Titanium(IV) Chloride Induced Reactions of Ketones and *C*-Acylimines with Dimethylcyanamide

Monika Mazik[a], Roland Boese[b], and Reiner Sustmann*[a]

Institut für Organische Chemie der Universität Essen[a], D-45117 Essen, Germany

Institut für Anorganische Chemie der Universität Essen[b], D-45117 Essen, Germany

Received March 20, 1996

Key Words: *C*-Acylimines / Ketones / Titanium(IV) chloride / Dimethylcyanamide

The reactions of ketones (benzophenone, 4-methylbenzophenone, acetophenone, acetone, and 2,2,4,4-tetramethyl-3-pentanone) and *C*-acylimines with dimethylcyanamide in the presence of titanium(IV) chloride were investigated. Benzophenone and 4-methylbenzophenone react with dimethylcyanamide to give 4,4-disubstituted 2-dimethylamino-3-aza-1-oxa-1,3-butadienes **5** and 4,4-disubstituted 2-dimethylamino-1-*N,N*-dimethylcarbamoyl-1,3-diaza-1,3-butadienes **9**. Ketones with enolizable hydrogen atoms undergo aldol reactions under these conditions. *C*-Acylimines **11b–11e**, derived from benzil and substituted anilines, undergo [2 + 2] cycloaddition to dimethylcyanamide with subsequent ring opening to 1-(*N,N*-dimethylcarbamoyl)-2,3,4-triaryl-1,4-diaza-1,3-butadienes **15**. 1,2-Diphenyl-2-(isopropylimino)ethanone (**11a**) reacts with dimethylcyanamide to give 2-dimethylamino-1-isopropyl-4,4-diphenyl-2-imidazolin-5-one (**23**) in a hitherto unknown multistep reaction. The structure of **23** was confirmed by an X-ray analysis.

Recently, we reported on the reaction of 1,2-diketones with dimethylcyanamide in the presence of a Lewis acid. In the presence of titanium(IV) chloride 1,2-diketones participate in [2 + 2] cycloadditions to dimethylcyanamide with subsequent ring opening of the cycloadducts to *N'*-alkylidene-*N,N*-dimethylurea derivatives[1]. We now investigated the reaction of monoketones and *C*-acylimines (1,2-diphenylethanodione monoimines) with dimethylcyanamide.

The reaction of monoketones with *N,N*-disubstituted cyanamides has been very rarely described in the literature. A few reactions of monoketones with cyanamide are known. Typical examples are the condensation reactions of simple aliphatic ketones with cyanamide which give the corresponding cyanoimines in moderate yield[2–4]. Reactions of 1,3-diketones[5], β-aminoenones[6], α-hydroxy ketones[7–10], and α-amino ketones[11,12] with cyanamide lead to 2-aminopyrimidine, 1,3-oxazole, and imidazole derivatives via cyanoimino compounds. Literature reports on the reaction of *N,N*-disubstituted cyanamides with monoketones involve the thermal reaction with perhaloketones[13–15] and the reaction with phosphorylated ketones[16]. Hermes and Braun[13] reported that the thermal reaction of perhaloketones with disubstituted cyanamides leads to 2*H*-1,3,5-oxadiazine derivatives **8** (R = R^1 = CF_3, CF_2Cl, Scheme 1). The results of Hermes and Braun are in contrast to those of Burger and Simmerl[14,15], who suggested the 4*H*-1,3,5-oxadiazine structure **10** as the structure of the reaction product.

C-Acylimines can be regarded as 4-aza-1-oxabutadiene systems which might undergo [4 + 2] cycloadditions with electron-rich dienophiles, Diels-Alder reactions with inverse electron demand[17]. The [4 + 2] cycloaddition of 4-aza-1-oxabutadienes, bearing an oxygen and a nitrogen atom at the diene termini, have not been investigated extensively. With the exception of studies of *o*-quinone monoimines, which display a high reactivity in [4 + 2] cycloaddition reactions with electron-rich dienophiles[18,19], only two [4 + 2] cycloaddition reactions of 4-aza-1-oxabutadienes have been reported, namely the reaction of benzilhydrazones with diphenylketene[20] and the reaction of dimethyl 2,3-dioxosuccinate monophenylimine with tetraethoxyethylene[21]. *C*-Acylimines may, however, also be considered as potential partners in [2 + 2] cycloadditions, reactions which have not been described so far.

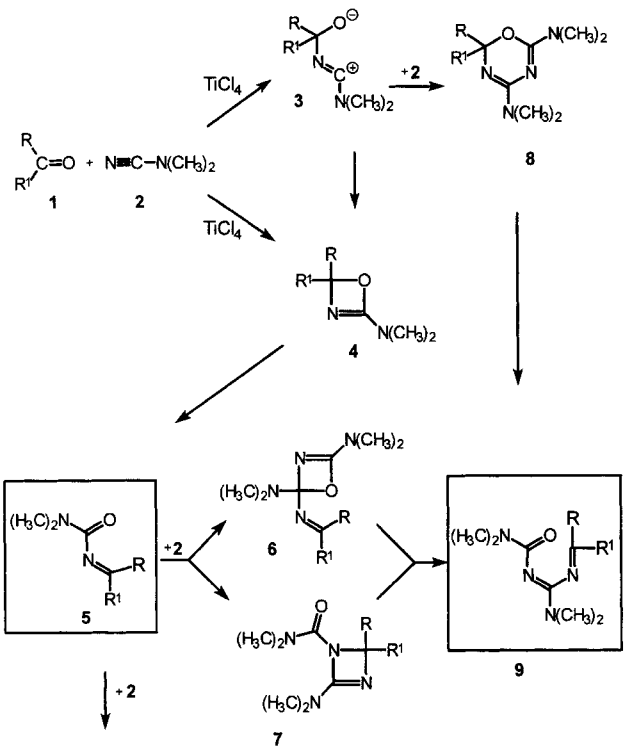
Results and Discussion

We investigated the reaction of aliphatic and aromatic ketones **1a–1e** with dimethylcyanamide in the presence of titanium(IV) chloride. The reactions were carried out in benzene at 25–75 °C employing a ketone **1**, dimethylcyanamide **2**, and titanium(IV) chloride in a 1:1:1 ratio. We found that under our conditions the reaction of benzophenone **1a** and 4-methylbenzophenone **1b** with dimethylcyanamide leads to 1:1 and 1:2 adducts, as shown by elemental analysis and mass spectrometry. In a similar reaction of dimethylcyanamide with acetone **1d** either at 25 °C or at 75 °C only condensation products of acetone, 4-methyl-3-penten-2-one, 4-hydroxy-4-methyl-2-pentanone, and 2,6-dimethyl-2,5-heptadien-4-one were isolated in 82, 8, and 2%, respectively. In the reaction of acetophenone **1c** with dimethylcyanamide the condensation product of acetophenone, 1,3-diphenyl-2-buten-1-one, was also isolated in

  0947–3440/96/1010–1665 $ 15.00+.25/0

10% yield. In this case the addition product of 1,3-diphenyl-2-buten-1-one and dimethylcyanamide could be detected by the GLC/MS. The reaction of 2,2,4,4-tetramethyl-3-pentanone **1e** with dimethylcyanamide gives only traces of the 1:1 and 1:2 adducts as observed by GLC/MS.

