Alkoxy-Substituted *N*-Acyliminium Salts – Synthesis, Structure, Reactivity☆

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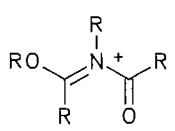
Alkylation of aliphatic imides **5** by use of oxonium salts takes place at one of the carbonyl oxygen atoms, leading to alkoxy-substituted *N*-acyliminium salts **1**. These new reactive intermediates are fully characterized by IR, ^{1}H- and ^{13}C-NMR spectroscopy and X-ray analysis. The stereochemical and dynamical properties of the model compounds **6**, **7** are investigated by ab initio model calculations (MP2/6-31G*//6-31G*). The barrier of rotation around the central C–N bond in **6** is calculated to 10.2 kcal/mol. The reaction with CH acids **8** yields new types of enamides (**9**); primary amines **10** are converted to *N*-acylamidines **11**. Primary amidines **12** react with **1** to form new 1,3-diazabutadiene derivatives **13**. The reaction with primary amides **14** gives *N,N'*-bisacylamidines **15**. With primary *N*-acylamidines **16** new doubly azavinylogous imides **17** (1-oxa-3,5-diazahexatriene derivatives) are formed.

N-Acyliminium salts are valuable electrophilic reactive intermediates; they have found widespread use in organic synthesis, mainly in heterocyclic and natural product chemistry[1,2]. In comparison with iminium salts[3], they are characterized by an enhanced electrophilicity, resulting from the presence of the electron-withdrawing acyl group attached to the iminium nitrogen atom. Therefore, *N*-acyliminium salts are usually not isolated, but generated and trapped in situ[1,2]. Their structural and dynamic behavior in solution is known from spectroscopic investigations. Recently, X-ray studies of sufficiently stable derivatives have been reported[4,5]. The electronic structure and dynamics in the gas phase were studied by ab initio calculations, indicating the preference of a planar *s-cis* conformation and a barrier of rotation for the C–N bond of 8.7 kcal/mol, which is high compared to that of butadiene, but surprisingly low in comparison with amides[6].

In this study we report on the synthesis, structural elucidation and reactions of alkoxy-substituted *N*-acyliminium salts **1**; to our knowledge, there have been no previous reports on such systems in the literature. In these new salts **1**, the C=NR–C=O skeleton of *N*-acyliminium salts is enlarged by an additional donor function, which will lower the electrophilicity at the iminium carbon atom ("push-pull iminium salts"), but will also serve as a potential leaving group. In this sense, the salts **1** may be understood as synthetic equivalents of the dications **I**, indicating considerable synthetic potential. The synthesis and isolation of another species with a leaving group, an α-chloro *N*-acyliminium salt, derived from phthalimide, have been reported very recently[7].



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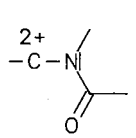
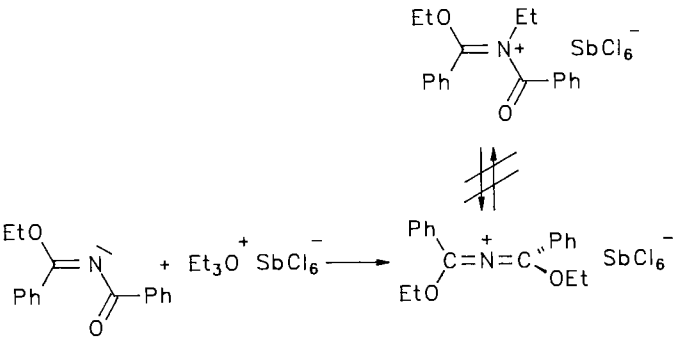


I

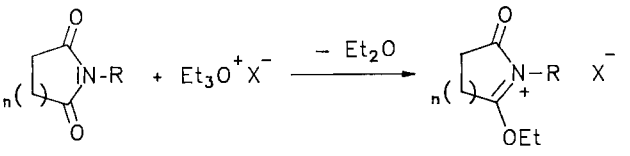
Imides **5** or alkoxy-substituted *N*-acylimines **2** (alkyl *N*-acylimidates) seemed to be the ideal precursors of these new salts. However, alkylation of *N*-acylimines **2** using oxonium salts **3** offers no synthetic route to the salts **1**; instead, *O*-alkylation is observed, yielding the unusually structured 1,3-dialkoxy-2-azapropenylium salts **4**, which do not rearrange to the corresponding *N*-acyliminium salts[8,9].



