (Scheme 11). Although the compounds are structurally related to **33a**, the loss of an oxygen at C-5 is an surprising



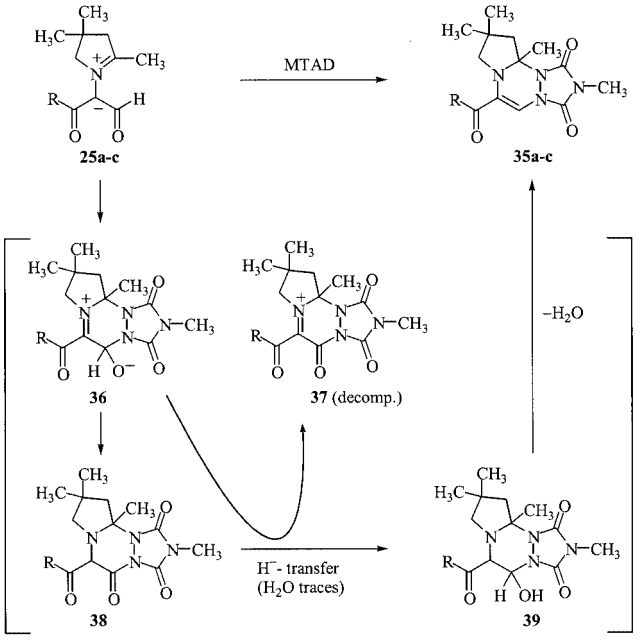
Scheme 10

discrepancy (indicated by the elemental analysis and the MS). That difference aside, the NMR spectroscopic data are very comparable (see Table 5).

Table 6. Selected NMR spectroscopic data (δ values, in $CDCl_3$) of the cycloadducts **33a** and **35a−c**

	^{1}H-shift				^{13}C-shift			
	5-OH[a] 5-H[b]	8-H	11-H[a] 10-H[b]	11a-CH_3 [a] 10a-CH_3 [b]	C-5	C-6	C-8	C-11a[a] C-10a[b]
33a	13.5	2.70 3.19	1.66 2.70	1.56	162.4	110.8	52.0	76.6
35a	7.32	2.65 3.36	2.12 2.98	1.42	125.9	114.7	65.0	81.7
35b	7.37	2.59 3.30	2.02 3.06	1.35	125.5	112.3	66.5	81.9
35c	7.63	2.62 3.60	2.07 3.00	1.32	117.7	112.6	65.7	82.1

[a] **33a**. [b] **35a−c**.



Scheme 11

Mechanistically, the most difficult problem lies in the fact that a reduction step has to be involved. Because there is no particular reduction agent present, we tentatively propose the route outlined in Scheme 12. The pathway includes a Cannizzaro-type hydride transfer between the dipole **36** and product **38** (keto tautomer), resulting in the formation of the iminium derivative **37** (which might be responsible for the polymeric material) and the alcohol **39**, the direct precursor of the final products **35a−c**. In view of the 50% loss of starting material by this pathway, the low experimental yield of **35** would find a reasonable explanation.

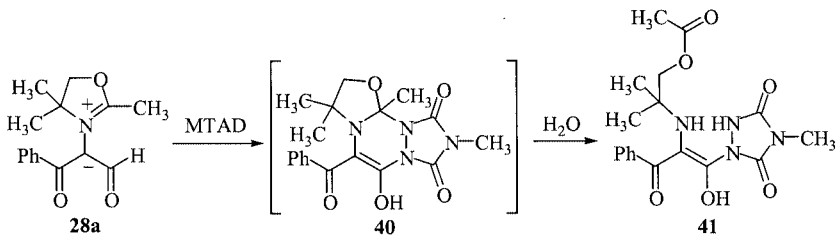
Treatment of the oxazolino derivative **28a** with MTAD at room temperature for 3 days again resulted in a formal [4+2] addition, but the isolation of the corresponding triazine **40**, the diaza analogue of an orthoester, was not successful. Instead, the hydrolyzed compound **41** was isolated after chromatographic separation (Scheme 12). As in the case of **33**, but in contrast to that of **35**, no reduction process is involved in the reaction pathway.

It is generally accepted that the thermal transformation of 3-alkyl-substituted 2,3-dihydrooxazolines into pyrroles proceeds through azomethine ylides as intermediates (see Scheme 1. **1→5→6**).[9,10] In order to lend further support to this assumption, we performed investigations with some of the dipolar systems described above. Transformations of the piperidino derivatives **22a−d** were successfully achieved by heating them at reflux in toluene solutions for 1.5−6 h. Depending on the nature of R^1 and R^2, either the two tetrahydroindolizines **42** and **43** (**a**,**b**) or only one isomer (**43c**,**d**) were isolated (Scheme 13). This result can be explained by assuming a 1,4-H-shift to the enamine **44** as the first step, followed by a cyclocondensation process. The observed chemoselectivity is in agreement with the decreasing reactivity of the carbonyl component in the order CHO > COR > CO_2CH_3.

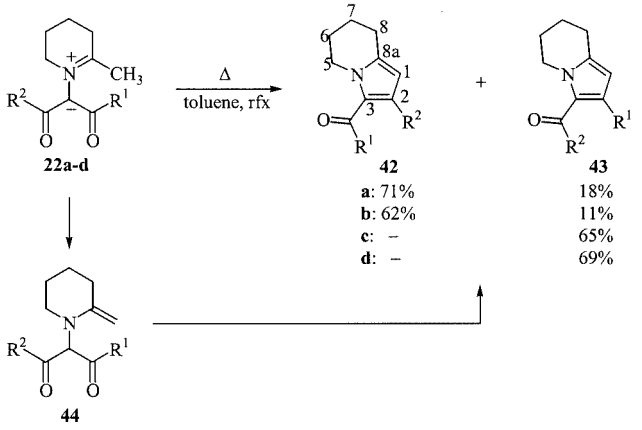
The transformation of azomethine ylides into annulated pyrrole derivatives adds a new alternative to the synthesis of such heterocycles. In this context the question arose of whether the same result might be achieved by direct transformation of the bicyclic 2,3-dihydroisoxazoles used in this work. Experiments performed with the piperidino compounds **19a−d** were unsuccessful, however, complex product mixtures with only traces of the expected pyrroles **42/43** being detected after toluene solutions of **19** had been heated at reflux. This failure, though, is probably due to side reactions: if the transformation of **19a** is performed under short-time thermolysis conditions (330 °C/ca. 10 s contact time), the pyrroles **42a/43a** are similarly formed in high yield.[37] Interestingly, heating of toluene solutions of **19** with simultaneous irradiation with a daylight 500 W lamp also resulted in the formation of the indolizines **42/43**, albeit in lower yield (Scheme 14).

The thermal behavior of the pyrrolidine dipoles **25** parallels that of the higher homologues **22**, with the exception of significantly longer reaction times (3 days vs. 1.5−6 h, in refluxing toluene), and the additional formation of the enamines **45a−d** (Scheme 15). It was shown by independent experiments that the latter compounds can be transformed into the pyrrolizidines **46/47** on heating benzene solutions of **45** in an autoclave for 12 h at 200 °C. The high thermal stability of the products follows from the observation that the yields of the heterocycles are still quite high despite the harsh conditions (**46a/47a**: 70%/5%; **46b/47b**: 80%/4%; **47c**: 60%, **47**d: 65%).

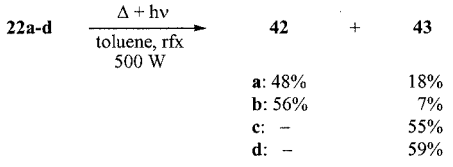
The dihydrooxazole system **28** turned out to be much more stable, and so the thermal reactions of **28a** and **28b** were performed with benzene solutions in an autoclave at 200 °C for 12 and 3 h, respectively. Chromatographic purification of the reaction mixtures resulted in each case in the isolation of three products: the pyrroles **48a/48b** (13%, 20%) and **49a/49b** (13%, 13%), as well as the non-cyclic *N*-formyl derivatives **52a/52b** (45%, 38%). Whereas the formation of the two annulated pyrroles follows the same pathway as dis-



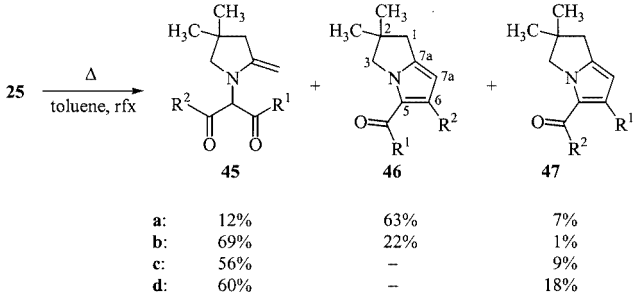
Scheme 12



Scheme 13

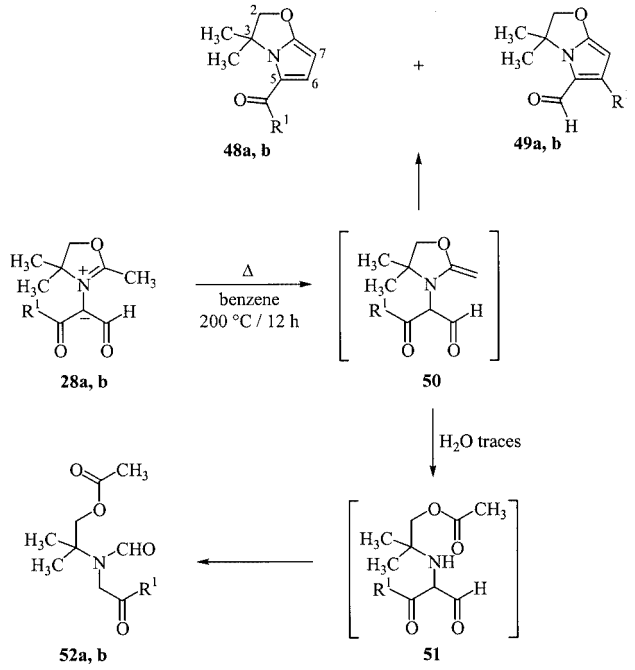


Scheme 14



Scheme 15

cussed for the related compounds **42/43**, the occurrence of the major components **52a** and **52b** is quite unexpected. Our tentative explanation includes the hydrolysis of the enamines **50** by traces of water to afford compounds **51**, which undergo rearrangement to the observed products **52** (Scheme 16). The latter transformation can be regarded as an intramolecular cleavage of a 1,3-dicarbonyl compound by a secondary amine, a reaction documented for the bimolecular alternative.[38]



Scheme 16

Conclusion

The aim of this work was to investigate the photochemical behavior of 2,3-dihydroisoxazoles. On irradiation of annulated heterocycles of this type, substituted at C-4 with keto, aldehyde, or ester functions, transformations to stable azomethine ylides take place as the main reaction pathway. For the first time, compounds of this type with stabilizing groups at only one terminus of the 1,3-dipolar system were isolated under ambient conditions. On the basis of the NMR spectroscopic data, and in particular a crystal structure analysis of **25b**, evidence for the non-planarity of the iminium and the anionic parts of the molecules was obtained. The twist angle in **25b** amounts to 73°, a clear indication of almost no conjugative interaction between the polar centers. In the case of **25d**, the rotation barrier around the central CN bond was determined to be 16 kcal/mol at

333 K. In view of the significantly reduced electronic interaction within the dipolar structures, which is also documented in the relatively short-wavelength UV absorptions ($\lambda_{max} < 335$ nm), the unusual stability of the dipolar compounds **22**, **25**, and **28** is very surprising. Along the same lines, but in contrast to other isolable azomethine ylides, is their low reactivity towards dipolarophiles such as dimethyl acetylenedicarboxylate or *N*-phenylmaleimide. With *N*-phenyltriazolinedione, however, formal Diels−Alder additions do take place, finally affording the products **33a**, **35a−c**, and **41**, respectively.