Scheme 1

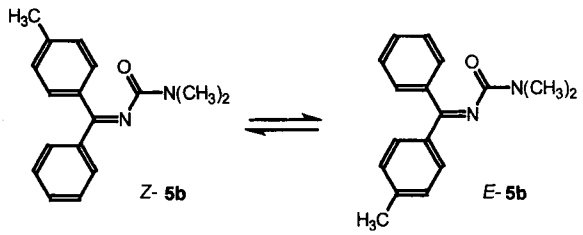


	R	R¹
1a	C_6H_5	C_6H_5
1b	C_6H_5	4-CH_3-C_6H_4
1c	C_6H_5	CH_3
1d	CH_3	CH_3
1e	$C(CH_3)_3$	$C(CH_3)_3$

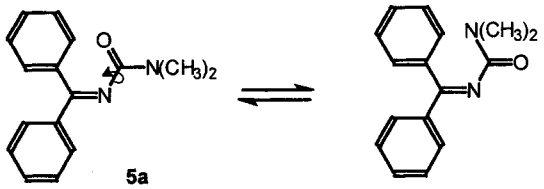
	R	R¹
5a	C_6H_5	C_6H_5
5b	C_6H_5	4-CH_3-C_6H_4
9a	C_6H_5	C_6H_5
9b	C_6H_5	4-CH_3-C_6H_4

The ^{13}C-NMR spectra of the 1:1 adducts from **1a** and **1b** with **2** obtained in 8% and 49% yield exhibit signals at ca. δ = 163 and 169 which can be assigned to the C atom of a CN double bond and the C atom of an amide carbonyl group characteristic of structure **5**. The presence of the two signals excludes the oxazete structure **4**. In the ^{13}C-NMR spectrum two signals at ca. δ = 35 and 36 are observed for the dimethylamino group. The signals of all aromatic carbon atoms can only be observed at low temperature in the ^{13}C-NMR spectrum. At 228 K the ^{1}H-NMR and the ^{13}C-NMR spectrum of the 1:1 adduct from **1b** and **2** show the presence of two isomers. We assign structures (*Z*)-**5b** and (*E*)-**5b** (Scheme 2) to these isomers, because the ^{13}C-NMR spectrum of the 1:1 adduct from **1a** and **2** at 228 K shows the presence of only one compound, which excludes an isomerization as shown in Scheme 3. The 1:1 adducts display a characteristic IR absorption at about 1650 cm^{-1} (C=N, N−C=O). It can be stated that no other structure than 2-dimethylamino-4,4-diphenyl-3-aza-1-oxa-1,3-butadiene **5a** and 2-dimethylamino-4-(p-methylphenyl)-4-phenyl-3-aza-1-oxa-1,3-butadiene **5b** is in agreement with the spectroscopic data. Thus, after an initial [2 + 2] cycloaddition, an electrocyclic ring opening to **5** takes place.

Scheme 2



Scheme 3



The second type of reaction product, the 1:2 adducts from **1a** and **1b** with **2** isolated in 45% and 10% yield, might possess either the 2*H*-1,3,5-oxadiazine structure **8**, the 4*H*-1,3,5-oxadiazine structure **10**, or the acyclic structure **9**. The ^{13}C-NMR spectra display, among others, three signals at ca. δ = 159, 162, and 169. The signals at ca. δ = 159 and 162 can be assigned to the C atoms of two CN double bonds and the signal at ca. δ = 169 to the C atom of the amide carbonyl group. The presence of these three signals supports structure **9** for the 1:2 adducts. The absence of a signal with a ^{13}C-chemical shift characteristic of the sp^3 C atom in the heterocycles **8** or **10** excludes the 1,3,5-oxadiazine structure. In the ^{13}C-NMR spectrum one dimethylamino group gives rise to two signals at ca. δ = 35 and 36 whereas for the second dimethylamino group only one signal at ca. δ = 37 is observed. At higher temperatures (383 K, DMSO), only one signal is observed each for both dimethylamino groups at ca. δ = 36 and 37, respectively. In the ^{1}H-NMR spectrum recorded at 294 K the proton signals of one dimethylamino group appear as a singlet at ca. δ = 2.90 and those of the second dimethylamino group as two singlets at ca. δ = 2.30 and 2.60. At 383 K the second dimethylamino group gives also rise to a singlet in the ^{1}H-NMR spectrum. The IR spectra show the presence of the C=N bonds and the amide carbonyl vibration around 1570−1640 cm^{-1}. 4,4-Disubstituted-2-dimethylamino-1-*N*,*N*-dimethylcarbamoyl-1,3-diaza-1,3-butadienes **9** may be formed in two ways, either via an intermediate 1,4-dipole **3** and electrocyclic ring opening of oxadiazine **8** or via a second [2 + 2] cycloaddition of **2** to **5** and ring opening of the oxazete derivative **6** or **7**. We tested the reaction of **5a** and **5b** with dimethylcyanamide in the presence of titanium(IV) chloride in order to check the latter hypothesis.

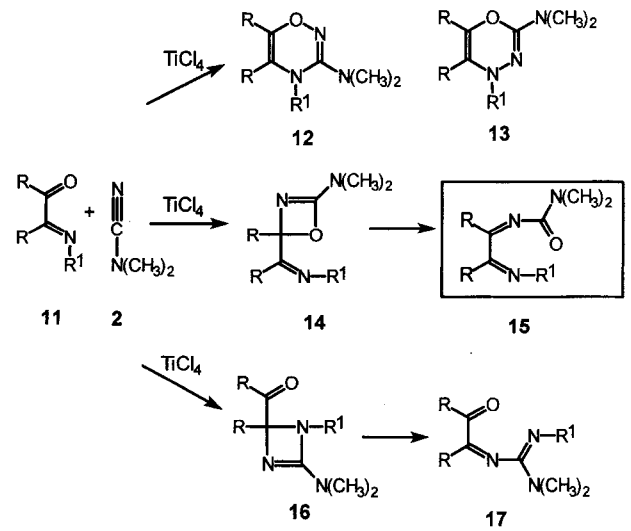
It leads in only 2–5% yield to the 1:2 adduct **9**, which may be an indication that **9** is formed mainly via ring opening of **8**.