2 **3a** **4**

Contrary to this the cyclic imides **5**[10–12], when treated with oxonium salts **3** in dichloromethane for 24–66 hours at room temperature, form after very careful addition of diethyl ether hygroscopic, well-shaped crystals of the salts **1** growing at the interface of the two solvent layers. After completion of the crystallization they are collected in 50–60% yield. Aromatic imides like phthalimide are unreactive under these conditions.

According to IR-, ^{1}H- and ^{13}C-NMR spectroscopic data the alkylation products have the expected structure of the cyclic alkoxy-substituted *N*-acyliminium salts **1**; isomeric 1,3-dialkoxy-2-azapropenylium structures (like **4**) can be excluded[8,9].



5 **3** **1aa-1cb**

5	n	R
a	1	Me
b	1	Et
c	2	Et

3	X
a	$SbCl_6$
b	BF_4

1	n	R	X
aa	1	Me	$SbCl_6$
ab	1	Me	BF_4
ba	1	Et	$SbCl_6$
ca	2	Et	$SbCl_6$
cb	2	Et	BF_4

The IR spectra are dominated by strong absorptions of the C=O valences at 1770–1810 cm^{-1}; the C=N bonds give rise to characteristic resonances at 1560–1660 cm^{-1} with the more strained five-membered ring systems showing the higher values. Two sets of ethyl signals in the NMR spectra of **1ba** are a direct proof of the postulated *O*-alkylation (C_S symmetry). Even at higher temperature (100°C) there is no indication of an ethyl migration from nitrogen to oxygen.

The alkylation of the imides **5** increases their electrophilicity considerably. This is well documented by the shift of the ^{13}C resonance of the iminium carbon atom of salt **1aa** at $\delta = 193.9$ (imides **5**: $\delta = 172-177$); the assignment for this line was achieved by a HOESY experiment, giving Nuclear Overhauser enhancements between the *O*-ethyl protons and the iminium carbon signal at $\delta = 193.9$ (for NMR data of *N*-acyliminium salts, see ref.[13]). The signal for the other carbonyl carbon atom remains at $\delta = 175.6$.

Configuration and conformation of salt **1ba** in the crystalline state were determined by X-ray crystallography (Figure 1)[14]. **1ba** crystallizes in the monoclinic space group $P2_1/c$ with four formula units in the unit cell. Hence, the postulated *N*-acyliminium structure of **1ba** is well established. Its heterobutadiene O=C–NR=C–OR subunit shows an *all-trans* arrangement with twisted ethyl groups. The electronic properties of the planar O=C–NR=C–OR system are reflected by the corresponding bond lengths (O=C: 1.184, C–N: 1.439, N=C: 1.308, C–O: 1.262 Å). The C–N bond linking the C=O and C=N part is relatively short, indicating strong conjugative interaction of these two π systems. In acyclic systems, these bonds were found to be considerably longer (1.49–1.50 Å), but these cations prefer nonplanar C=NR–C=O structures[4,5]. On the other hand, the alkoxy substituent at the iminium carbon atom of **1ab** contributes significantly to a stabilization of the positive charge in this part of the molecule as derived from the relatively long C=N and very short C–O bond. In *N*-acyliminium salts without hetero substituent, the corresponding C=N bond length was determined to 1.287 Å[4].

There are no close contacts between chlorine atoms of the anion and ethyl hydrogen atoms of the cation ($r_{H-Cl} > 2.9$ Å).