Although the formation of pyrroles by thermal transformation of simple 2,3-dihydrooxazoles is a well known procedure, only the methodology involving a photochemical and a thermal step is successful for obtaining annulated pyrroles such as **42/43**, **46/47**, and **48/49**.

Experimental Section

General: Melting points are uncorrected. IR: Perkin−Elmer 257 Infracord. ^{1}H NMR: Bruker WM 250 (250 MHz), ^{13}C NMR: Bruker WM 400 (100 MHz). $CDCl_3$ as solvent and TMS as internal standard. MS: Finnigan MAT 44 S (70 eV) with Datasystem MAT SS 200. Elemental analyses: Perkin−Elmer Elemental Analyzer 240. Products were isolated by flash chromatography on silica gel (Silica 32−36, ICN Biomedicals) or alumina oxide /Alumina N, Biomedicals). TLC: SiO_2 60 F-254, 0.2 mm (Merck). Irradiation was performed with a 150 W high-pressure mercury lamp (Hanau TQ 150) at 20 °C with either a Vycor ($\lambda >$ ca. 230 nm) or a Jena glass filter ($\lambda >$ ca. 280 nm) at ca. 20 °C; the solutions were saturated with dry nitrogen before irradiation.

General Procedure for the Preparation of the Dihydrooxazoles 19 by 1,3-Dipolar Cycloaddition: A solution of the nitrone **15** (ca. 5 mmol) and the alkyne derivative **18** (1.1 equivalent) in ethanol (30−80 mL) was heated at reflux until complete conversion (0.5−2 h). After concentration, the remaining solution was poured into water (ca. 20 mL) and then extracted with dichloromethane. The combined organic solutions were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The crude material was purified by flash chromatography (SiO_2).

3a-Methyl-2-phenyl-4,5,6,7-tetrahydro-3a*H*-isoxazolo[2,3-*a*]-pyridine-3-carbaldehyde (19a): Treatment of 6-methyl-2,3,4,5-tetrahydropyridine *N*-oxide (**15**)[39] (0.70 g, 6.2 mmol) with **18a** (0.87 g, 6.7 mmol) in boiling ethanol (30 mL, 30 min) gave **19a** (1.20 g, 80%) as a colorless solid after flash chromatography (SiO_2, cyclohexane/ethyl acetate, 25:1) and subsequent recrystallization, m.p. 80 °C (ethyl acetate). IR (CCl_4): $\tilde{\nu}$ = 2960, 2940, 2850, 2820, 2740 (OC-H), 1650 (C=O), 1620, 1590, 1490, 1450, 1440, 1390, 1370, 1350, 1340, 1275, 1115, 1065, 690 cm^{-1}. ^{1}H NMR: δ = 1.32 (m, 1 H, 4-H), 1.46 (s, 3 H, CH_3), 1.58 (m, 2 H, 5-H), 1.72 (m, 2 H, 6-H), 2.73 (m, 1 H, 4-H), 2.99 (m, 1 H, 7-H), 3.48 (m, 1 H, 7-H), 7.45−7.66 (m, 5 H, Ph-H), 9.80 (s, 1 H, CHO). ^{13}C NMR: δ = 19.8/22.3 (C-5, C-6), 27.5 (CH_3), 30.8 (C-4), 52.0 (C-7), 69.1 (C-3a), 119.0 (C-3), 127.2 (Ph-C), 128.9 (Ph-C), 129.5 (Ph-C), 132.0 (Ph-C), 171.3 (C-2), 186.3 (CHO). UV (CH_3CN): λ = 302 nm (ε = 9200), 252 nm (ε = 7000), 224 nm (ε = 11900). MS (70 ev. EI): *m*/*z* (%) = 243 (8%) [M$^+$], 228 (64), 200 (15), 187 (15), 105 (76), 82 (11), 78 (13), 77 (78), 70 (10), 69 (11), 67 (13). $C_{15}H_{17}NO_2$ (243.3): calcd. C 74.05, H 7.04, N 5.76; found C 73.83, H 7.04, N 5.70.

2-*tert*-Butyl-3a-methyl-4,5,6,7-tetrahydro-3a*H*-isoxazolo[2,3-*a*]-pyridine-3-carbaldehyde (19b): Treatment of **15**[39] with **18b** (0.78 g, 7.1 mmol) in boiling ethanol (30 mL, 30 min) gave **19b** (0.82 g, 83%) as a pale yellow oil after flash chromatography (SiO_2, cyclohexane/ethyl acetate, 15:1). IR (CCl_4): $\tilde{\nu}$ = 2960, 2920, 2890, 2840, 1640 (C=O), 1580, 1460, 1445, 1390, 1365, 1320, 1270, 1125, 1075, 950, 790, 745 cm^{-1}. ^{1}H NMR: δ = 1.23 (m, 1 H, 4-H), 1.30 (s, 3 H, CH_3), 1.38 (s, 9 H, *t*Bu), 1.43−1.73 (m, 4 H, 5-H, 6-H), 2.64 (m, 1 H, 4-H), 2.75 (m, 1 H, 7-H), 3.29 (m, 1 H, 7-H), 10.16 (s, 1 H, CHO). UV (CH_3CN): δ = 233 nm (ε = 4100), 282 nm (ε = 7500). MS (70 eV, EI): *m*/*z* (%) = 224 (6%) [M$^+$ + 1], 223 (32), 209 (53), 168 (31), 166 (61), 152 (61), 138 (43), 125 (22), 124 (25), 122 (27). HRMS ($C_{13}H_{21}NO_2$): calcd. 223.1572; found 223.1571.

Methyl 3a-Methyl-4,5,6,7-tetrahydro-3a*H*-isoxazolo[2,3-*a*]pyridine-3-carboxylate (19c): Treatment of **15**[39] with **18c** (0.50 g, 5.9 mmol) in boiling ethanol (20 mL, 10 h) gave **19c** (0.26 g, 59%) as a yellow oil after flash chromatography (SiO_2, cyclohexane/ethyl acetate, 15:1). IR (CCl_4): $\tilde{\nu}$ = 2960, 2940, 2900, 2850, 1710 (C=O), 1620, 1605, 1435, 1350, 1335, 1325, 1280, 1150, 1125, 1110, 1090, 1070 cm^{-1}. ^{1}H NMR: δ = 1.32 (m, 1 H, 4-H), 1.35 (s, 3 H, CH_3), 1.47−1.75 (m, 4 H, 5-H, 6-H), 2.45 (m, 1 H, 4-H), 2.92 (m, 1 H, 7-H), 3.32 (m, 1 H, 7-H), 3.74 (s, 3 H, OCH_3), 7.36 (s, 1 H, 2-H). UV (CH_3CN): λ = 269 nm (ε = 5300). MS (70 eV, EI): *m*/*z* (%) = 197 (5%) [M$^+$], 182 (59), 149 (11), 138 (7), 124 (9), 122 (9), 110 (18), 109 (13), 96 (12), 94 (9), 93 (7). HRMS ($C_{10}H_{15}NO_3$): calcd. 197.1052; found 197.1049.

Dimethyl 3a-Methyl-4,5,6,7-tetrahydro-3a*H*-isoxazolo[2,3-*a*]pyridine-2,3-dicarboxylate (19d): Treatment of **15**[39] (0.50 g, 4.4 mmol) with dimethyl acetylenedicarboxylate (**18d**, 0.69 g, 4.9 mmol) in boiling ethanol (40 mL, 2 h) gave **19d** (0.87 g, 77%) as a pale yellow oil after flash chromatography (SiO_2, cyclohexane/ethyl acetate, 15:1). IR (CCl_4): $\tilde{\nu}$ = 2940, 2850, 1760 (C=O), 1715 (C=O), 1635, 1450, 1430, 1350, 1330, 1280, 1230, 1200, 1170, 1140, 1090, 1040, 1010 cm^{-1}. ^{1}H NMR: δ = 1.31 (m, 1 H, 4-H), 1.40 (s, 3 H, CH_3), 1.46−1.76 (m, 4 H, 5-H, 6-H), 2.40 (m, 1 H, 4-H), 2.64 (m, 1 H, 7-H), 3.38 (m, 1 H, 7-H), 3.77 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3). UV (CH_3CN): λ = 268 nm (ε = 2900). MS (70 eV, EI): *m*/*z* (%) = 255 (5%) [M$^+$], 241 (6), 240 (52), 196 (38), 164 (14), 154 (26), 108 (11), 96 (42), 82 (25), 81 (16). HRMS ($C_{12}H_{17}NO_5$): calcd. 255.1107; found 255.1106.

General Procedure for the Preparation of the Dihydrooxazoles 20 by 1,3-Dipolar Cycloaddition: A solution of the alkyne derivative **18** (1.01 equivalent) in diethyl ether (1 mL) was added dropwise under N_2 at room temperature to a stirred solution of 3,3,5-trimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide (**16**)[40,41] (ca. 8 mmol) in pure diethyl ether (5 mL). The mixture was stirred until complete conversion and then concentrated in vacuo (removal of the solvent and the remaining starting materials). The crude material was purified by flash chromatography (SiO_2).

3a,5,5-Trimethyl-2-phenyl-3a,4,5,6-tetrahydropyrrolo[1,2-*b*]-isoxazole-3-carbaldehyde (20a): Treatment of **16**[40,41] (1.00 g, 7.9 mmol) with **18a** (1.04 g, 8.0 mmol) for 17 h gave **20a** (1.72 g, 85%) as a yellow oil after flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1). IR (CCl_4): $\tilde{\nu}$ = 2960, 2930, 2870, 2820/2720 (aldehyde), 1650 (C=O), 1620 (C=C), 1595, 1490, 1440, 1390, 1370, 1340, 1290, 1270, 1125, 1065, 915 cm^{-1}. ^{1}H NMR: δ = 1.12 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 1.58 (s, 3 H, CH_3), 1.89 (d, 1 H, 4-H), 2.30 (d, 1 H, 4-H), 3.03 (d, 1 H, 6-H), 3.42 (d, 1 H, 6-H), 7.54 (m, 5 H, Ph-H), 9.72 (s, 1 H, CHO), $J_{4,4}$ = 13.3, $J_{6,6}$ = 9.8 Hz. UV (CH_3CN): λ = 303 nm (ε = 8000), 248 nm (ε = 7200). MS (70 eV, EI): *m*/*z* (%) = 257 (25%) [M$^+$], 242 (30), 201 (14), 200

(100), 173 (16), 172 (16), 145 (39), 144 (25), 131 (10), 124 (29). HRMS ($C_{16}H_{19}NO_2$): calcd. 257.1416; found 257.1411.

2-*tert*-Butyl-3a,5,5-trimethyl-3a,4,5,6-tetrahydropyrrolo[1,2-*b*]-isoxazole-3-carbaldehyde (20b): Treatment of **16** (1.00 g, 7.9 mmol)[40,41] with **18b** (0.88 g, 8.0 mmol) for 17 h gave **20b** (1.55 g, 83%) as pale yellow crystals after flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1) and crystallization, m.p. 55 °C (*n*-pentane, subl.). IR (CCl_4): $\tilde{\nu}$ = 2960, 2920, 2860, 2830/2740 (aldehyde), 1640 (C=O), 1595 (C=C), 1460, 1455, 1390, 1360, 1325, 1280, 1270, 1140, 1080, 970, 925, 695 cm^{-1}. ^1H NMR: δ = 1.07 (s, 3 H, CH_3), 1.15 (s, 3 H, CH_3), 1.37 (s, 9 H, *t*Bu), 1.45 (s, 3 H, CH_3), 1.82 (d, 1 H, 4-H), 2.19 (d, 1 H, 4-H), 2.76 (d, 1 H, 6-H), 3.30 (d, 1 H, 6-H), 10.07 (s, 1 H, CHO), $J_{4,4}$ = 13.3, $J_{6,6}$ = 9.8 Hz. UV (CH_3CN): λ = 285 nm (ε = 8800), 230 nm (ε = 4200). $C_{14}H_{23}NO_2$ (237.4): calcd. C 70.85, H 9.77, N 5.90; found C 70.35, H 9.72, N 6.10.