To summarize, we observed a strong influence of the methyl group of the phenyl ring of 4-methylbenzophenone on the relative yields of products **5** and **9**. If the reactants **1a–b** and **2** were employed in a 1:1 molar ratio the yields of isolated 1:1 adducts **5** ranged from 8% (benzophenone) to 49% (4-methylbenzophenone), and the yields of isolated 1:2 adducts **9** from 45% (benzophenone) to 10% (4-methylbenzophenone). In the case of ketones bearing a hydrogen atom in the α-position to the C=O group a condensation reaction takes place. Steric effects, for example in the case of 2,2,4,4-tetramethyl-3-pentanone, suppress the reaction with dimethylcyanamide almost completely.

The *C*-acylimines used in this study were obtained by the reaction of benzil with isopropylamine or aniline derivatives substituted on the benzene ring. In the case of anilines carrying electron-withdrawing groups titanium(IV) chloride was necessary for the reaction. The latter is a more effective water scavenger than molecular sieves and it may also act catalytically as Lewis acid to polarize the carbonyl bond.

The reaction of **11** with **2** may produce four different types of 1:1 cycloadducts: 1,2,4-oxadiazines **12**, 1,3,4-oxadiazines **13**, 4*H*-1,3-oxazete derivatives **14**, and 4*H*-1,3-diazete derivatives **16** (Scheme 4). 1-*N,N*-Dimethylaminocarbamoyl-1,4-diaza-1,3-butadiene derivatives **15** and 4-(*N,N*-dimethylamino-*N'*-alkyl(aryl)-amidino)-2,3-disubstituted-4-aza-1-oxa-1,3-butadiene derivatives **17** may be formed via ring opening of compounds **14** and **16**, respectively.

Scheme 4



	R	R^1
11a	C_6H_5	$CH(CH_3)_2$
11b	C_6H_5	C_6H_5
11c	C_6H_5	4-CH_3-C_6H_4
11d	C_6H_5	4-Cl-C_6H_4
11e	C_6H_5	3-NO_2-C_6H_4

	R	R^1
15b	C_6H_5	C_6H_5
15c	C_6H_5	4-CH_3-C_6H_4
15d	C_6H_5	4-Cl-C_6H_4
15e	C_6H_5	3-NO_2-C_6H_4

In order to prove this *C*-acylimines **11a–11e** were allowed to react with an equimolar amount of dimethylcyanamide **2** in the presence of $TiCl_4$ and products which were 1:1 adducts of compounds **11** and **2** according to the M^+ peaks in the mass spectra could be isolated. No reaction took place in the absence of the Lewis acid.

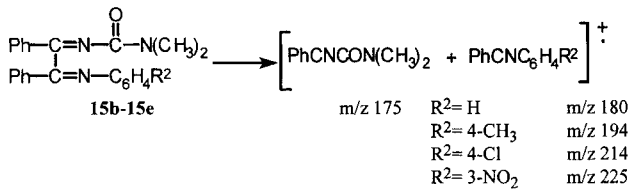
The reactions of the *C*-acylimines were carried out at 25–60°C in benzene employing the reactants and titanium(IV) chloride in a 1:1:1 ratio. Equimolar amounts of the Lewis acid are required because the final products are complexed in a 1:1 manner, as shown by MS analysis. From these titanium complexes the 1:1 adducts were liberated by hydrolysis. It was found that the adducts are subject to hydrolytic attack which lowers the yields of isolated products (70–85%).

The products were fully characterized by elemental analysis and spectroscopic methods. The spectral data show that the compounds obtained from **11b–11e** (1,2-diphenyl-2-phenyliminoethanone and its substituted derivatives) and **2** have a structure different from that of the product isolated in the reaction of 1,2-diphenyl-2-isopropyliminoethanone **11a** and **2**.

^{13}C-NMR spectra of the 1:1 adducts from **11b–11e** and **2** exhibit signals at about δ = 162, 165, and 169 which may be assigned to two C=N carbon atoms and to the C atom of an amide carbonyl group which are characteristic of structure **15**. The spectrum shows two signals at ca. δ = 35 and 36 for the dimethylamino group. In the ^{1}H-NMR spectra the protons of the dimethylamino group appear as two singlets. The chemical shifts of these singlets depend on the substituent on the phenyl ring of the phenylimino group. At high temperature (383 K, DMSO) the protons of the dimethylamino group show only a singlet. All compounds display a IR absorption at about 1650 cm^{-1} (C=N, N–C=O). The mass spectra of the 1:1 adducts from **11b–11e** and **2** obtained by the direct inlet system show a base peak at a *m/z* of 180 (R^2 = H), 194 (R^2 = 4-CH_3), 214 (R^2 = 4-Cl), and 225 (R^2 = 3-NO_2) in agreement with a $PhCNC_6H_4R^2$ fragment which is characteristic of structure **15** (Scheme 5). Another peak characteristic of structure **15** assigned to a $PhCNCON(CH_3)_2$ fragment is present with lower intensity because of its fragmentation to *m/z* of 103 and *m/z* of 72 in accordance with PhCN and $CON(CH_3)_2$ fragments, respectively. The mass spectra of the initial *C*-acylimines **11b–11e** show a similar fragmentation pattern. These spectra display two characteristic peaks at *m/z* in agreement with $PhCNC_6H_4R^2$ and PhCO. The presence of a peak at *m/z* = 72 in the mass spectra of the 1:1 adducts from **11b–11e** and **2** is also typical of 2,3-disubstituted 4-*N,N*-dimethylcarbamoyl-1-oxa-4-aza-1,3-butadienes and 2,3-disubstituted-1,4-di-(*N,N*-dimethylcarbamoyl)-1,4-diaza-1,3-butadienes obtained by the reaction of 1,2-diketones with dimethylcyanamide, the structure of the latter adduct being established by an X-ray analysis[1].

It can be concluded that no other structure than 1-*N,N*-dimethylcarbamoyl-2,3,4-triphenyl-1,4-diaza-1,3-butadiene **15b** and its derivatives **15c–15e** is in agreement with the spectroscopic data. *C*-Acylimines **11b–11e**, therefore, undergo [2 + 2] cycloaddition to the C=O bond to give **14** which further rearranges to **15**. Interestingly, the mass spectra of **15b–15e** obtained by GLC/MS show a different frag-

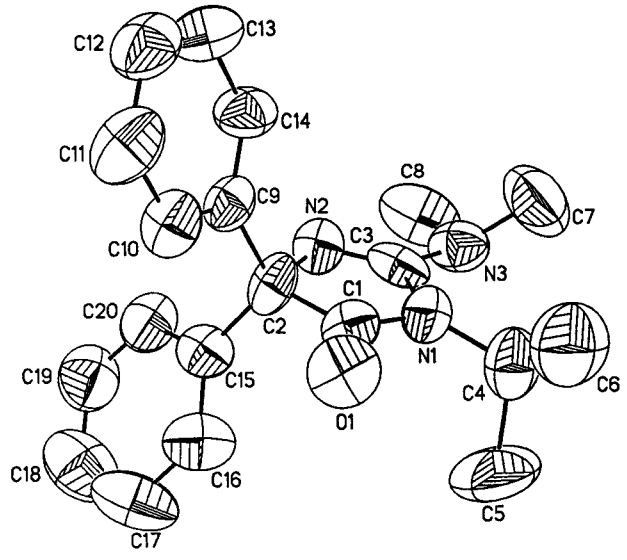
Scheme 5



mentation pattern than mass spectra obtained by the direct inlet system (see Experimental).