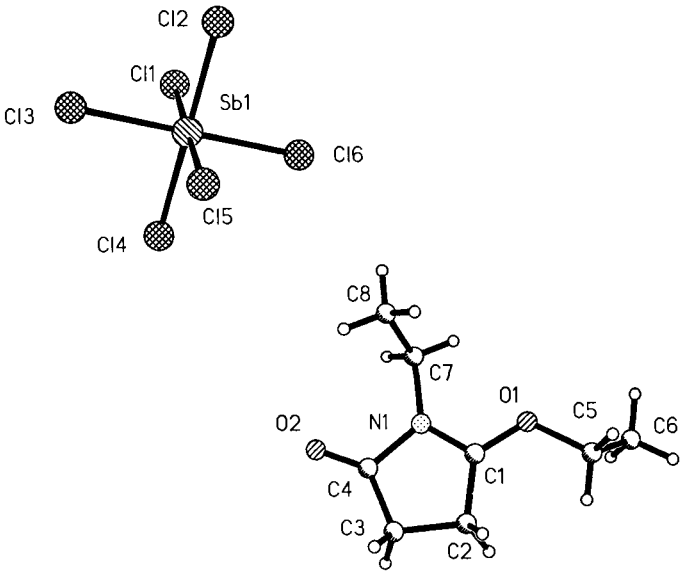


Figure 1. XS-molecular plot for **1ba** with crystallographic numbering (SHELX-PLUS[26]); bond lengths [Å]: C(1)–O(1) 1.262(6), N(1)–C(4) 1.439(9), O(1)–C(5) 1.483(8), N(1)–C(7) 1.483(7), O(2)–C(4) 1.184(10), C(1)–C(2) 1.477(7), N(1)–C(1) 1.308(7), C(2)–C(3) 1.505(12); bond angles [°]: O(1)–C(1)–N(1) 118.2(5), N(1)–C(1)–C(2) 113.7(5), O(1)–C(5)–C(6) 108.4(6), C(1)–N(1)–C(4) 109.8(5), O(2)–C(4)–N(1) 120.2(8), C(4)–N(1)–C(7) 123.3(5); torsional angles [°]: N(1)–C(1)–C(2)–C(3) 0.4(6), C(4)–N(1)–C(1)–C(2) 0.0(6), C(1)–O(1)–C(5)–C(6) 130.9(6), C(5)–O(1)–C(1)–N(1) 180.0(5), C(1)–N(1)–C(7)–C(8) –104.8(6), C(7)–N(1)–C(4)–C(3) 179.7(5), C(1)–N(1)–C(4)–O(2) 179.7(6)

Quantum-chemical ab initio Calculations

In order to better understand the conformational and dynamic properties and to rationalize the crystallographic and spectroscopic results quantum-chemical model calculations were performed. The 6-31G* basis set[15] of the GAUSSIAN 92 program[16] was used throughout. Effects of electron correlation were estimated by using second-order Møller-Plesset theory (MP2)[17]. All molecules were completely geometry-optimized within C_S symmetry. Alkyl groups at nitrogen and oxygen were replaced by hydrogen atoms; in the following section, results for the experimentally not easily accessible hydroxy-substituted *N*-acyliminium ions **6** and **7** (*O*-protonated diformylamine) are discussed (Table 1). The numbering follows the relative MP2 energies, on which the following discussion is based.

Eight planar conformations are possible for the ion **6**; according to frequency analyses, they all correspond to minima on the potential energy hyperface (Figure 2). Lowest in energy is structure **6a**, where an intramolecular hydrogen bridge leads to additional stabilization ($E_{rel} = -2.72$ kcal/mol); this form is therefore no model for the alkoxy derivatives **1**. Among the other conformers, **6b** is best in energy and taken as the reference structure for all other forms

Table 1. MP2/6-31G*//6-31G* results for the $C_2H_4NO_2^+$ conformers **6a–h** and **7a, b**: Total energies (6-31G*//6-31G* and MP2/6-31G*//6-31G*) [a.u.], relative energies [kcal/mol], torsional angles [°], and dipole moments [Debye]