Methyl 3a,5,5-Trimethyl-3a,4,5,6-tetrahydropyrrolo[1,2-*b*]isoxazole-3-carboxylate (20c): Treatment of **16**[40,41] (1.00 g, 7.9 mmol) with **18c** (0.67 g, 8.0 mmol) for 20 h gave **20c** (1.41 g, 83%) as colorless crystals after flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1) and crystallization, m.p. 33 °C (*n*-pentane, subl.). IR (CCl_4): $\tilde{\nu}$ = 2960, 2930, 2860, 1715 (C=O), 1620 (C=C), 1470, 1440, 1370, 1350, 1300, 1290, 1220, 1210, 1190, 1110, 1090, 1065 cm^{-1}. ^1H NMR: δ = 1.10 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.79 (d, 1 H, 4-H), 2.18 (d, 1 H, 4-H), 2.88 (d, 1 H, 6-H), 3.35 (d, 1 H, 6-H), 3.74 (s, 3 H, OCH_3), 7.22 (s, 1 H, 2-H), $J_{4,4}$ = 13.3, $J_{6,6}$ = 9.8 Hz. UV (CH_3CN): λ = 261 nm (ε = 6100). MS (70 eV, EI): *m*/*z* (%) = 211 (70%) [M^+], 197(11), 196 (100), 164 (18), 142 (22), 136 (18), 124 (93), 123 (48), 123 (48), 97 (25).

Dimethyl 3a,5,5-Trimethyl-3a,4,5,6-tetrahydropyrrolo[1,2-*b*]isoxazole-2,3-dicarboxylate (20d): Treatment of **16**[40,41] (1.00 g, 7.9 mmol) with **18d** (1.14 g, 8.0 mmol) for 3 h gave 20d (1.95 g, 92%) as colorless crystals after flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1) and crystallization, m.p. 63 °C (diethyl ether/*n*-pentane). IR (CCl_4): $\tilde{\nu}$ = 2960, 2930, 2870, 1760 (C=O), 1715 (C=O), 1650 (C=C), 1440, 1370, 1350, 1295, 1280, 1260, 1200, 1165, 1120, 1100, 1070 cm^{-1}. ^1H NMR: δ = 1.11 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 1.78 (d, 1 H, 4-H), 2.22 (d, 1 H, 4-H), 2.93 (d, 1 H, 6-H), 3.36 (d, 1 H, 6-H), 3.76 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3); $J_{4,4}$ = 13.3 Hz; $J_{6,6}$ = 9.8 Hz. UV (CH_3CN): λ = 269 nm (ε = 3800). $C_{13}H_{19}NO_5$ (269.3): calcd. C 57.98, H 7.11, N 5.20; found. C 57.93, H 7.08, N 5.22.

General Procedure for the Preparation of the Dihydrooxazoles 21 by 1,3-Dipolar Cycloaddition. (a) 2,4,4-Trimethyloxazoline *N*-Oxide (17):[42] A solution of triethyl orthoacetate (1.2 equivalent) in dichloromethane (2.5 mL) was added under N_2 at room temperature to a stirred solution of 2-(hydroxyamino)-2-methyl-1-propanol hydrochloride (ca. 5 mmol) in pure dichloromethane (2.5 mL).
(b) Compound 21: After 1 h, the above mixture was treated with pure triethylamine (1 equivalent) and the alkyne derivative **18** (ca. 1.3 equivalent), and stirring was continued until complete conversion. The mixture was concentrated in vacuo (removal of the solvent and the remaining starting materials), and the crude material was purified by flash chromatography (SiO_2).

3,3,7a-Trimethyl-6-phenyl-2,3-dihydro-7a*H*-[1,3]oxazolo[3,2-*b*]-isoxazole-7-carbaldehyde (21a): A reaction mixture of freshly prepared **17** (5.3 mmol),[42] 3-phenylpropynal (**18a**, 0.84 g, 6.5 mmol), and triethylamine (0.74 g, 5.3 mmol), stirred for 24 h, gave **21a** (1.17 g, 85%) as a yellow oil after flash chromatography (SiO_2, cyclohexane/ethyl acetate, 5:1). IR (CCl_4): $\tilde{\nu}$ = 3080, 3060, 2980, 2940, 2850, 2760/2730 (aldehyde), 1665 (C=O), 1630 (C=C), 1590, 1490, 1390, 1375, 1350, 1260, 1120, 1040, 690 cm^{-1}. ^1H NMR: δ = 1.36 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 2.00 [s, 3 H, C(7a)-CH_3), 3.33 (d, 1 H, 2-H), 3.82 (d, 1 H, 2-H), 7.58 (m, 5 H, Ph-H), 9.72 (s, 1 H, CHO); $J_{2,2}$ = 9.0 Hz. UV (CH_3CN): λ = 289 nm (ε = 8700), 250 nm (ε = 8400). MS (70 eV, EI): *m*/*z* (%) = 259 (2%) [M^+] 244 (8), 229 (3), 228 (37), 200 (4), 188 (13), 187 (32), 186 (16), 158 (7), 145 (3).

6-*tert*-Butyl-3,3,7a-trimethyl-2,3-dihydro-7a*H*-[1,3]oxazolo[3,2-*b*]-isoxazole-7-carbaldehyde (21b): A reaction mixture of freshly prepared **17** (7.1 mmol),[42] 4,4-dimethyl-2-pentynal (**18b**, 1.17 g, 10.6 mmol), and triethylamine (0.72 g, 7.1 mmol), stirred for 10 h, gave **21b** (1.16 g, 69%) as a yellow oil after flash chromatography (SiO_2, cyclohexane/ethyl acetate, 5:1); pale yellow crystals from cyclohexane/*n*-pentane, m.p. 59 °C. IR (CCl_4): $\tilde{\nu}$ = 2980, 2940, 2900, 2850, 2760 (H-CO), 1660 (C=O), 1610 (C=C), 1580, 1470, 1390, 1370, 1340, 1300, 1270, 1180, 1140, 1040 cm^{-1}. ^1H NMR (250 MHz. $CDCl_3$): δ = 1.30 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 1.40 (s, 9 H, *t*Bu), 1.91 [s, 3 H, C(7a)-CH_3), 3.17 (d, 1 H, 2-H), 3.73 (d, 1 H, 2-H), 10.04 (s, 1 H, CHO); $J_{2,2}$ = 9.0 Hz. UV (CH_3CN): λ = 278 nm (ε = 10400). $C_{13}H_{21}NO_3$ (239.4): calcd. C 65.25, H 8.85, N 5.85; found C 64.88, H 8.87, N 5.83.

Dimethyl 3,3,7a-Trimethyl-2,3-dihydro-7a*H*-[1,3]oxazolo[3,2-*b*]isoxazole-6,7-dicarboxylate (21d): A reaction mixture of freshly prepared **17** (7.1 mmol),[42] **18d** (1.30 g, 9.1 mmol), and triethylamine (0.72 g, 7.1 mmol), stirred for 5 h, gave **21d** (1.32 g, 69%) as a yellow oil after flash chromatography (SiO_2, cyclohexane/ethyl acetate, 20:1/10:1).[22] IR (CCl_4): $\tilde{\nu}$ = 2990, 2970, 2950, 2860, 1760 (C=O), 1720 (C=O), 1660 (C=C), 1440, 1380, 1350, 1300, 1270, 1210, 1200, 1170, 1110, 1080, 1040 cm^{-1}. ^1H NMR): δ = 1.31 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.90 [s, 3 H, C(7a)-CH_3), 3.34 (d, 1 H, 2-H), 3.78 (s, 3 H, OCH_3), 3.79 (d, 1 H, 2-H), 3.92 (s, 3 H, OCH_3); $J_{2,2}$ = 9.0 Hz. UV (CH_3CN): λ = 265 nm (ε = 4400). MS 70 eV, EI): *m*/*z* (%) = 271 (4%) [M^+] 256 (24), 200 (19), 183 (18), 182 (100), 170 (14), 150 (64), 125 (13), 112 (14), 83 (13).

Photolysis of 19a: A solution of **19a** (105 mg, 0.43 mmol) in pure benzene (200 mL, Jena filter) was irradiated until complete conversion (36 min, TLC monitoring). After concentration, a solid crude material was obtained. According to the ^1H NMR spectrum, this contained the azomethine ylide **22a** and 7-benzoyl-6-methyl-1-azabicyclo[4.1.0]heptane-7-carbaldehyde (**23a**) in the ratio ca. 10:1. Crystallization from ethanol/ethyl acetate (1:1) gave **22a** (92 mg, 88%) as yellow crystals, m.p.133 °C. IR (CCl_4): $\tilde{\nu}$ = 2950, 2850, 1600 (C=O), 1570 (C=C), 1510, 1440, 1400, 1340, 1300, 1290, 1270, 1220, 1180, 890, 860 cm^{-1}. ^1H NMR: δ = 1.93 (m, 2 H, 3′-H), 2.09 (m, 2 H, 4′-H), 2.34 (s, 3 H, CH_3), 2.91 (t, 2 H, 5′-H), 3.90 (m, 2 H, 2′-H), 7.41 (m, 3 H, Ph-H), 7.58 (m, 2 H, Ph-H), 8.91 (s, 1 H, CHO). ^{13}C NMR: δ = 17.6/21.5 (C-3′, C-4′), 23.8 (CH_3), 33.4 (C-5′), 53.7 (C-2′), 123.0 (C-2), 128.0 (Ph-C), 128.4 (Ph-C), 129.1 (Ph-C), 129.7 (Ph-C), 140.3 (C-6′), 176.7 (CHO), 186.6 (CO). UV (CH_3CN): λ = 333 nm (ε = 3500), 280 nm (ε = 13500). MS (70 eV, EI): *m*/*z* (%) = 244 (8%) [M^+] 243 (46), 229 (16), 228 (100), 215 (5), 214 (25), 200 (33), 186 (6), 78 (7), 77 (55), 70 (5). $C_{15}H_{17}NO_2$ (243.3): calcd. C 74.05, H 7.04, N 5.76; found C 73.98, H 7.07 N 5.71.
Data of 23a: ^1H NMR (taken from the mixture with **22a**): δ = 2.56 (s, 3 H, CH_3); 3.55 (m, 2 H, 5-H), 3.80 (m, 2 H, 2-H), 9.29 (s, 1 H, CHO).

Photolysis of 19b: A solution of **19b** (120 mg, 0.54 mmol) in pure benzene (200 mL, Jena filter) was irradiated until complete conversion (46 min, TLC monitoring). After concentration, a solid crude material was obtained. According to the ^1H NMR spectrum, this

contained the azomethine ylide **22b** and 7-(2,2-dimethylpropanoyl)-6-methyl-1-aza-bicyclo[4.1.0]heptane-7-carbaldehyde (**23b**) in the ratio ca. 60:1. Crystallization from diethyl ether/dichloromethane gave **22b** (90 mg, 75%) as light brown crystals, m.p.104 °C. IR (KBr): $\tilde{\nu}$ = 2960, 2860, 1640, 1590, 1530, 1510, 1480, 1460, 1380, 1310, 1280, 1200, 1140, 1000, 800 cm^{-1}. ^1H NMR: δ = 1.31 (s, 9 H, *t*Bu), 1.89 (m, 2 H, 3′-H), 2.00 (m, 2 H, 4′-H), 2.18 (s, 3 H, CH_3), 2.81 (m, 2 H, 5′-H), 3.67 (m, 2 H, 2′-H), 9.41 (s, 1 H, CHO). UV (CH_3CN): λ = 330 (ε = 1500), 274 nm (ε = 17900). MS (70 eV, EI): *m*/*z* (%) = 224 (3%) $[M + 1]^+$, 223 (21), 209 (13), 208 (100), 194 (12), 180 (19), 152 (9), 138 (63), 124 (16), 122 (10). HRMS ($C_{13}H_{21}NO_2$): Calcd. 223.1571; found. 223.1569. $C_{13}H_{21}NO_2$ (223.3): calcd. C 69.92, H 9.48, N 6.27; found C 68.97, H 9.48, N 6.05.