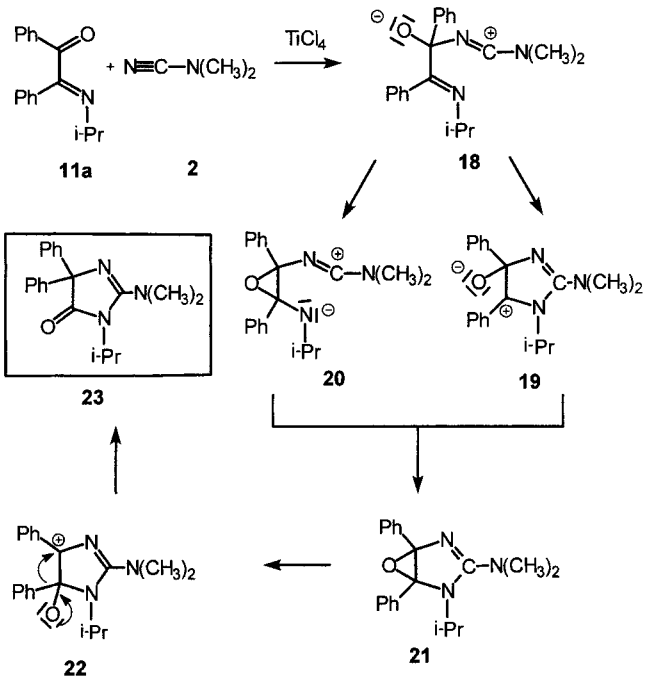
The ^{13}C-NMR spectrum of the 1:1 adduct from **11a** and **2** displays, among others, signals at δ = 76, 162, and 183. The first signal can be assigned to a sp^3 C atom and the two latter signals to C=N and C=O carbon atoms, respectively. The presence of these signals suggested at first structure **16a** (2-dimethylamino-3*H*, 4*H*-4-benzoyl-3-isopropyl-4-phenyl-1,3-diazete). The absence of a signal for a second C=N carbon atom excludes the formation of products **15a** and **17a**. The resonances at δ = 19 (CH_3) and at δ = 47 (CH) are assigned to the isopropyl group. In the ^{13}C-NMR spectrum a signal at δ = 40 is observed for the dimethylamino group and the ^{1}H-NMR spectrum shows a singlet at δ = 2.86. The doublet at δ = 1.43 (CH_3) and a septet at δ = 3.98 (CH) in the ^{1}H-NMR spectrum indicate the presence of the isopropyl group. The IR spectrum shows the presence of a C=N bond at 1624 cm^{-1} and a carbonyl vibration at 1720 cm^{-1}. In order to prove structure **16a**, derived from the spectroscopic data, we carried out an X-ray analysis, which showed structure **16a** to be wrong. Instead of a 1,3-diazete ring, 2-dimethylamino-1-isopropyl-4,4-diphenyl-2-imidazolin-5-one (**23**) represents the isolated 1:1 adduct of compounds **11a** and **2**. The question remains, how this molecule is formed from **11a** and **2** in the presence of $TiCl_4$. A hypothetical mechanism of a multistep reaction involves formation of a bicyclic structure **21**, which rearranges further to **23** (Scheme 6). A similar reaction course was observed earlier in the reaction of dimethyl-2,3-dioxosuccinate with ethyl vinyl ether[22]. 2-Dimethylamino-1-isopropyl-4,4-diphenyl-2-imidazolin-5-one has not been described so far. Literature reports on the preparation of other 2-aminoimidazolin-5-one derivatives involve the cyclization of diaminomethylenehydrazones with dimethyl acetylenedicarboxylate[23], thermal ring closure of *N*-aryl-*N'*-(β-arylvinyl)carbodiimides[24], reaction of carbodiimides with 3-dimethylamino-2*H*-azirines[25], cyclization of *N*-methylamidinoglycine ethyl ester[26] and heating of 2-dimethylamino-2-imidazolin-4-one with dimethyl sulfate[26].

Figure 1. ORTEP Representation of 1:1 adduct (**23**) from **11a** and **2** according to the X-ray analysis[a]



[a] Selected bond lengths [Å] and bond angles [°]: N(1)–C(1) 1.320(10), N(1)–C(3) 1.451(14), N(1)–C(4) 1.449(12), N(2)–C(2) 1.502(16), N(2)–C(3) 1.275(14), N(3)–C(3) 1.376(14), O(1)–C(1) 1.262(16), C(1)–C(2) 1.526(17), C(2)–C(9) 1.539(15); C(1)–N(1)–C(3) 105.4(7), C(1)–N(1)–C(4) 125.8(9), C(3)–N(1)–C(4) 126.8(8), C(2)–N(2)–C(3) 105.7(10), C(3)–N(3)–C(7) 116.0(14), C(7)–N(3)–C(8) 115.6(10), N(1)–C(1)–O(1) 125.4(10), N(1)–C(1)–C(2) 109.5(9), N(2)–C(2)–C(1) 103.0(8), C(1)–C(2)–C(9) 109.4(12), O(1)–C(1)–C(2) 125.1(9), N(1)–C(3)–N(2) 116.3(9), N(2)–C(2)–C(15) 109.0(12), N(1)–C(3)–N(3) 118.4(9), C(1)–C(2)–C(15) 113.7(8), N(2)–C(2)–C(9) 108.2(7), N(1)–C(4)–C(5) 110.7(10), C(2)–C(9)–C(14) 122.2(5).

Scheme 6



Experimental

Melting points uncorrected. – ^{1}H- and ^{13}C-NMR spectra: Varian Gemini 200 and a Bruker AMX 300 spectrometer; internal standard TMS (solvent $CDCl_3$, unless indicated otherwise). – Mass spectra: Fisons VG Prospec 3000 and a Hewlett Packard HP 5971A MSD spectrometer. – IR spectra: Perkin-Elmer FT-IR 1600 spectrometer. – Column chromatography: silica gel 70–230 mesh (Fluka), eluent benzene/ethyl acetate mixture (3:1) unless indicated otherwise. Preparative TLC and analytical TLC: Merck Kieselgel 60 F_{254} plates (1 mm and 0.2 mm thick, respectively), eluent a benzene/ethyl acetate (3:1).