Nr.	Θ_1[a]	Θ_2[a]	Θ_3[a]	E_{tot} 6-31G*//6-31G* [a.u.]	E_{rel} [kcal/mol]	Dipolmoment [Debye]	E_{tot} MP2/6-31G*//6-31G* [a.u.]	E_{rel} [kcal/mol]
6a	0.	0.	0.	-281.98996	-1.71	5.038	-282.73658	-2.72
6b	0.	180.	180.	-281.98723	0.00	3.913	-282.73224	0.00
6c	180.	0.	180.	-281.98106	3.87	7.390	-282.72754	2.89
6d	180.	180.	180.	-281.98036	4.31	6.828	-282.72718	3.17
6e	0.	180.	0.	-281.98069	4.10	5.472	-282.72569	4.11
6f	0.	0.	180.	-281.97862	5.40	7.010	-282.72564	4.14
6g	180.	180.	0.	-281.97624	6.90	4.299	-282.72269	5.99
6h	180.	0.	0.	-281.97138	9.95	4.043	-282.71807	8.89
7a	180.	180.	180.	-358.92768	0.00	6.136	-359.92663	0.00
7b	180.	180.	0.	-358.92561	1.41	4.637	-359.92403	1.63

[a] $\Theta_1 = \Theta_{C=N-C=O}$, $\Theta_2 = \Theta_{O-C=N-C}$, $\Theta_3 = \Theta_{H-O-C=N}$.

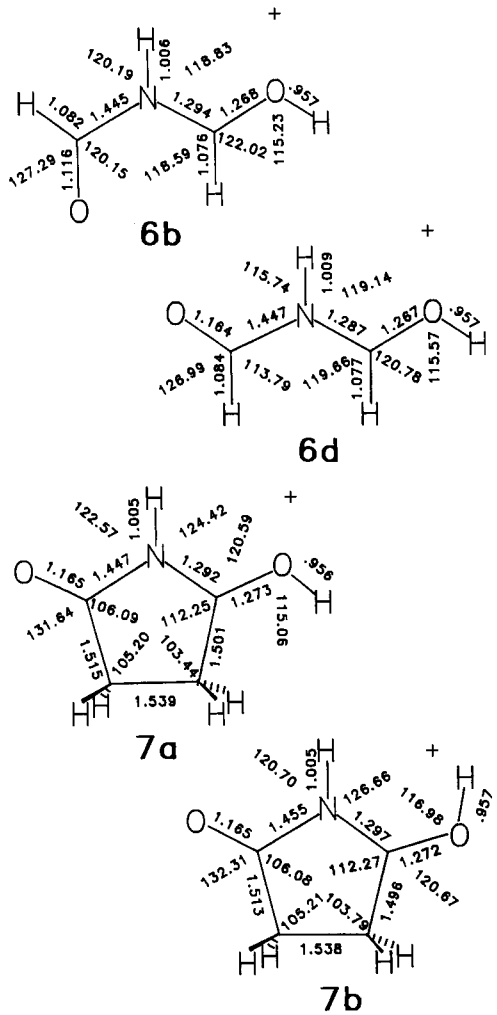


Figure 2. Ab initio-optimized structures of the conformers **6b**, **d** and **7a**, **b**. Bond lengths [Å], bond angles [°], torsional angles [°], and relative energies (E_{rel}) [kcal/mol] (MP2/6-31G*//6-31G* ab initio results)

(E_{rel} = 0.00 kcal/mol) (Figure 2). It also has the lowest calculated dipole moment in this series. In comparison with the *s-trans* forms (**6c,d,g,h**), the *s-cis* arrangement of the C=O and C=N units is favorable (**6a,b,e,f**), in a manner similar to that of simple *N*-acyliminium ions[6,18]. A hydroxy group showing *s-trans* conformation seems also to be a preferred subunit (**6b,c,d,f**), compared to an *s-cis* hydroxy group (**6a,e,g,h**). Stereoelectronic effects and bond dipole compensations govern the relative energies of these species. The energy richest isomer **6h** suffers additionally from steric 1,6-repulsions between two hydrogen atoms.