Data of 23b: ^1H NMR (taken from the mixture with **22b**): δ = 2.41 (s, 3 H, CH_3), 9.71 (s, 1 H, CHO).

Photolysis of 19c: A solution of **19c** (400 mg, 2.0 mmol) in pure benzene (200 mL, Vycor filter) was irradiated until complete conversion (170 min, TLC monitoring). After concentration a crude material was obtained. According to the ^1H NMR spectrum, this contained the azomethine ylide **22c** and 7-methoxy-6-methyl-1-aza-bicyclo[4.1.0]heptan-7-carbaldehyde (**23c**) in the ratio ca. 6:1. Flash chromatography (neutral Al_2O_3, activity III, dichloromethane/methanol, 50:1) gave **22c** (100 mg, 25%) as a light brown oil. IR (CCl_4): $\tilde{\nu}$ = 2980, 2930, 1730 (br., C=O), 1640, 1570, 1530, 1430, 1330, 1295, 1230, 1180, 1130, 1100, 1070, 1030 cm^{-1}. ^1H NMR: δ = 1.88 (m, 2 H, 3′-H), 2.02 (m, 2 H, 4′-H), 2.32 (s, 3 H, CH_3), 2.80 (m, 1 H, 5′-H), 2.89 (m, 1 H, 5′-H), 3.70 (s, 3 H, OCH_3), 3.73 (m, 2 H, 2′-H), 9.00 (s, 1 H, CHO). MS (70 eV, EI): *m*/*z* (%) = 197 (31) $[M^+]$ 182 (100), 138 (37), 136 (14), 110 (29), 108 (36), 100 (12).

Data of 23c: ^1H NMR (taken from the mixture with **22c**): δ = 2.47 (s, 3 H, CH_3), 3.57 (m, 2 H, 5-H), 3.90 (m, 2 H, 2-H), 3.74 (s, 3 H, OCH_3), 9.54 (s, 1 H, CHO).

Photolysis of 19d: A solution of **19d** (200 mg, 0.78 mmol) in pure benzene (200 mL, Vycor filter) was irradiated until complete conversion (2.5 h, TLC monitoring). After concentration a crude material was obtained. According to the ^1H NMR spectrum, this contained the azomethine ylide **22d**. Flash chromatography (SiO_2, dichloromethane/methanol, 15:1) gave **22d** (105 mg, 58%) as a light brown oil. IR (CCl_4): $\tilde{\nu}$ = 2980, 2940, 2860, 1740 (ROC=O), 1650, 1530, 1430, 1400, 1340, 1280, 1210, 1180, 1140, 1070, 1040, 900 cm^{-1}. ^1H NMR: δ = 1.90 (m, 2 H, 3′-H), 2.03 (m, 2 H, 4′-H), 2.36 (m, 3 H, CH_3), 2.87 (m, 2 H, 5′-H), 3.67 (s, 3 H, OCH_3), 3.81 (m, 2 H, 2′-H), 3.84 (s, 3 H, OCH_3). MS (70 eV, EI): *m*/*z* (%) = 256 (3%) $[M + 1]^+$, 255 (22), 241 (8), 240 (66), 197 (11), 196 (100), 164 (64), 140 (16), 136 (8), 108 (24). HRMS ($C_{12}H_{17}NO_5$), calcd. 255.1107; found 255.1108.

Photolysis of 20a: A solution of **20a** (250 mg, 0.97 mmol) in pure benzene (200 mL, Jena filter) was irradiated until complete conversion (90 min, TLC monitoring). After concentration, crystallization of the solid residue afforded **25a** (220 mg, 88%) as yellow, hygroscopic crystals, m.p. 120 °C (diethyl ether/dichloromethane). IR (CCl_4): $\tilde{\nu}$ = 3050, 2960, 2870/2800 (OC-H), 1600 (C=O), 1580 (C=C), 1530, 1420, 1355, 1340, 1300, 1290, 1180, 1080, 1030 cm^{-1}. ^1H NMR: δ = 1.32 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 2.98 (s, 2 H, 4′-H), 4.10 [d (br), 1 H, 2′-H], 4.22 [d (br), 1 H, 2′-H], 7.40 (m, 3 H, Ph-H), 7.58 (m, 2 H, Ph-H), 8.98 (s, 1 H, CHO); $J_{2',2'}$ = 13.3 Hz. ^{13}C NMR: δ = 18.7 (CH_3), 27.0 (CH_3), 35.7 (C-3′), 52.7 (C-4′), 71.7 (C-2′), 116.8 (C-2), 127.9 (Ph-C), 128.5 (Ph-C), 129.8 (Ph-C), 140.2 (Ph-C), 177.5 (CHO), 184.9 (C-5′), 186.7 (C=O). UV (CH_3CN): λ = 330 nm (ε = 3600), 278 nm (ε = 13400). MS (70 eV, EI): *m*/*z* (%) = 257 36%) $[M^+]$ 242 (14), 229 (41), 228 (11), 215 (13), 214 (83), 212 (13), 173 (64), 131 (10), 124 (59). HRMS ($C_{16}H_{19}NO_2$): calcd. 257.1416; found 257.1413. $C_{16}H_{19}NO_2$ (257.4): calcd. C 74.68, H 7.44, N 5.44; found C 74.04, H 7.43, N 5.32.

Photolysis of 20b: A solution of **20b** (240 mg, 1.01 mmol) in pure benzene (200 mL, Jena filter) was irradiated until complete conversion (100 min, TLC monitoring). After concentration, crystallization of the solid residue afforded **25b** (220 mg, 91%) as yellow, hygroscopic crystals, m.p. 109 °C (diethyl ether). IR (CCl_4): $\tilde{\nu}$ = 2960, 2860, 2810 (OC-H), 1590 (C=O), 1510 (C=C), 1520, 1470, 1460, 1410, 1380, 1360, 1320, 1200, 1180, 1090 cm^{-1}. ^1H NMR: δ = 1.29 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.31 (s, 9 H, *t*Bu), 2.17 (s, 3 H, CH_3), 2.82 (m, 1 H, 4′-H), 2.98 (m, 1 H, 4′-H), 3.84 (m, 1 H, 2′-H), 4.05 (m, 1 H, 2′-H), 9.46 (s, 1 H, CHO). ^{13}C NMR: δ = 18.1 (CH_3), 26.9 (CH_3), 27.3 (CH_3), 29.5 (*t*−Bu−CH_3), 35.4 (C-3′), 41.4 (C-2), 52.4 (C-4′), 71.5 (C-2′), 115.2 (C-4), 173.6 (CHO), 186.4 (C-5′), 194.4 (C=O). UV (CH_3CN): λ = 331 nm (ε = 1600), 274 nm (ε = 16600). MS (70 eV, EI): *m*/*z* (%) = 237 (22%) $[M^+]$ 222 (14), 194 (20), 181 (12), 180 (100), 162 (10), 153 (14), 152 (89), 138 (12), 136 (12). HRMS ($C_{14}H_{23}NO_2$): calcd. 237.1729; found 237.1724. $C_{14}H_{23}NO_2$ (237.4): calcd. C 70.85, H 9.77, N 5.50; found C 69.98, H 9.56, N 5.68.

Photolysis of 20c: A solution of **20c** (220 mg, 1.04 mmol) in pure acetonitrile (200 mL, Vycor filter) was irradiated until complete conversion (220 min, TLC monitoring). After concentration, flash chromatography of the residue (neutral Al_2O_3, activity III, ethyl acetate/ethanol, 20:1) gave **25c** (132 mg, 60%) and methyl 3-oxo-2-(1,4,4-trimethyl-2-pyrrolidinylidene)propanoate (**26c**,18 mg, 8%).

Data for 25c: Light brown oil. IR (CCl_4): $\tilde{\nu}$ = 2960, 2880, 2820 (OC-H), 1655 (C=O), 1580 (C=C), 1560, 1440, 1420, 1390, 1350, 1330, 1305, 1195, 1135, 1080, 1045, 900 cm^{-1}. ^1H NMR: δ = 1.25 (s, 6 H, CH_3), 2.28 (s, 3 H, CH_3), 2.80 (d, br., 1 H, 4′-H), 3.00 (d, br., 1 H, 4′-H), 3.70 (s, 3 H, OCH_3), 3.85 (d, br., 1 H, 2′-H), 4.28 (d, br., 1 H, 2′-H), 9.07 (s, 1 H, CHO), $J_{4',4'}$ = 20.2 Hz; $J_{2',2'}$ = 13.3 Hz. ^{13}C NMR: δ = 18.9 (CH_3), 26.5 (CH_3), 27.1 (CH_3), 35.3 (C-3′), 50.1 (C-4′), 52.5 (OCH_3), 72.1 (C-2′), 101.8 (C-2), 165.5 (CO_2R), 171.8 (CHO), 185.4 (C-5′). UV (CH_3CN): λ = 335 nm (ε = 2100), 256 nm (ε = 13700). MS (70 eV, EI): *m*/*z* (%) = 211 (31%) $[M^+]$ 196 (28), 194 (18), 180 (18), 152 (100), 151 (34), 136 (33), 124 (20), 108 (15), 96 (18). HRMS ($C_{11}H_{17}NO_3$: calcd. 211.1208; found 211.1202.

Data for 26c: Yellow oil. IR (CCl_4): $\tilde{\nu}$ = 2960, 2920, 2860, 2780, 1690 (OC=O), 1630 (C=O), 1545, 1450, 1400, 1320, 1290, 1260, 1230, 1190, 1120, 1060, 1050, 960 cm^{-1}. ^1H NMR: δ = 1.17 (s, 6 H, CH_3), 3.06 (s, 3 H, NCH_3), 3.12 (s, 2 H, 3′-H), 3.46 (s, 2 H, 5′-H), 3.75 (s, 3 H, OCH_3), 9.69 (s, 1 H, CHO). MS (70 eV, EI): *m*/*z* (%) = 211 (36%) $[M^+]$ 196 (12), 194 (13), 180 (18), 168 (12), 153 (12), 152 (100).

Photolysis of 20d: A solution of **20d** (280 mg, 1.04 mmol) in pure acetonitrile (200 mL, Vycor filter) was irradiated until complete conversion (270 min, TLC monitoring). After concentration, flash chromatography of the residue (SiO_2, ethyl acetate/methanol, 20:1/10:1) gave **25d** (210 mg, 75%) and dimethyl 2-(1,4,4-trimethyl-2-pyrrolidinylidene)malonate (**26d**, 48 mg, 17%).

Data for 25d: Yellow oil. IR (CCl_4): $\tilde{\nu}$ = 2960, 2940, 2840, 1740 (OC=O), 1660 (OC=O), 1530, 1440, 1330, 1220, 1195, 1150, 1080, 1050, 990 cm^{-1}. ^1H NMR: δ = 1.29 (s, 6 H, CH_3), 2.33 (s, 3 H, CH_3), 2.86 (d, br., 1 H, 4′-H), 3.04 (d, br., 1 H, 4′-H), 3.68 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 3.89 (d, br., 1 H, 2′-H), 4.20 (d, br., 1 H, 2′-H); $J_{4',4'}$ = 19.5 Hz; $J_{2',2'}$ = 13.3 Hz. ^{13}C NMR: δ =

18.7 (CH_3), 26.5 (CH_3), 27.8 (CH_3), 35.5 (C-3′), 50.6 (OCH_3), 51.8 (OCH_3), 52.6 (C-4′), 72.3 (C-2′), 97.7 (C-2), 163.9 (CO_2R), 168.0 (CO_2R), 171.0 (C-5′), 188.2 (C=O). UV (CH_3CN): λ= 326 nm (ε = 1700), 261 nm (ε = 11800). MS (70 eV, EI): *m*/*z* (%) = 269 (11%) [M^+], 211 (12), 210 (100), 179 (6), 178 (55), 150 (4). HRMS ($C_{13}H_{19}NO_5$): calcd. 269.1263; found. 269.1258.