General Procedure for the Synthesis of Compounds **5** *and* **9**: A solution of $TiCl_4$ (1.9 g, 0.01 mol) in 10 ml of dry benzene was added dropwise to a well-stirred mixture of the ketone (0.01 mol) and dimethylcyanamide (0.7 g, 0.01 mol) in 20 ml of dry benzene. After the addition was complete the mixture was stirred at room temperature for 1 h, heated at 70 °C for 1 h, cooled to room temp., and the benzene was evaporated. About 50 ml of water was added to the residue and the resulting solution was alkalized with 5% NaOH and extracted with chloroform. The mixture of products was separated by preparative TLC and crystallized from petroleum ether.

2-Dimethylamino-4,4-diphenyl-3-aza-1-oxa-1,3-butadiene (**5a**): Yield: 0.20 g (8%), m.p. 102–103 °C. R_f = 0.31. – ^{1}H NMR (300 MHz, 294 K): δ = 2.84 (s, 3H, NCH_3), 2.85 (s, 3H, NCH_3), 7.30–7.70 (m, 10H, aromatic H). – ^{13}C NMR (75 MHz, 294 K): δ = 35.28 (NCH_3), 36.89 (NCH_3), 128.21, 163.85 (C=N), 169.43 [O=*C*-N(CH_3)$_2$]. – ^{13}C NMR (75 MHz, 228 K): δ = 35.68 (NCH_3), 37.39 (NCH_3), 128.19, 128.63, 128.79, 130.13, 130.53, 132.07, 136.04, 137.79, 164.36 (C=N), 170.15 [O=*C*-N(CH_3)$_2$]. – IR (KBr): $\tilde{\nu}$ = 2923, 1650, 1575, 1494, 1434, 1382, 1255, 1173, 1136, 1054, 1017, 943, 779, 697 cm^{-1}. – MS; *m/z* (%): 252 (7) [M$^+$], 208 (100), 180 (10), 175 (12), 165 (11), 147 (1), 105 (4), 77 (18), 72 (15), 51 (6), 44 (2). – $C_{16}H_{16}N_2O$ (252.2): calcd. C 76.19, H 6.35, N 11.11; found C 76.40, H 6.43, N 11.10. – Mol. mass: calcd. 252.1261; found 252.1257 (HRMS).

2-Dimethylamino-4-(p-methylphenyl)-4-phenyl-3-aza-1-oxa-1,3-butadiene (**5b**): Yield: 1.30 g (49%), m.p. 98–99 °C. R_f = 0.28. – ^{1}H NMR (300 MHz, 294 K): δ = 2.32 (s, 3H, *p*-CH_3), 2.78 (s, 3H, NCH_3), 2.80 (s, 3H, NCH_3), 7.11–7.50 (m, 9H, aromatic H). – ^{1}H NMR (228 K): δ = 2.31, 2.32 [*p*-CH_3, isomers (*E*) and (*Z*)], 2.81, 2.82 [NCH_3, isomers (*E*) and (*Z*)], 2.83, 2.86 [NCH_3, isomers (*E*) and (*Z*)], 7.10–7.50 (m, 9H, aromatic H). – ^{13}C NMR (75 MHz, 294 K): δ = 21.42 (*p*-CH_3), 35.22 (NCH_3), 36.83 (NCH_3), 128.10, 128.88, 163.94 (C=N), 169.37 [O=*C*-N(CH_3)$_2$]. – ^{13}C NMR (228 K): δ = 21.50, 21.54 [*p*-CH_3, isomers (*E*) and (*Z*)], 35.08, 35.10 [NCH_3, isomers (*E*) and (*Z*)], 36.79, 36.82 [NCH_3, isomers (*E*) and (*Z*)], 127.54, 127.74, 127.98, 128.18, 128.75, 128.94, 129.54, 129.60, 129.85, 131.37, 132.61, 134.43, 135.59, 137.51, 140.32, 142.13, 163.94 and 163.97 [C=N, isomers (*E*) and (*Z*)], 169.50 and 169.85 [O=*C*-N(CH_3)$_2$, isomers (*E*) and (*Z*)]. – IR (KBr): $\tilde{\nu}$ = 2922, 1650, 1577, 1492, 1445, 1386, 1315, 1296, 1269, 1188, 1136, 1059, 996, 955, 829, 755, 700 cm^{-1}. – MS; *m/z* (%): 266 (6) [M$^+$], 235 (1), 222 (100), 207 (1), 194 (6), 189 (5), 179 (5), 165 (2), 152 (1), 133 (1), 119 (2), 105 (1), 91 (8), 86 (7), 77 (7), 72 (12), 65 (5), 51 (3), 44 (2). – $C_{17}H_{18}N_2O$ (266.2): calcd. C 76.69, H 6.76, N 10.53; found C 76.85, H 6.84, N 10.50. – Mol. mass: calcd. 266.1418; found 266.1414 (HRMS).

2-Dimethylamino-1-dimethylcarbamoyl-4,4-diphenyl-1,3-diaza-1,3-butadiene (**9a**): Yield: 1.45 g (45%), m.p. 110–111 °C. R_f 0.06. – ^{1}H NMR (300 MHz, 294 K): δ = 2.31 (s, 3H, NCH_3), 2.63 (s, 3H, NCH_3), 2.92 [s, 6H, N(CH_3)$_2$], 7.30–7.50 (m, 10H, aromatic H). – ^{13}C NMR (75 MHz, 294 K): δ = 35.23 (NCH_3), 36.73 (NCH_3), 37.13 [N(CH_3)$_2$], 128.04, 128.28, 129.14, 129.14, 130.04, 130.56, 132.43, 137.22, 159.69 (C=N), 162.51 (C=N), 169.15 [O=*C*-N(CH_3)$_2$]. – IR (KBr): $\tilde{\nu}$ = 2922, 1638, 1628, 1572, 1491, 1446, 1367, 1318, 1283, 1178, 1141, 1031, 966, 952, 924, 862, 823, 779, 762, 696, 683 cm^{-1}. – MS; *m/z* (%): 322 (7) [M$^+$], 278 (100), 208 (3), 180 (3), 165 (7), 104 (2), 77 (6), 72 (13). – $C_{19}H_{22}N_4O$ (322.2): calcd. C 70.80, H 6.83, N 17.39; found C 71.03, H 6.90, N 17.35. – Mol. mass: calcd. 322.1792; found 322.1788 (HRMS).