To study the dynamic properties of **6** we also simulated the rotation around the C–N bond from **6b** to **6d** by a stepwise fixing of the C=N–C=O torsional angle and otherwise complete geometry relaxation (Figure 3). The barrier of activation for this process is calculated to 10.2 kcal/mol, which is higher by 3.2 kcal/mol than in the unsubstituted *N*-acyliminium ion[19] (see also ref.[6,18]); since the HO–CH=NH– moiety is a more powerful electron donor than the simple H_2C=NH– group, a stronger interaction between both π systems is expected, raising the barrier of rotation (ground-state stabilization). In hydroxy-substituted *N*-acylimines[19,20], the neutral analog to **6** without a nitrogen substituent, a barrier of 3.7 kcal/mol is calculated[19], indicating the pre-eminent influence of the nitrogen lone pair on the energy of the transition state in these amide-type molecules. Similar effects of protonation on the rotational barrier of *N*-formylmethyleneamine were observed by Wiberg et al.[21].

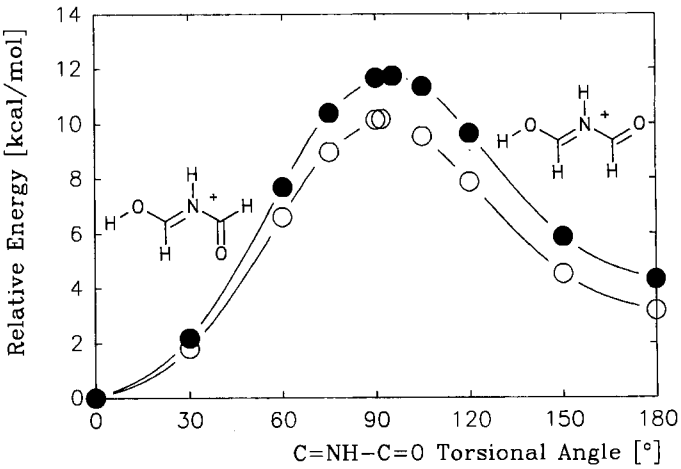


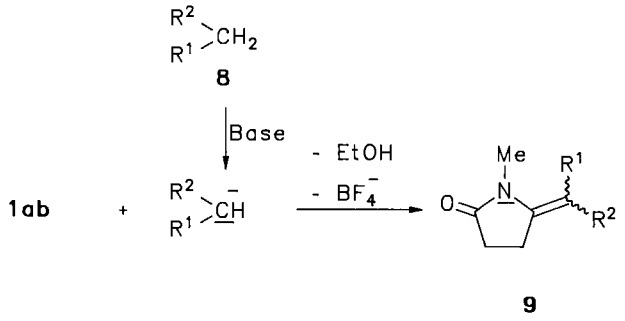
Figure 3. Calculated energies [kcal/mol] for the interconversion of **6b** to **6d**, depending on the C=NH–C=O torsional angle [°]. ●–● 6-31G*//6-31G*, ○–○ MP2/6-31G*//6-31G*

The cations **7** are model compounds, which are more closely related to the experimentally studied salts **1** than the model ions **6**. In Figure 2 the calculated bond parameters for **7a** are given; **7a** is the direct analogue to **1ba**, for which the crystal structure was determined (vide supra). A comparison with structure **6b** shows, that in the cations **1** the energy-lowest conformation (*s-cis*) cannot be realized, but an additional strain of ca. 3 kcal/mol (as in **6d**) is operative. The corresponding *s-cis* hydroxy conformer **7b** is only 1.6

kcal/mol higher in energy, whereas **6g** is 2.8 kcal/mol more energy-rich than **6d**.