Data for 26d: Colorless crystals, m.p. 98 °C (diethyl ether/dichloromethane). IR (CCl_4): ṽ = 2940, 2860, 1730, 1690, 1620, 1540, 1460, 1450, 1430, 1400, 1390, 1325, 1290, 1200, 1150, 1130, 1100, 1070, 1000 cm^{-1}. ^1H NMR: δ = 1.18 (s, 6 H, CH_3), 3.01 (s, 3 H, NCH_3), 3.09 (s, 2 H, 3-H), 3.52 (s, 2 H, 5-H), 3.68 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3). ^{13}C NMR: δ = 26.7 (CH_3), 35.9 (C-4), 40.0 (NCH_3), 50.9 (OCH_3), 51.6 (C-3), 51.9 (OCH_3), 70.4 (C-5), 93.8 (C-1′), 167.1 (CO_2R), 167.4 (CO_2R), 176.6 (C-2), 181.4 (CO). UV (CH_3CN): λ = 315 nm (ε = 12500), 252 nm (ε = 8700). MS (EI): *m*/*z* (%) = 269 (25%) [M^+], 211 (80), 210 (100), 180 (22), 178 (16), 152 (25). $C_{13}H_{19}NO_5$ (269.3): calcd. C 57.98, H 7.11, N 5.20; found C 57.79, H 7.07, N 5.20.

Photolysis of 21a: A solution of **21a** (1.19 g, 4.6 mmol) in pure benzene (200 mL, Jena filter) was irradiated until complete conversion (440 min, TLC monitoring). After concentration, crystallization of the solid residue from diethyl ether/dichloromethane gave 1.06 g (89%) of the azomethine ylide **28a** as yellow crystals, m.p. 135 °C. IR ($CHCl_3$): ṽ = 2960, 2930, 2840, 1640 (C=O), 1590 (C=C), 1570, 1530, 1440, 1370, 1360, 1330, 1300, 1280, 980 cm^{-1}. ^1H NMR: δ = 1.53 (s, 3 H, CH_3), 1.57 (s, 3 H, CH_3), 2.28 [s, 3 H, C(2′)-CH_3), 4.70 (s, 2 H, 5′-H), 7.40 (m, 3 H, Ph-H), 7.62 (m, 2 H, Ph-H), 9.08 (s, 1 H, CHO). ^{13}C NMR: δ = 13.6 (CH_3), 25.1 (CH_3), 25.2 (CH_3), 69.9 (C-4′), 82.1 (C-5′), 108.8 (C-2), 128.0 (Ph-C), 128.5 (Ph-C), 129.8 (Ph-C), 140.4 (Ph-C), 176.8 (C-2′), 179.3 (CHO), 186.7 (CO). UV (CH_3CN): λ = 278 nm (ε = 12000). MS (70 eV, EI): *m*/*z* (%) = 260 (8%) [M + 1] $^+$, 259 (40), 232 (5), 231 (28), 204 (17), 189 (5), 176 (16), 163 (10), 162 (22), 135 (12). $C_{15}H_{17}NO_3$ (259.3): calcd. C 69.48, H 6.61, N 5.40; found C 69.27, H 6.70, N 5.37.

Photolysis of 21b: A solution of **21b** (1.10 g, 4.6 mmol) in pure benzene (200 mL, Jena filter) was irradiated until complete conversion (370 min, TLC monitoring). After concentration, flash chromatography (basic Al_2O_3, activity III, ethyl acetate) afforded the azomethine ylide **28b** (0.66 g, 60%) as a yellow, hygroscopic, wax-like solid. IR (CCl_4): ṽ = 2980, 2940, 2900, 2880, 1690 (C=O), 1600 (C=C), 1530, 1480, 1460, 1390, 1380, 1310, 1230, 1170, 1050 cm^{-1}. ^1H NMR: δ = 1.34 (s, 9 H, *t*Bu), 1.36 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 2.15 [s, 3 H, C(2′)-CH_3), 4.64/4.62 (AB-d, 2 H, 5′-H), 9.47 (s, 1 H, CHO); $J_{5',5'}$ = 9 Hz. ^{13}C NMR (100 MHz. $CDCl_3$): δ = 13.3 (CH_3), 24.9 (CH_3), 25.2 (CH_3), 29.6 (*t*Bu), 41.4 (C-2), 69.6 (C-4′), 82.0 (C-5′), 110.3 (C-4), 175.6 (CHO), 176.6 (C-2′), 195.9 (CO). UV (CH_3CN): λ = 279 nm (ε = 11200). MS (70 eV, EI): *m*/*z* (%) = 239 (10%) [M^+] 183 (6), 182 (54), 156 (6), 144 (19), 140 (9), 128 (6), 127 (5), 115 (20), 114 (37), 112 (9).

Photolysis of 21d: A solution of **21d** (0.62 g, 2.3 mmol) in pure acetonitrile (200 mL, Vycor filter) was irradiated until complete conversion (8.5 h, TLC monitoring). After concentration, a residue was obtained. According to the ^1H NMR analysis, this contained the azomethine ylide **28d** as the only identifiable compound (ca. 90%, yellow oil). Because of its great instability towards SiO_2 and Al_2O_3 the spectroscopic identification of **28d** was accomplished without further purification. IR ($CHCl_3$): ṽ = 2980, 2940, 1730 (OC=O), 1660 (OC=O), 1630, 1540, 1480, 1440, 1400, 1370, 1345, 1320, 1150, 1050, 990, 890 cm^{-1}. ^1H NMR: δ = 1.52 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 2.33 [s, 3 H, C(2′)-CH_3), 3.67 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 4.63/4.72 (AB-d, 2 H, 5′-H); $J_{5',5'}$ = 9 Hz. ^{13}C NMR: δ = 13.6 (CH_3), 24.6 (CH_3), 25.2 (CH_3), 50.4 (OCH_3), 51.7 (OCH_3), 70.1 (C-4′), 82.4 (C-5′), 89.1 (C-2), 165.4 (CO_2R), 168.4 (CO_2R), 174.1 (CO), 178.1 (C-2′). UV (CH_3CN): λ = 261 nm. MS (70 eV, EI): *m*/*z* (%) = 272 (3%) [M + 1]$^+$, 271 (23), 213 (11), 212 (100), 174 (13), 142 (6), 140 (15), 138 (4), 130 (10), 115 (3). HRMS ($C_{12}H_{17}NO_6$): calcd. 271.1056; found 271.1047.

Reaction between 22a and Methyltriazolinedione (MTAD): A solution of MTAD (25 mg, 0.20 mmol) in dichloromethane (2 mL) was slowly added to a solution of **22a** (48 mg, 0.20 mmol) in pure dichloromethane (5 mL). The mixture was stirred for 20 min at room temp. and then concentrated. Flash chromatography of the residue (SiO_2, cyclohexane/ethyl acetate, 3:2) gave 6-benzoyl-5-hydroxy-2,11a-dimethyl-9,10,11,11a-tetrahydro-1*H*,8*H*-pyrido[2,1-*c*][1,2,4]-triazolo[1,2-*a*][1,2,4]triazine-1,3(2*H*)-dione (**33a**, 55 mg, 78%) as yellow crystals, m.p. 155 °C (cyclohexane/ethyl acetate, 3:2). IR (KBr): ṽ = 2940, 1795 (C=O), 1730 (C=O), 1720 (C=O), 1600, 1450, 1440, 1390, 1360, 1320, 1270, 1250, 1220, 1190, 1170, 1120 cm^{-1}. ^1H NMR: δ = 1.56 (s, 3 H, CH_3), 1.66 (m, 5 H, 9-H, 10-H, 11-H), 2.70 (m, 2 H, 8-H, 11-H), 3.14 (s, 3 H, NCH_3), 3.19 (m, 1 H, 8-H), 7.46 (m, 3 H, Ph-H), 8.22 (m, 2 H, Ph-H), 13.49 (s, 1 H, OH). ^{13}C NMR: δ = 20.1 (C-10), 24.8 (CH_3), 25.3 (CH_3), 25.3 (C-9), 34.4 (C-11), 52.0 (C-8), 76.6 (C-11a), 110.8 (C-6), 128.2 (Ph-C), 129.0 (Ph-C), 131.7 (Ph-C), 132.6 (Ph-C), 146.2 (NCO), 148.8 (NCO), 162.4 (C-5), 169.6 (CO). MS (70 eV, EI): *m*/*z* (%) = 357 (3%) [M + 1]$^+$, 356 (15), 341 (5), 243 (6), 242 (33), 214 (5), 167 (4), 149 (10), 105 (100), 82 (3). $C_{18}H_{20}N_4O_4$ (356.4): calcd. C 60.66, H 5.66, N 15.72; found C 60.51, H 5.62, N 15.58.

Reaction between 25a and MTDA: A solution of MTAD (45 mg, 0.40 mmol) in dichloromethane (2 mL) was slowly added to a solution of **25a** (100 mg, 0.39 mmol) in pure dichloromethane (5 mL). The mixture was stirred for 30 min at room temp. and then concentrated. Flash chromatography of the residue (neutral Al_2O_3, activity III, dichloromethane/ethanol, 10:1) gave 6-benzoyl-2,9,9,10a-tetramethyl-8,9,10,10a-tetrahydro-1*H*-pyrrolo[2,1-*c*][1,2,4]-triazolo[1,2-*a*][1,2,4]triazine-1,3(2*H*)-dione (**35a**, 20 mg, 14%) as a yellow oil, and **25a** (40 mg, 40%). Data for **35a**: IR (CCl_4): ṽ = 2960, 2930, 2860, 1780, 1730, 1650 (C=O), 1610 (C=C), 1455, 1380, 1290, 1270, 1230, 1180, 1150, 1050, 1010 cm^{-1}. ^1H NMR: δ = 1.12 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.42 (s, 3 H, 10a-CH_3), 2.12 (d, 1 H, 10-H), 2.65 (d, 1 H, 8-H), 2.98 (d, 1 H, 10-H), 3.12 (s, 3 H, NCH_3), 3.36 (d, 1 H, 8-H), 7.32 (s, 1 H, 5-H), 7.50 (m, 3 H, Ph-H), 7.75 (m, 2 H, Ph-H); $J_{10,10}$ = 14.3, $J_{8,8}$ = 9.3 Hz. ^{13}C NMR: δ = 22.3 (CH_3), 25.4 (NCH_3), 27.1 (CH_3), 28.0 (CH_3), 37.0 (C-9), 50.5 (C-10), 65.0 (C-8), 81.7 (C-10a), 114.7 (C-6), 125.9 (C-5), 128.3 (Ph-C), 129.0 (Ph-C), 132.1 (Ph-C), 137.8 (Ph-C), 146.8 (N-CO), 153.0 (N-CO), 190.6 (CO). MS (70 eV, EI): *m*/*z* (%) = 354 (60%) [M^+] 339 (11), 282 (10), 255 (62), 254 (11), 240 (17), 226 (11), 212 (13), 198 (7), 136 (14). HRMS ($C_{19}H_{22}N_4O_3$): calcd. 354.1692; found 354.1688.