2-Dimethylamino-1-dimethylcarbamoyl-4-(p-methylphenyl)-4-phenyl-1,3-diaza-1,3-butadiene (**9b**): Yield: 0.35 g (10%), m.p. 107–108 °C. R_f 0.05. – ^{1}H NMR (300 MHz, 294 K): δ = 2.38 (broad s, 6H, *p*-CH_3, NCH_3), 2.68 (s, 3H, NCH_3), 2.96 [s, 6H, N(CH_3)$_2$], 7.15–7.50 (m, 9H, aromatic H). – ^{13}C NMR (75 MHz, 294 K): δ = 21.46 (*p*-CH_3), 35.23 (NCH_3), 36.50 (NCH_3), 37.14 [N(CH_3)$_2$], 127.91, 128.20, 128.73, 128.98, 129.94, 130.32, 159.81 (C=N), 162.57 (C=N); 169.13 [O=*C*-N(CH_3)$_2$]. – IR (KBr): $\tilde{\nu}$ = 2923, 1636, 1508, 1458, 1262, 1179, 1142, 1033, 799, 694 cm^{-1}. – MS; *m/z* (%): 336 (0.5) [M$^+$], 292 (100), 264 (0.5), 222 (4), 181 (5), 165 (4), 152 (1), 119 (1), 91 (3), 77 (2), 72 (15). – $C_{20}H_{24}N_4O$ (336.3): calcd. C 71.43, H 7.14, N 16.67; found C 71.60, H 7.24, N 16.70. – Mol. mass: calcd. 336.1948; found 366.2008.

General Procedures for the Synthesis of C-Acylimines (**11**): a) A solution of benzil (6.3 g, 0.03 mol) and the amine (0.03 mol) in diethyl ether was kept over 4-Å molecular sieves at 30 °C. The course of the reaction was monitored by TLC. The reaction time was ca. 72 h. Diethyl ether was removed by evaporation and the product was isolated by crystallization from *n*-hexane.

b) A mixture of the benzil (6.3 g, 0.03 mol) and the aniline derivative (0.03 mol) was refluxed in 80 ml of benzene with continuous removal of water by azeotropic distillation. The course of the reaction was monitored by TLC. After ca. 15 h benzene was separated in a rotary evaporator and the product was isolated by column chromatography or by crystallization from *n*-hexane.

c) To a 0.5-l four-necked flask fitted with stirrer, reflux condenser, thermometer, and dropping funnel 250 ml of solvent (benzene or diethyl ether), benzil (6.3 g, 0.03 mol) and the aniline derivative (0.03 mol) were added. Then a solution of $TiCl_4$ (2.8 g, 0.015 mol) in 20 ml of benzene was added to the reaction mixture over a 20–60 min period. The temperature was kept between 0 and 10 °C during this addition. When the $TiCl_4$ addition was complete, the mixture was stirred at room temp. for 20 h. The reaction mixture was filtered and the solvent was removed. The residual product was crystallized from hexane or purified by column chromatography.

1,2-Diphenyl-2-isopropyliminoethanone (**11a**): Procedure (a). Yield: 4.52 g (60%), m.p. 86–87 °C (ref.[27] 86–88 °C). R_f = 0.4.

1,2-Diphenyl-2-phenylimino-ethanone (**11b**): Procedure (b). Yield: 0.85 g (10%). Procedure (c). Yield: 2.57 g (30%), m.p. 98–100 °C (ref.[28] 103–106 °C). R_f = 0.8.

2-[(4-methylphenyl)imino]-1,2-diphenylethanone (**11c**): Procedure (b). Yield: 3.14 g (35%), m.p. 85–86 °C. R_f = 0.78. – ^{1}H NMR (200 MHz): δ = 2.17 (s, 3H, *p*-CH_3), 6.80–7.00 (4H, aromatic H), 7.33–8.00 (10H, aromatic H). – ^{13}C NMR (75 MHz): δ = 20.50 (CH_3), 120.33, 127.82, 128.52, 128.60, 128.81, 129.05, 129.65, 131.26, 132.81, 134.01, 134.66, 146.36, 161.21 and 165.61 [C=N, isomer (*E*) and (*Z*)], 197.83 (C=O). – MS; *m/z* (%): 299 (36) [M$^+$], 194 (100), 105 (1), 91 (44), 65 (46). – $C_{21}H_{17}NO$ (299.4): calcd. C 84.28, H 5.68, N 4.68; found C 84.57, H 5.60, N 4.71.

2-[(4-Chlorphenyl)imino]-1,2-diphenylethanone (**11d**): Procedure (c). Yield: 2.78 g (29%), m.p. 88–90 °C. R_f 0.70. – ^{1}H NMR (200 MHz): δ = 6.40–6.90 (4H, aromatic H), 7.00–8.05 (10H, aromatic H). – ^{13}C NMR (75 MHz): δ = 121.31, 121.66, 127.98, 128.22, 128.35, 128.53, 128.83, 129.06, 129.69, 130.20, 130.41, 131.41, 131.85, 132.82, 134.27, 134.39, 134.68, 137.03, 162.10 and 166.81 [C=N, isomer (*E*) and (*Z*)], 196.08 (C=O). – MS; *m/z* (%): 319 (2) [M$^+$], 214 (100), 111 (15), 105 (1), 75 (10), 51 (3). – $C_{20}H_{14}ClNO$ (319.8): calcd. C 75.23, H 4.39, N 4.39; found C 75.49, H 4.32, N 4.45.

2-[(3-Nitrophenyl)imino]-1,2-diphenylethanone (**11e**): Procedure (c). Yield: 2.38 g (24%), m.p. 98–101 °C. R_f 0.77. – ^{1}H NMR (200 MHz): δ = 7.15–7.95 (14H, aromatic H). – ^{13}C NMR (75 MHz):

δ = 115.20, 118.92, 126.09, 128.17, 128.84, 129.32, 129.69, 130.09, 132.30, 132.75, 134.05, 134.17, 134.71, 148.06, 150.17, 168.41 (C=N), 195.86 (C=O). – MS; *m/z* (%): 330 (1) [M$^+$], 225 (100), 195 (6), 179 (24), 105 (2), 76 (20), 50 (4). – $C_{20}H_{14}N_2O_3$ (330.3): calcd. C 72.72, H 4.24, N 8.48; found C 72.50, H 4.17, N 8.50.

General Procedure for the Synthesis of 1:1 Adducts from Compounds **11** *and* **2**: To a solution of a *C*-acylimine derivative (**11a–e**) (3.3 mmol) in 20 ml of dry benzene, dimethylcyanamide (0.23 g, 3.3 mmol) was added. Then a solution of $TiCl_4$ (0.67 g, 3.3 mmol) in 20 ml of dry benzene was added dropwise to the well-stirred reaction mixture. The mixture was stirred at room temp. for 3 h, heated at 60°C for 1.5 h, cooled, and the benzene was evaporated. to the residue, titanium complexes of the products, about 20 ml of water was added. The mixture was alkalized with 5% NaOH and extracted several times with chloroform. The products were purified by preparative TLC and crystallized from petroleum ether (40–60°C).