Reactivity of Alkoxy-Substituted *N*-Acyliminium Salts

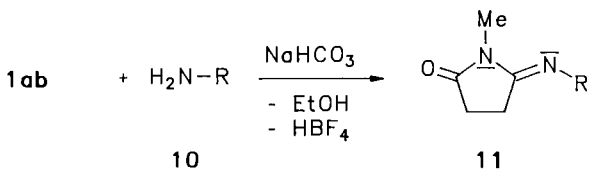
N-Acyliminium salts without an alkoxy group at the iminium carbon atom are valuable electrophilic reagents for C–C bond formation[1,2]; the intramolecular addition to aromatic and heterocyclic systems is often the key step in alkaloid syntheses[2]. However, similar as with iminium salts **3**, the addition of metallated carbon nucleophiles (lithium alkyls, Grignard compounds) is difficult because of solubility problems and side reactions occurring in these cation-anion combination reactions. Much easier to perform are reactions of the salts **1** with C–H acids **8** in the presence of sterically hindered bases (Hünig bases[22]). With malononitrile (**8a**) and ethyl cyanoacetate (**8b**) at room temperature an immediate reaction with the formation of **9a** and **9b** is observed. With the less reactive diethyl malonate (**8c**) separate deprotonation with *n*-butyllithium and subsequent reaction with **1** in a heterogeneous mixture are recommended.



8,9	R^1	R^2
a	CN	CN
b	CN	CO_2Et
c	CO_2Et	CO_2Et

Compound **9b** was prepared earlier under much more drastic conditions[23]. Wittig reactions of imides are known in the literature, but only unstabilized ylides are sufficiently nucleophilic. Substances like **9** with two electron-withdrawing groups are not obtainable by Wittig reactions[24].

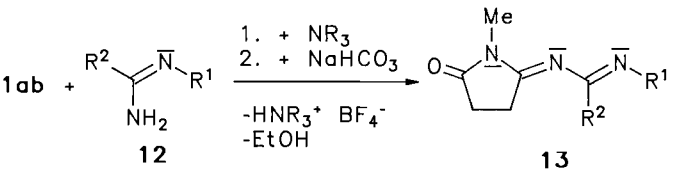
Reactions with different nitrogen nucleophiles are easy to perform and demonstrate the synthetic utility of the new



10,11	R
a	iPr
b	nBu
c	

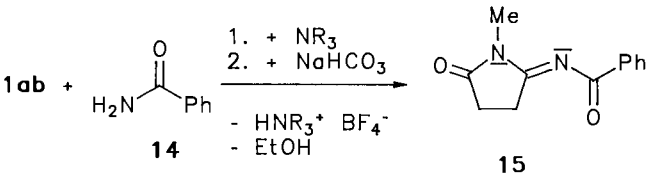
salts **1**. With primary amines **10** the corresponding cyclic *N*-acylamidines **11** are formed; again the ethoxy group serves as an efficient leaving group. Migration of the C=N double bond into the ring, giving the related α-amino enamides, has not been observed.

Similarly, amidines **12** react with **1** at the iminium center, giving rise to the formation of the 1,3-diazabutadiene derivatives **13**. In these reactions, to obtain an optimum yield the addition of an additional mole of base is essential; otherwise, half of the amidine is blocked by the proton which is liberated during the reaction.



12,13	R^1	R^2
a	Ph	Ph
b	Ph	tBu
c	tBu	Ph

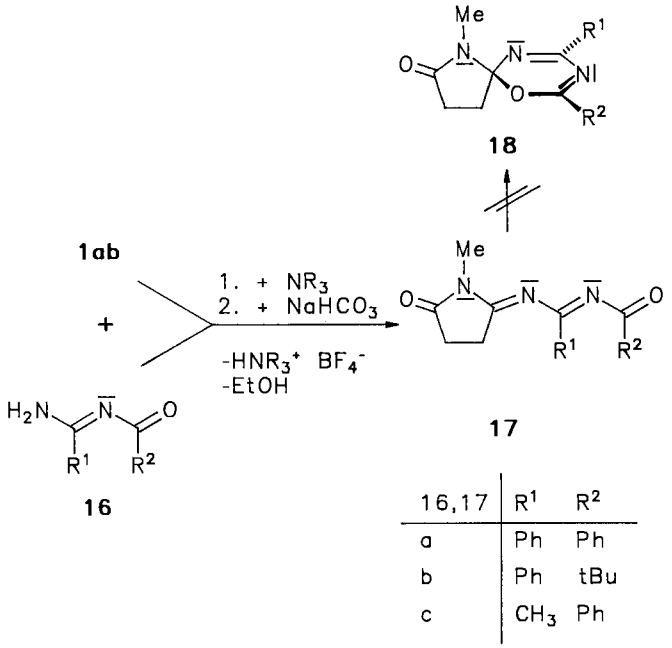
In the presence of an additional base the salts **1**, surprisingly, also react with simple primary amides **14** in spite of their low nucleophilicity at the nitrogen atom. In these reactions diacylated amidines **15** are formed. Without an additional base, no reaction occurs. Obviously, the deprotonation of the intermediate ammonium salts shifts the equilibrium towards the products.