Reaction between 25b and MTDA: A solution of MTAD (170 mg, 1.50 mmol) in dichloromethane (5 mL) was slowly added to a solution of **25b** (350 mg, 1.47 mmol) in pure dichloromethane (15 mL). The mixture was stirred for 30 min at room temp. and then concentrated. Flash chromatography of the residue (neutral Al_2O_3, activity III, dichloromethane/ethanol, 10:1) gave 6-(2,2-dimethylpropanoyl)-2,9,9,10a-tetramethyl-8,9,10,10a-tetrahydro-1*H*-pyrrolo-[2,1-*c*][1,2,4]triazolo[1,2-*a*][1,2,4]-triazine-1,3(2*H*)-dione (**35b**, 70 mg, 14%) as a yellow solid and **25b** (165 mg, 47%). Data for **35b**: m.p. 124 °C (diethyl ether/*n*-pentane). IR (CCl_4): ṽ = 2960, 2940, 2880, 1780, 1730, 1670 (C=O), 1615 (C=C), 1460, 1400, 1350, 1300, 1270, 1200, 1150, 1060, 1010 cm^{-1}. ^1H NMR: δ = 1.12 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 1.30 (s, 9 H, *t*Bu), 1.35 (s, 3 H,

10a-CH_3), 2.02 (d, 1 H, 10-H), 2.59 (d, 1 H, 8-H), 3.06 (d, 1 H, 10-H), 3.12 (s, 3 H, NCH_3), 3.30 (d, 1 H, 8-H), 7.37 (s, 1 H, 5-H); $J_{10,10}$ = 14.3, $J_{8,8}$ = 9.3 Hz. ^{13}C NMR: δ = 21.9 (CH_3), 25.3 (NCH_3), 27.5 (CH_3), 28.2 (t−Bu−CH_3), 29.0 (CH_3), 36.5 (C-9), 43.9 (t−Bu−C), 50.2 (C-10), 66.5 (C-8), 81.9 (C-10a), 112.3 (C-6), 125.5 (C-5), 146.9 (N-CO), 153.2 (N-CO), 203.0 (CO). MS 70 eV, EI): *m*/*z* (%) = 335 (13%) [M + 1]$^+$, 334 (68), 319 (30), 262 (13), 236 (12), 235 (92), 220 (25), 137 (25), 136 (38), 82 (16). $C_{17}H_{26}N_4O_3$ (334.5): calcd. C 61.06, H 7.84, N 16.75; found C 60.94, H 7.83, N 16.51.

Reaction between 25c and MTDA: A solution of MTAD (180 mg, 1.59 mmol) in dichloromethane (7 mL) was slowly added to a solution of **25c** (330 mg, 1.56 mmol) in pure dichloromethane (20 mL). The mixture was stirred for 30 min at room temp. and then concentrated. Flash chromatography of the residue (neutral Al_2O_3, activity III, cyclohexane/dichloromethane, 1:1; dichloromethane/ethanol, 10:1) gave methyl 6-[(2,9,9,10a-tetramethyl-1,3-dioxo-2,3,8,9,10,10a-hexahydro-1*H*-pyrrolo[2,1-*c*][1,2,4]triazolo[1,2-*a*]-[1,2,4]triazine]carboxylate (**35c**, 50 mg, 10%) as a yellow oil and **25c** (130 mg, 39%). IR (CCl_4): ṽ = 2960, 2860, 2820, 1780 and 1730 (N-C=O), 1720 (OC=O), 1625 (C=C), 1450, 1430, 1400, 1360, 1280, 1260, 1185, 1140, 995 cm^{-1}. ^{1}H NMR: δ = 1.14 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 2.07 (d, 1 H, 10-H), 2.62 (d, 1 H, 8-H), 3.00 (d, 1 H, 10-H), 3.10 (s, 3 H, NCH_3), 3.60 (d, 1 H, 8-H), 3.80 (s, 3 H, OCH_3), 7.63 (s, 1 H, 4-H), $J_{10,10}$ = 14.3, $J_{8,8}$ = 9.3 Hz. ^{13}C NMR: δ = 22.2 (CH_3), 25.3 (NCH_3), 27.3 (CH_3), 28.4 (CH_3), 36.8 (C-9), 50.4 (C-10), 51.9 (OCH_3), 65.7 (C-8), 82.1 (C-10a), 112.6 (C-6), 117.7 (C-5), 146.7 (N-CO), 153.1 (N-CO), 164.3 (CO). MS (70 eV, EI): *m*/*z* (%) = 308 (84%) [M$^+$], 293 (36), 209 (100), 195 (39), 194 (81), 162 (39).

Reaction between 28a and MTAD: A solution of MTAD (235 mg, 2.08 mmol) in dichloromethane (3 mL) was slowly added to a solution of **28a** (215 mg, 0.83 mmol) in pure dichloromethane (5 mL). The mixture was stirred for 3 days at room temp. and then concentrated. Flash chromatography of the residue (SiO_2, ethyl acetate) gave 2-[(*E*)-1-benzoyl-2-hydroxy-2-(4-methyl-3,5-dioxo-1,2,4-triazolan-1-yl)ethenyl]amino-2-methylpropyl acetate (**41**, 114 mg, 35%) as a yellow foam. IR ($CHCl_3$): ṽ = 3340 (br., N−H, O−H), 1780 (C=O), 1730 (br., C=O), 1650 (C=O), 1600 (C=C), 1570, 1450, 1380, 1360, 1310, 1260, 990 cm^{-1}. ^{1}H NMR: δ = 1.37 (s, 6 H, 2-CH_3), 2.11 (s, 3 H, $COCH_3$), 3.08 (s, 3 H, NCH_3), 4.18 (s, 2 H, 1-H), 5.60 (br. s, 2 H, NH), 7.47 (m, 2 H, Ph-H), 7.59 (m, 1 H, Ph-H), 8.10 (m, 2 H, Ph-H). MS (CI, isobutane): *m*/*z* (%) = 391 (10%) [M$^+$] 390 (25), 389 (100), 388 (5), 361 (3), 277 (9), 276 (50), 248 (15).

Thermolysis of 22a: A solution of **22a** (80 mg, 0.3 mmol) in toluene (50 mL) was heated at reflux for 6 h. After concentration in vacuo, the residue was separated by flash chromatography (cyclohexane/ethyl acetate, 25:1), affording phenyl-(5,6,7,8-tetrahydroindolizin-3-yl)methanone (**42a**, 53 mg, 71%) and 2-phenyl-5,6,7,8-tetrahydroindolizine-3-carbaldehyde (**43a**, 13 mg, 18%).

Data for 42a: Colorless crystals, m.p. 83 °C (*n*-pentane/diethyl ether). IR (CCl_4): ṽ = 2950, 2860, 1625 (C=O), 1600, 1580, 1490, 1470, 1445, 1430, 1390, 1340, 1320, 1310, 1240, 1190, 1170, 1040, 1025, 880, 700, 655 cm^{-1}. ^{1}H NMR: δ = 1.86 (m, 2 H, 6-H), 1.99 (m, 2 H, 7-H), 2.87 (t, 2 H, 8-H), 4.50 (t, 2 H, 5-H), 5.93 (d, 1 H, 1-H), 6.71 (d, 1 H, 2-H), 7.44 (m, 3 H, Ph-H), 7.77 (m, 2 H, Ph-H), $J_{1,2}$ = 4.5 Hz. MS (70 eV, EI): *m*/*z* (%) = 226 12%) [M + 1]$^+$ 225 (78), 224 (100), 208 (6), 197 (8), 196 (23), 184 (5), 120 (12), 106 (8), 105 (16). $C_{15}H_{15}NO$ (225.3): calcd. C 79.97, H 6.71, N 6.22; found C 79.91, H 6.73, N 6.16.

Data for 43a: Colorless crystals, m.p. 72 °C (cyclohexane/ethyl acetate, 3:1). IR (CCl_4): ṽ = 2940, 2840, 1650 (C=O), 1600, 1505, 1490, 1455, 1440, 1420, 1370, 1350, 1310, 1190, 1125, 1020, 870 cm^{-1}. ^{1}H NMR: δ = 1.90 (m, 2 H, 6-H), 2.00 (m, 2 H, 7-H), 3.16 (t, 2 H, 8-H), 3.99 (t, 2 H, 5-H), 6.56 (s, 1 H, 1-H), 7.34 (m, 5 H, Ph-H), 9.91 (s, 1 H, CHO), $J_{5,6}$ = $J_{7,8}$ = 5.9 Hz. MS (70 eV, EI): *m*/*z* (%) = 226 (17%) [M + 1]$^+$, 225 (100), 224 (65), 210 (8), 196 (20), 115 (9), 105 (7), 77 (11). $C_{15}H_{15}NO$ (225.3): calcd. C 79.97, H 6.71, N 6.22; found C 79.85, H 6.68, N 6.02.

Thermolysis of 22b: A solution of **22b** (480 mg, 2.1 mmol) in toluene (300 mL) was heated at reflux for 3.5 h. After concentration in vacuo, the residue was separated by flash chromatography (cyclohexane/ethyl acetate, gradient from 25:1 → 15:1), affording 2,2-dimethyl-(5,6,7,8-tetrahydroindolizin-3-yl)propan-1-one (**42b**, 273 mg, 62%) and 2-*tert*-butyl-5,6,7,8-tetrahydroindolizine-3-carbaldehyde (**43b**, 50 mg, 11%).

Data for 42b: Colorless crystals, m.p. 59 °C (diethyl ether/*n*-pentane). IR (CCl_4): ṽ = 2940, 2920, 2900, 2860, 1630 (C=O), 1485, 1465, 1440, 1425, 1390, 1365, 1345, 1335, 1315, 1305, 1200, 1085 cm^{-1}. ^{1}H NMR: δ = 1.36 (s, 9 H, *t*Bu), 1.79 (m, 2 H, 6-H), 1.91 (m, 2 H, 7-H), 2.81 (t, 2 H, 8-H), 4.34 (t, 2 H, 5-H), 5.91 (d, 1 H, 1-H), 7.04 (d, 1 H, 2-H), $J_{1,2}$ = 4.0, $J_{5,6}$ = 6.6 Hz. MS (70 eV, EI): *m*/*z* (%) = 205 (12%) [M$^+$], 149 (10), 148 (100), 120 (6), 118 (4), 106 (6), 93 (4), 79 (5), 78 (5), 77 (5). HRMS ($C_{13}H_{19}NO$): calcd. 205.1467, found 205.1463. $C_{13}H_{19}NO$ (205.3): calcd. C 76.05, H 9.33, N 6.82; found C 75.83, H 9.48, N 6.79.

Data for 43b: Colorless crystals, m.p. 71 °C (diethyl ether/*n*-pentane). IR (CCl_4): ṽ = 2940, 2900, 2860, 1670 (C=O), 1650, 1500, 1460, 1450, 1390, 1360, 1310, 1210, 1135, 1110, 970 cm^{-1}. ^{1}H NMR: δ = 1.36 (s, 9 H, *t*Bu), 1.86 (m, 2 H, 6-H), 1.95 (m, 2 H, 7-H), 3.07 (t, 2 H, 8-H), 3.87 (t, 2 H, 5-H), 6.24 (s, 1 H, 1-H), 10.09 (s, 1 H, CHO), $J_{5,6}$ = $J_{7,8}$ = 6.6 Hz. MS (70 eV, EI): *m*/*z* (%) = 206 (6%) [M + 1]$^+$, 205 (37), 190 (100), 172 (6), 162 (54), 134 (8), 132 (6), 120 (20), 118 (9), 95 (6), 93 (9). $C_{13}H_{19}NO$ (205.3): calcd. C 76.05, H 9.33, N 6.82; found C 75.85, H 9.36, N 6.79.