1-Dimethylcarbamoyl-2,3,4-triphenyl-1,4-diaza-1,3-butadiene (**15b**): Yield: 0.94 g (80%), m.p. 100–101°C. R_f 0.40. – ^{1}H NMR (300 MHz): δ = 2.41 (3H, s, NCH_3), 2.76 (3H, s, NCH_3), 6.90–7.8 (m, 15H, aromatic H). – ^{13}C NMR (75 MHz): δ = 35.22 (NCH_3), 36.27 (NCH_3), 119.65, 128.40, 128.46, 128.50, 128.72, 128.80, 129.00, 130.99, 132.18, 135.78, 136.89, 150.05, 162.37 (C=N), 165.66 (C=N), 169.69 [O=*C*-N(CH_3)$_2$]. – IR (KBr): $\tilde{\nu}$ = 1654, 1616, 1576, 1447, 1388, 1263, 1153, 775, 695, 636 cm^{-1}. MS; *m/z* (%): (direct inlet system) 355 (12) [M$^+$], 312 (4), 250 (4), 180 (100), 175 (1), 103 (4), 77 (36), 72 (21); (GLC/MS) 355 (100) [M$^+$], 327 (72), 283 (56), 250 (39), 235 (4), 223 (32), 192 (8), 180 (39), 161 (41), 147 (95), 132 (50), 120 (39), 104 (7), 77 (49), 51 (12), 44 (6). – $C_{23}H_{21}N_3O$ (355.2): calcd. C 77.72, H 5.95, N 11.82; found C 77.40, H 6.00, N 11.90. – Mol. mass: calcd. 355.1683; found 355.1686 (HRMS).

1-Dimethylcarbamoyl-4-(p-methylphenyl)-2,3-diphenyl-1,4-diaza-1,3-butadiene (**15c**): Yield: 1.04 g (85%), m.p. 54–55°C. R_f 0.36. – ^{1}H NMR (200 MHz): δ = 2.22 (s, 3H, *p*-CH_3), 2.40 (s, 3H, NCH_3), 2.75 (s, 3H, NCH_3), 6.80–7.00 (4H, aromatic H), 7.34–7.83 (10H, aromatic H). – ^{13}C NMR (75 MHz): δ = 20.84 (*p*-CH_3), 35.19 (NCH_3), 36.21 (NCH_3), 119.72, 128.35, 128.43, 128.71, 128.80, 129.06, 130.84, 132.13, 134.13, 135.75, 137.03, 147.54, 162.43 (C=N), 165.23 (C=N), 169.89 [O=*C*-N(CH_3)$_2$]. – IR (KBr): $\tilde{\nu}$ = 1654, 1622, 1578, 1507, 1447, 1393, 1148, 1023, 690 cm^{-1}. – MS; *m/z* (%): (direct inlet system) 369 (13) [M$^+$], 325 (3), 194 (100), 180 (45), 175 (1), 103 (3), 91 (20), 77 (14), 72 (20), 65 (9); (GLC/MS) 369 (68) [M$^+$], 341 (70), 297 (52), 264 (36), 237 (32), 221 (10), 194 (24), 180 (22), 161 (100), 146 (55), 134 (67), 118 (18), 77 (25). – $C_{24}H_{23}N_3O$ (369.4): calcd. C 78.02, H 6.27, N 11.37; found C 77.88, H 6.20, N 11.40. – Mol. mass: calcd. 369.1839; found 369.1824 (HRMS).

4-(p-Chlorophenyl)-1-dimethylcarbamoyl-2,3-diphenyl-1,4-diaza-1,3-butadiene (**15d**): Yield: 1.05 g (82%), m.p. 115–118°C. R_f 0.36. – ^{1}H NMR (200 MHz): δ = 2.58 (s, 3H, NCH_3), 2.74 (s, 3H, NCH_3), 6.91–7.11 (4H, aromatic H), 7.34–7.81 (m, 10H, aromatic H). – ^{13}C NMR (75 MHz): δ = 35.24 (NCH_3), 36.50 (NCH_3), 121.17, 127.11, 128.31, 128.50, 128.69, 128.78, 129.86, 131.24, 132.41, 135.33, 136.64, 148.60, 162.27 (C=N), 166.06 (C=N), 169.71 [O=C-N(CH_3)$_2$]. – IR (KBr): $\tilde{\nu}$ = 1654, 1616, 1577, 1490, 1394, 1262, 1152, 1012, 692 cm^{-1}. – MS; *m/z* (%): (direct inlet system) 389 (12) [M$^+$], 346 (3), 284 (3), 214 (100), 181 (3), 131 (3), 111 (18), 103 (3), 77 (7), 72 (31); (GLC/MS) 389 (51) [M$^+$], 361 (67), 317 (25), 312 (30), 284 (22), 257 (18), 214 (10), 181 (100), 166 (78), 154 (44), 118 (4), 77 (20), 44 (4). – $C_{23}H_{20}ClN_3O$ (389.8): calcd. C 70.86, H 5.17, N 10.78; found 389.1380. – Mol. mass: calcd. 389.1294; found 389.1380 (HRMS).

1-Dimethylcarbamoyl-4-(p-nitrophenyl)-2,3-diphenyl-1,4-diaza-1,3-butadiene (**15e**): Yield: 1.04 g (79%), m.p. 132–133°C. R_f 0.33. – ^{1}H NMR (300 MHz): δ = 2.72 (s, 3H, NCH_3), 2.79 (s, 3H, NCH_3), 7.24–7.90 (m, 14H, aromatic H). – ^{13}C NMR (75 MHz): δ = 35.46 (NCH_3), 36.80 (NCH_3), 115.13, 119.02, 125.56, 127.38, 128.43, 128.66, 128.90, 129.30, 131.79, 132.77, 134.94, 136.10, 148.24, 151.29, 162.00 (C=N), 167.85 (C=N), 169.40 [O=*C*-N(CH_3)$_2$]. – IR (KBr): $\tilde{\nu}$ = 1654, 1527, 1448, 1348, 1202, 1152, 684 cm^{-1}. – MS; *m/z* (%): (direct inlet system) 400 (10) [M$^+$], 225 (100), 175 (1), 122 (7), 103 (3), 77 (8), 72 (20); (GLC/MS) 400 (44) [M$^+$], 371 (51), 342 (25), 323 (33), 295 (42), 268 (24), 238 (6), 207 (21), 192 (100), 165 (77), 146 (40), 135 (21), 118 (25), 92 (6), 77 (32), 44 (20). – $C_{23}H_{20}N_4O_3$ (400.2): calcd. C 68.99, H 5.03, N 13.99; found C 68.67, H 4.98, N 14.01. – Mol. mass: calcd. 400.1534; found 400.1580 (HRMS).