Thermolysis of 22c: A solution of **22c** (100 mg, 0.51 mmol) in toluene (80 mL) was heated at reflux for 1.5 h. After concentration in vacuo, the residue was separated by flash chromatography (cyclohexane/ethyl acetate, 25:1 → 15:1), affording methyl 5,6,7,8-tetrahydroindolizine-3-carboxylate (**43c**, 59 mg, 65%) as a light yellow oil. IR (CCl_4): ṽ = 2940, 2920, 2880, 2850, 1700 (C=O), 1485, 1470, 1440, 1430, 1425, 1395, 1355, 1320, 1305, 1230, 1180, 1145, 1040 cm^{-1}. ^{1}H NMR: δ = 1.80 (m, 2 H, 6-H), 1.96 (m, 2 H, 7-H), 2.81 (t, 2 H, 8-H), 3.79 (s, 3 H, CH_3), 4.33 (t, 2 H, 5-H), 5.86 (d, 1 H, 1-H), 6.92 (d, 1 H, 2-H), $J_{1,2}$ = 4.0, $J_{5,6}$ = $J_{7,8}$ = 6.6 Hz. MS (70 eV, EI): *m*/*z* (%) = 180 (7%) [M + 1]$^+$, 179 (64), 164 (14), 148 (47), 146 (9), 121 (17), 120 (100), 119 (12), 118 (19), 106 (20). HRMS ($C_{10}H_{13}NO_2$): calcd. 179.0947; found 179.0946.

Thermolysis of 22d: A solution of **22d** (90 mg, 0.35 mmol) in toluene (50 mL) was heated at reflux for 3 h. After concentration in vacuo, the residue was separated by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1), affording dimethyl 5,6,7,8-tetrahydroindolizine-2,3-dicarboxylate (**43d**, 58 mg, 69%) as a yellow oil. IR (CCl_4): ṽ = 2980, 2930, 1730 (C=O), 1700 (C=O), 1480, 1440, 1430, 1395, 1340, 1310, 1280, 1250, 1200, 1150, 1120, 1060 cm^{-1}. ^{1}H NMR: δ = 1.81 (m, 2 H, 6-H), 1.95 (m, 2 H, 7-H), 2.78 (t, 2 H, 8-H), 3.81 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 4.21 (t, 2 H, 5-H), 6.20 (s, 1 H, 1-H), $J_{5,6}$ = $J_{7,8}$ = 6.6 Hz. MS (70 eV, EI): *m*/*z* (%) = 238 (8%) [M + 1]$^+$, 237 (62), 206 (97), 205 (69), 176 (16), 164 (18), 147 (63), 134 (20), 119 (58), 106 (12). HRMS ($C_{12}H_{15}NO_4$): calcd. 237.1001; found 237.1003.

Thermolysis of 25a: A solution of **25a** (450 mg, 1.75 mmol) in toluene (250 mL) was heated at reflux for 3 days. After concentration in vacuo, the residue was separated by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1, ethyl acetat/methanol, 20:1), affording (2,2-dimethyl-2,3-dihydro-1*H*-pyrrolizin-5-yl)(phenyl)methanone (**46a**, 264 mg, 63%), 2,2-dimethyl-6-phenyl-2,3-dihydro-1*H*-pyrrolizine-5-carbaldehyde (**47a**, 29 mg, 7%), and 2-(4,4-dimethyl-2-methylene-1-pyrrolidinyl)-3-oxo-3-phenylpropanal (**45a**, 54 mg, 12%).

Data for 46a: Yellow crystals, m.p. 57 °C (diethyl ether/*n*-pentane). IR (CCl_4): $\tilde{\nu}$ = 3025, 2960, 2860, 1620 (C=O), 1600 (C=C), 1460, 1430, 1400, 1380, 1300, 1270, 1150, 1040, 1020, 890, 690, 660 cm^{-1}. ^1H NMR: δ = 1.29 (s, 6 H, CH_3), 2.69 (s, 2 H, 1-H), 4.20 (s, 2 H, 3-H), 5.92 (d, 1 H, 7-H), 6.81 (d, 1 H, 6-H), 7.48 (m, 3 H, Ph-H), 7.82 (m, 2 H, Ph-H), $J_{6,7}$ = 4.5 Hz. MS (70 eV, EI): *m*/*z* (%) = 240 (12%) $[M + 1]^+$, 239 (70), 238 (9), 225 (13), 224 (78), 222 (22), 196 (10), 184 (27), 162 (24), 154 (14). $C_{16}H_{17}NO$ (239.3): calcd. C 80.30, H 7.16, N 5.85; found C 80.28, H 7.16, N 5.83.

Data for 47a: Yellow crystals, m.p. 145 °C (diethyl ether/*n*-pentane). IR (CCl_4): $\tilde{\nu}$ = 3030, 2960, 2860, 2800/2730, 1660 (C=O), 1620 (C=C), 1520, 1460, 1440, 1390, 1370, 1250, 1170 cm^{-1}. ^1H NMR: δ = 1.31 (s, 6 H, CH_3), 2.99 (s, 2 H, 1-H), 3.75 (s, 2 H, 3-H), 6.63 (s, 1 H, 7-H), 7.40 (m, 5 H, Ph-H), 9.94 (s, 1 H, CHO). MS (70 eV, EI): *m*/*z* (%) = 240 (9%) $[M + 1]^+$, 239 (51), 238 (14), 225 (17), 224 (100), 196 (13), 184 (7), 183 (6), 182 (23), 180 (7). $C_{16}H_{17}NO$ (239.3): calcd. C 80.30, H 7.16, N 5.85; found C 80.19, H 7.13, N 5.93.

Data for 45a: IR (CCl_4): $\tilde{\nu}$ = 3060, 2960, 2920, 2760/2710, 1700 (HC=O), 1640 (RC=O), 1600 (C=C), 1550, 1450, 1400, 1340, 1320, 1220, 1170, 1155 cm^{-1}. ^1H NMR: δ = 1.25 (s, 6 H, CH_3), 2.94 (m, 2 H, $=CH_2$), 3.33 (s, 2 H, 3-H), 4.68 (s, 2 H, 5-H), 4.93 (d (br), 1 H, 2-H), 7.50 (m, 2 H, Ph-H), 7.63 (m, 1 H, Ph-H), 7.92 (m, 2 H, Ph-H), 9.34 (d (br), 1 H, CHO), $J_{2,CHO}$ = 7.5 Hz.

Thermolysis of 25b: A solution of **25b** (450 mg, 1.90 mmol) in toluene (250 mL) was heated at reflux for 3 days. After concentration in vacuo, the residue was separated by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1, ethyl acetate/methanol, 30:1), affording (2,2-dimethyl-2,3-dihydro-1*H*-pyrrolizin-5-yl)-2,2-dimethylpropan-1-one (**46b**, 91 mg, 22%), 6-*tert*-butyl-2,2-dimethyl-2,3-dihydro-1*H*-pyrrolizine-5-carbaldehyde (**47b**, 5 mg, 1%), and 2-(4,4-dimethyl-2-methylene-1-pyrrolidinyl)-3-oxo-4,4-dimethylpentanal (**45b**, 312 mg, 69%).

Data for 46b: Light yellow crystals, m.p. 71 °C (diethyl ether/*n*-pentane). IR (CCl_4): $\tilde{\nu}$ = 2960, 2920, 2900, 2860, 1630 (C=O), 1460, 1450, 1440, 1430, 1390, 1360, 1300, 1270, 1200, 1160, 1060, 910 cm^{-1}. ^1H NMR: δ = 1.23 (s, 6 H, CH_3), 1.37 (s, 9 H, *t*Bu), 2.61 (s, 2 H, 1-H), 4.09 (s, 2 H, 3-H), 5.87 (d, 1 H, 7-H), 7.02 (d, 1 H, 6-H), *J*6,7 = 4.5 Hz. MS (70 eV, EI): *m*/*z* (%) = 219 (12%) $[M^+]$, 163 (12), 162 (100), 120 (7), 106 (15), 86 (7), 84 (10), 79/6), 78 (8), 77 (9). $C_{14}H_{21}NO$ (219.4): calcd. C 76.67, H 9.65, N 6.39; found C 76.40, H 9.60, N 6.25.

Data for 47b: Yellow oil. IR (CCl_4): $\tilde{\nu}$ = 2960, 2900, 2880, 2820, 2710, 1680 (C=O), 1650 (C=C), 1520, 1470, 1440, 1390, 1360, 1310, 1220, 1180, 1120 cm^{-1}. ^1H NMR: δ = 1.28 (s, 6 H, CH_3), 1.37 (s, 9 H, *t*Bu), 2.91 (s, 2 H, 1-H), 3.65 (s, 2 H, 3-H), 6.32 (s, 1 H, 7-H), 9.90 (s, 1 H, CHO). MS (70 eV, EI): *m*/*z* (%) = 219 (35%) $[M^+]$, 205 (17), 204 (100), 190 (9), 177 (14), 176 (59), 120 (13), 91 (14), 86 (11), 84 (17).

Data for 45b: Colorless crystals, m.p. 123 °C (diethyl ether/*n*-pentane). IR (CCl_4): $\tilde{\nu}$ = 2960, 2930, 2880, 2750/2710, 1720 (HC=O), 1640 (RC=O), 1600 (C=C), 1470, 1400, 1370, 1320, 1260, 1170, 1150, 1060 cm^{-1}. ^1H NMR: δ = 1.22 (s, 15 H, CH_3), 2.89 (m, 2 H, $C=CH_2$), 3.22 (s, 2 H, 3′-H), 4.21 (s, 2 H, 5′-H), 4.80 (d, 1 H, 2-H), 9.30 (d, 1 H, CHO), $J_{2,CHO}$ = 7.5 Hz. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.3 (CH_3), 26.9 (CH_3), 36.3 (C-4′), 43.4 (C-4), 44.6 (br., $=CH_2$), 50.2 (C-3′), 66.3 (C-5′), 95.3 (br., C-2), 168.5 (C-2′), 187.4 (CHO), 208.0 (CO). MS (70 eV, EI): *m*/*z* (%) = 237 (17%) $[M^+]$, 153 (29), 152 (100), 136 (19), 124 (16), 122 (8), 109 (7), 108 (16), 95 (13), 94 (9). $C_{14}H_{23}NO_2$ (237.4): calcd. C 70.85, H 9.77, N 5.90; found C 70.77, H 9.71, N 5.90.

Thermolysis of 25c: A solution of **25c** (290 mg, 1.37 mmol) in toluene (175 mL) was heated at reflux for 3 days. After concentration in vacuo, the residue was separated by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 5:1, ethyl acetate/methanol, 20:1), affording methyl 2,2-dimethyl-2,3-dihydro-1*H*-pyrrolizine-5-carboxylate (**47c**, 24 mg, 9%) and methyl 2-(4,4-dimethyl-2-methylene-1-pyrrolidinyl)-3-oxopropanoate (**45c**, 163 mg, 56%).

Data for 45c: Light yellow crystals, m.p. 92 °C (diethyl ether/*n*-pentane). IR (CCl_4): $\tilde{\nu}$ = 2960, 2940, 2880, 2760/2710, 1755 (OC=O), 1650 (HC=O), 1600 (C=C), 1550, 1440, 1410, 1370, 1320, 1260, 1210, 1180, 940 cm^{-1}. ^1H NMR: δ = 1.21 (s, 6 H, CH_3), 2.88 (s, br., 2 H, $C=CH_2$), 3.31 (s, 2 H, 3′-H), 3.77 (s, 3 H, OCH_3), 3.98 (s, 2 H, 5′-H), 4.98 (d, 1 H, 2-H), 9.38 (d, 1 H, CHO), $J_{2,CHO}$ = 7.5 Hz. MS (70 eV, EI): *m*/*z* (%) = 211 (40%) $[M^+]$, 196 (46), 194 (28), 183 (13), 152 (100), 136 (26), 124 (46), 108 (25), 96 (13). $C_{11}H_{17}NO_3$ (211.3): calcd. C 62.54, H 8.11, N 6.63; found C 62.50, H 8.02, N 6.66.