2-Dimethylamino-1-isopropyl-4,4-diphenyl-2-imidazolin-5-one (**23**): Yield: 0.74 g (70%), m.p. 104–105°C. R_f 0.38. – ^{1}H NMR (300 MHz): δ = 1.43 [d, 6H, CH(CH_3)$_2$, *J* = 6.88 Hz], 2.86 [s, 6H, N(CH_3)$_2$], 3.98 [sept, 1H, C*H*(CH_3)$_2$], 7.23–7.55 (m, 10H, aromatic H). – ^{13}C NMR (75 MHz): δ = 19.46 [CH(*C*H_3)$_2$], 40.65 [N(CH_3)$_2$], 47.35 [*C*H(CH_3)$_2$], 76.34 (C-sp^3 of imidazoline ring), 127.20, 127.22, 128.17, 128.80, 129.01, 129.90, 134.89, 141.65, 161.71 (C=N), 182.88 (C=O). – IR (KBr): $\tilde{\nu}$ = 1720, 1624, 1447, 1381, 1294, 1243, 1057, 702 cm^{-1}. – MS; *m/z* (%): (direct inlet system) 321 (40) [M$^+$], 278 (50), 251 (2), 244 (7), 236 (36), 221 (14), 216 (9), 208 (7), 193 (7), 180 (16), 165 (18), 146 (18), 133 (9), 118 (21), 105 (100), 77 (25), 71 (33), 43 (10); (GLC/MS) 321 (100) [M$^+$], 278 (67), 244 (11), 236 (50), 221 (33), 207 (27), 202 (26), 180 (18), 165 (43), 133 (15), 118 (34), 104 (16), 71 (47), 43 (7), 44 (4). – $C_{20}H_{23}N_3O$ (321.3): calcd. C 74.74, H 7.21, N 13.07; found C 74.42, H 7.11, N 13.04. – Mol. mass: calcd. 321.1840; found 321.1843 (HRMS).

X-Ray Diffraction Analysis of **23**: The data of a crystal of **23** with the approximate dimensions 0.41 × 0.30 × 0.11 Å^3 were obtained with a Nicolet R3m/V four-circle diffractometer (Mo-K_α radiation, graphite monochromator) at 298 K. Cell dimensions were refined from diffractometer angles of 50 reflections in the 2Θ range 10–20°. Cell constants: a = 16.189(4), b = 8.009(2), c = 15.735(3) Å, α = 90, β = 115.582(10), γ = 90°. V = 1840.0(11) Å^3, space group *Cc* (Nr. 9), *Z* = 4, ρ_{calc} = 1.157 g/cm^3, absorption coefficient μ = 0.07 mm^{-1}, $2\Theta_{max}$ = 45°, 2379 unique intensities, of which 1204 ($F_o \geq 4\sigma(F_o)$) were observed, measured in 2Θ:ω-scan technique. The structure was solved by using direct methods and refined on *F* by using SHELXTL-Plus (Vers. 4.2). 194 parameters, anisotropic displacement parameters for all atoms except hydrogen atoms, groupewise isotropic displacement parameters all hydrogen atoms, treated as rigid groups. R = 0.0697, R_w = 0.0701, $w^{-1} = \sigma^2(F_o) + 0.004 \cdot F_o^2$, maximum residual electron density 0.35 e/Å^3. Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-405388.

[1] M. Mazik, R. Boese, R. Sustmann, *Tetrahedron* **1996**, *52*, 3939–3945.
[2] N. A. Gol'dberg, V. G. Gulov, *Khim. Nauk. Prom.* **1959**, *4*, 138.
[3] V. G. Golov, V. G. Vodop'yanov, Yu. J. Mushin, *Zh. Org. Khim.* **1971**, *7*, 2104–2108.
[4] B. I. Sukhorukov, A. I. Finkel'shtein, *Optika i Spektroskopiya* **1960**, *9*, 46–50.
[5] A. Miller, *J. Org. Chem.* **1984**, *49*, 4072–4074.

[6] A. Alberola, C. Andre's, A. G. Ortega, R. Pedrosa, M. Vicente, *Synth. Commun.* **1987**, *17*, 1309–1314.
[7] A. F. Cockerill, A. Deacon, R. G. Harrison, D. J. Osborne, D. M. Prime, W. J. Ross, A. Todd, J. P. Verge, *Synthesis* **1976**, 591–593.
[8] G. Crank, M. J. Foulis, *J. Med. Chem.* **1971**, *14*, 1075–1077.
[9] Yu. Sharanin, *Zh. Org. Khim.* **1980**, *16*, 2185–2188.
[10] V. Wolf, P. Hauschildt, W. Coop, *Chem. Ber.* **1962**, *95*, 2419–2423.
[11] A. Lawson, *J. Chem. Soc.* **1956**, 307–310.
[12] G. C. Lancini, E. Lazzari, *J. Heterocycl. Chem.* **1966**, *3*, 152–154.
[13] M. E. Hermes, R. A. Braun, *J. Org. Chem.* **1966**, *31*, 2568–2571.
[14] K. Burger, R. Simmerl, *Synthesis* **1983**, *3*, 237–238.
[15] K. Burger, R. Simmerl, *Liebigs Ann. Chem.* **1984**, 982–990.
[16] W. Zielinski, M. Mazik *Heterocycles* **1994**, *38*, 375–382.
[17] J. Sauer, R. Sustmann, *Angew. Chem.* **1980**, *92*, 773–801; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 779–807.
[18] H. W. Heine, B. J. Barchiesi, E. A. Williams, *J. Org. Chem.* **1984**, *49*, 2560–2565.
[19] A. Mc Killop, T. S. B. Sayer, *J. Org. Chem.* **1976**, *41*, 1079–1080.
[20] R. Gompper, K. P. Paul, unpublished observation, see R. Gompper, *Angew. Chem.* **1969**, *81*, 348–363; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 312–327.
[21] M. Felderhoff, Ph. D. Thesis, Universität Essen **1993**.
[22] R. Sustmann, M. Felderhoff, *Heterocycles* **1995**, *40*, 1027–1034.
[23] Y. Miyamoto, Ch. Yamazaki, *J. Heterocycl. Chem.* **1994**, *31*, 1445–1448.
[24] P. Molina, A. Tarraga, M. J. Lidon, *J. Chem. Soc., Perkin Trans. 1* **1990**, 1727–1731.
[25] E. Schaumann, S. Grabley, *Liebigs Ann. Chem.* **1981**, 290–305.
[26] G. L. Kenyon, G. L. Rowley, *J. Am. Chem. Soc.* **1971**, *93*, 5552–5560.
[27] W. B. Wheatley, W. E. Fitzgibbon, L. C. Cheney, *J. Org. Chem.* **1953**, *18*, 1564–1566.
[28] P. L. Julian, E. W. Meyer, A. Magnani, W. Cole, *J. Am. Chem. Soc.* **1945**, *67*, 1203–1211.

[96082]