Data for 47c: Yellow oil. IR (CCl_4): $\tilde{\nu}$ = 2960, 2930, 2900, 2880, 1705 (C=O), 1490, 1470, 1440, 1330, 1280, 1270, 1260, 1200, 1130, 1110, 1030, 940 cm^{-1}. ^1H NMR: δ = 1.25 (s, 6 H, CH_3), 2.65 (s, 2 H, 1-H), 3.80 (s, 3 H, OCH_3), 4.00 (s, 2 H, 3-H), 5.86 (d, 1 H, 7-H), 6.91 (d, 1 H, 6-H), $J_{6,7}$ = 4.5 Hz. MS (70 eV, EI): *m*/*z* (%) = 193 (87%) $[M^+]$, 192 (17), 178 (32), 162 (44), 160 (21), 138 (84), 134 (54), 118 (27), 107 (19), 106 (100).

Thermolysis of 25d: A solution of **25d** (500 mg, 1.86 mmol) in toluene (250 mL) was heated at reflux for 3 days. After concentration in vacuo, the residue was separated by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 3:1, ethyl acetate/methanol, 30:1), affording dimethyl 2,2-dimethyl-2,3-dihydro-1*H*-pyrrolizine-5,6-dicarboxylate (**47d**, 84 mg, 18%) and dimethyl 2-(4,4-dimethyl-2-methylene-1-pyrrolidinyl)-3-oxosuccinate (**45d**, 300 mg, 60%).

Data for 45d: Yellow crystals, m.p. 128 °C (diethyl ether/*n*-pentane). IR (KBr): $\tilde{\nu}$ = 3010, 2960, 2880, 1750 (C=O), 1720 (C=O), 1630 (C=C), 1550, 1480, 1420, 1320, 1250, 1220, 1170, 1100, 1050, 980 cm^{-1}. ^1H NMR: δ = 1.20 (s, 6 H, CH_3), 3.18 (s, 2 H, $C=CH_2$), 3.31 (s, 2 H, 3′-H), 3.79 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 4.08 (s, 2 H, 5′-H), 5.75 (s, 1 H, 2-H). MS (70 eV, EI): *m*/*z* (%) = 269 (M^+, 4%), 211 (13), 210 (100), 182 (15), 166 (4), 151 (3), 150 (8), 122 (6), 108 (5). $C_{13}H_{19}NO_5$ (269.3): calcd. C 57.98, H 7.11, N 5.20; found C 57.76, H 6.91, N 5.17.

Data for 47d: Yellow crystals, m.p. 52 °C (diethyl ether/*n*-pentane). IR (CCl_4): $\tilde{\nu}$ = 2960, 2930, 2900, 2870, 1730 (C=O), 1705 (C=O), 1485, 1470, 1450, 1290, 1250, 1200, 1190, 1140, 1120, 1110, 1060 cm^{-1}. ^1H NMR: δ = 1.25 (s, 6 H, CH_3), 2.64 (s, 2 H, 1-H), 3.83 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 4.01 (s, 2 H, 3-H), 6.26 (s, 1 H, 7-H). MS (70 eV, EI): *m*/*z* (%) = 251 (90%) $[M^+]$, 220 (100), 219 (26), 204 (64), 190 (16), 188 (32), 164 (70), 162 (16), 161 (34), 160 (89). $C_{13}H_{17}NO_4$ (251.3): calcd. C 62.14, H 6.82, N 5.57; found C 61.93, H 6.69, N 5.61.

Thermolysis of 45a: A solution of **45a** (100 mg, 0.39 mmol) in pure benzene (50 mL) was heated in an autoclave at 200 °C for 12 h. After concentration of the mixture in vacuo, the residue was separated by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1), affording **46a** (65 mg, 70%) and **47a** (5 mg, 5%).

Thermolysis of 45b: A solution of **45b** (100 mg, 0.42 mmol) in pure benzene (50 mL) was heated in an autoclave at 200 °C for 12 h. After concentration of the mixture in vacuo, the residue was separated by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1), affording **46b** (74 mg, 80%) and **47b** (4 mg, 4%).

Thermolysis of 45c: A solution of **45c** (100 mg, 0.47 mmol) in pure benzene (50 mL) was heated in an autoclave at 200 °C for 24 h. After concentration of the mixture in vacuo, the residue was separated by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1), affording **47c** (55 mg, 60%).

Thermolysis of 45d: A solution of **45d** (100 mg, 0.37 mmol) in pure benzene (50 mL) was heated in an autoclave at 200 °C for 24 h. After concentration of the mixture in vacuo, the residue was separated by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1), affording **47d** (61 mg, 65%).

Thermolysis of 28a: A solution of **28a** (650 mg, 2.51 mmol) in pure benzene (75 mL) was heated in an autoclave at 200 °C for 3.5 h. After concentration of the mixture in vacuo, the residue was separated by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1), affording (3,3-dimethyl-2,3-dihydropyrrolo[2,1-*b*][1,3]oxazol-5-yl)(phenyl)methanone (**48a**, 79 mg, 13%), 3,3-dimethyl-6-phenyl-2,3-dihydropyrrolo[2,1-*b*][1,3]oxazole-5-carbaldehyde (**49a**, 79 mg, 13%), and 2-[formyl(2-oxo-2-phenylethyl)amino]-2-methylpropyl acetate (**52a**, 313 mg, 45%).

Data for 48a: Yellow crystals, m.p. 102 °C (diethyl ether/*n*-pentane). IR (CCl_4): $\tilde{\nu}$ = 3060, 2960, 2930, 2880, 1620 (C=O), 1490, 1450, 1430, 1380, 1340, 1260, 1210, 1030, 1020, 880, 690, 670 cm^{-1}. ^1H NMR: δ = 1.79 (s, 6 H, CH_3), 4.68 (s, 2 H, 2-H), 5.33 (d, 1 H, 7-H), 6.73 (d, 1 H, 6-H), 7.45 (m, 3 H, Ph-H), 7.73 (m, 2 H, Ph-H), $J_{6,7}$ = 4.5 Hz. MS (70 eV, EI): *m*/*z* (%) = 242 (19%) $[M + 1]^+$, 241 (100), 240 (11), 226 (7), 212 (26), 198 (11), 187 (10), 186 (50), 184 (7), 158 (15). $C_{15}H_{15}NO_2$ (241.3): calcd. C 74.67, H 6.27, N 5.81; found C 74.55, H 6.22, N 5.72.

Data for 49a: Yellow crystals, m.p. 132 °C (diethyl ether/*n*-pentane). IR (KBr): $\tilde{\nu}$ = 3040, 2960, 2920, 2830, 2750, 1650 (C=O), 1600 (C=C), 1530, 1490, 1350, 1220, 1200, 970, 930, 860, 770, 700, 660 cm^{-1}. ^1H NMR: δ = 1.60 (s, 6 H, CH_3), 4.74 (s, 2 H, 2-H), 6.28 (s, 1 H, 7-H), 7.32 (m, 3 H, Ph-H), 7.47 (m, 2 H, Ph-H), 9.70 (s, 1 H, CHO). MS (70 eV, EI): *m*/*z* (%) = 242 (19%) $[M + 1]^+$, 241 (100), 240 (22), 198 (9), 186 (23), 185 (13), 184 (11), 170 (13), 158 (11), 144 (6). $C_{15}H_{15}NO_2$ (241.3): calcd. C 74.67, H 6.27, N 5.81; found C 74.49, H 6.19, N 5.77.

Data for 52a: Yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3080, 3060, 2980, 2940, 1750, 1710, 1665 (NC=O), 1590, 1450, 1380, 1350, 1300, 1220, 1100, 1050, 1000, 960, 910, 690 cm^{-1}. ^1H NMR: δ = 1.47 (s, 6 H, CH_3), 2.07 (s, 3 H, $COCH_3$), 4.08 (s, 2 H, CH_2), 4.80 (s, 2 H, OCH_2), 7.49 (m, 2 H, Ph-H), 7.61 (m, 1 H, Ph-H), 7.99 (m, 2 H, Ph-H), 8.54 (s, 1 H, NCHO). ^{13}C NMR: δ = 20.7 (CH_3), 24.6 (CH_3), 47.6 (C-1′), 57.0 (C-2), 68.9 (C-1), 127.9 (Ph-C), 128.7 (Ph-C), 133.5 (Ph-C), 135.1 (Ph-C), 162 (NCHO), 170.4 (CO_2R), 193.4 (CO). MS (70 eV, EI), *m*/*z* (%) = 277 (7%) $[M^+]$, 205 (5), 204 (40), 177 (6), 176 (46), 145 (7), 144 (65), 130 (6), 120 (16).

Thermolysis of 28b: A solution of **28b** (460 mg, 1.92 mmol) in pure benzene (75 mL) was heated in an autoclave at 200 °C for 3 h. After concentration of the mixture in vacuo, the residue was separated by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1), affording 1-(3,3-dimethyl-2,3-dihydropyrrolo[2,1-*b*][1,3]oxazol-5-yl)-2,2-dimethylpropan-1-one (**48b**, 87 mg, 20%), 6-(*tert*-butyl)-3,3-dimethyl-2,3-dihydropyrrolo[2,1-*b*][1,3]oxazole-5-carbaldehyde (**49b**, 55 mg, 13%), and 2-[(3,3-dimethyl-2-oxobutyl)(formyl)amino]-2-methylpropyl acetate (**52b**, 189 mg, 38%).

Data for 48b: Pale yellow crystals, m.p. 73 °C (diethyl ether/*n*-pentane). IR (CCl_4): $\tilde{\nu}$ = 2980, 2940, 2900, 2880, 1630 (C=O), 1570, 1490, 1480, 1440, 1400, 1350, 1260, 1200, 1130, 1080, 1040, 1000, 910 cm^{-1}. ^1H NMR: δ = 1.37 (s, 9 H, *t*Bu), 1.68 (s, 6 H, CH_3), 4.60 (s, 2 H, 2-H), 5.27 (d, 1 H, 7-H), 7.03 (d, 1 H, 6-H), $J_{6,7}$ = 4.5 Hz. MS (70 eV, EI): *m*/*z* (%) = 222 (5%) $[M + 1]^+$, 221 (35), 194 (1), 166 (1), 165 (12), 164 (100), 137 (2), 136 (3), 110 (10), 109 (2). $C_{13}H_{19}NO_2$ (221.3): calcd. C 70.56, H 8.65, N 6.33; found C 70.30, H 8.53, N 6.29.

Data for 49b: Yellow oil. IR (CCl_4): $\tilde{\nu}$ = 2960, 2900, 2860, 2740/2720, 1670 (C=O), 1630 (C=C), 1550, 1490, 1460, 1410, 1360, 1260, 1230, 1120, 1070, 990, 650 cm^{-1}. ^1H NMR: δ = 1.34 (s, 9 H, *t*Bu), 1.54 (s, 6 H, CH_3), 4.67 (s, 2 H, 2-H), 5.94 (s, 1 H, 7-H), 9.75 (s, 1 H, CHO). MS (70 eV, EI): *m*/*z* (%) = 222 (15%) $[M + 1]^+$, 221 (97), 207 (14), 206 (100), 180 (6), 179 (33), 178 (43), 166 (6), 164 (13).

Data for 52b: Yellow oil. IR (CCl_4): $\tilde{\nu}$ = 2980, 2900, 2870, 1750 (OC=O), 1730 (RC=O), 1665 (NC=O), 1480, 1390, 1380, 1350, 1260, 1225, 1190, 1060, 1050, 1000, 950 cm^{-1}. ^1H NMR: δ = 1.24 (s, 9 H, *t*Bu), 1.41 (s, 6 H, CH_3), 2.10 (s, 3 H, $COCH_3$), 4.02 (s, 2 H, CH_2), 4.30 (s, 2 H, OCH_2), 8.47 (s, 1 H, NCHO). MS (CI, isobutane): *m*/*z* (%) = 258 (100%) $[M + 1]^+$, 257 (2), 230 (3), 216 (3), 200 (3), 198 (2), 160 (3), 115 (2), 100 (2).

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