Finally, we used *N*-acylamidines **16** as nucleophiles in condensation reactions with the salts **1**. After stirring for 10 hours at room temperature the 1-oxa-3,5-diazahexatriene derivatives **17** were isolated in 22–52% yield. Again the presence of an additional base (triethylamine) is essential. The compounds **17** are not very stable, but decompose within two weeks forming black oils even at −25°C.

Because of their electronic system (doubly azavinylogous imide) and their manifold structural possibilities the compounds **17** are of special interest to us. They are not subject to ring-chain tautomerism leading to the spiro-2*H*-1,3,5-oxadiazines **18**[25]. As the ^{13}C-NMR spectrum (Table 2) definitely confirms, quaternary signals between $\delta = 157$ and 165 can only be attributed to the open-chain forms **17**, but not to the spiro isomers **18**, for which absorptions at lower field have to be expected[25].

Thus, alkoxy-substituted *N*-acyliminium salts **1** are easily obtainable by *O*-alkylation of imides with trialkyloxonium



16,17	R^1	R^2
a	Ph	Ph
b	Ph	tBu
c	CH_3	Ph

Table 2. Selected ^{13}C-NMR data of **17a**, **b**, **c**

	δ[C=N]	δ [C=O]
17a	159.8; 162.1	176.2; 180.4
17b	157.0; 162.4	176.4; 195.0
17c	161.1; 164.2	176.3; 179.1

salts. Their reactions with amines, amidines and their derivatives provide especially good access to new types of azavinylogous systems, for which interesting chemical and structural behavior may be expected. Further work in this area is in progress.

We thank the *Fonds der Chemischen Industrie* for financial support and the *BASF AG*, Ludwigshafen, for supplying us with chemicals.

Experimental

IR: Perkin Elmer PE 298. – ^1H NMR: Bruker WM-300 (300 MHz), internal reference tetramethylsilane or solvent. – ^{13}C NMR: Bruker WM-300 (75.5 MHz), internal reference tetramethylsilane or solvent. – MS: Finnigan MAT C 312. – CHN: Perkin Elmer CHN Analysator 240. – All experiments involving *N*-acyliminium salts are carried out with the exclusion of moisture (Ar). – All solvents are rigorously dried by standard methods.

General Procedure for the Synthesis of Alkoxy-Substituted N-Acyliminium Salts **1** *by Alkylation of Imides* **5** *with Trialkyloxonium Salts* **3**: 5–10 mmol of salt **3** is added to a solution of an equimolar amount of imide **5** in 30–60 ml of dichloromethane. The generation of the *N*-acyliminium salts **1** can be monitored by IR spectroscopy of the slightly turbid reaction mixture. At 25°C the salt is formed within a period of 24–66 h; after completion of the reaction the salts **1** are precipitated.

5-Ethoxy-3,4-dihydro-1-methyl-2-oxo-2H-pyrrolium Hexachloroantimonate (**1aa**): From 4.29 g (9.8 mmol) of $Et_3O^+SbCl_6^-$ (**3a**) and 1.11 g (9.8 mmol) of *N*-methylsuccinimide (**5a**)[7] in dichloromethane (60 ml). After 24 h the reaction mixture is carefully covered with an upper layer of diethyl ether (20 ml) and kept for 12 h at −25°C. At the interface of the two layers, the salt **1aa** is formed as a microcrystalline colorless powder (2.43 g, 52%), which is collected and dried under reduced pressure, m.p. 145 C (dec.). – IR (paraffin): $\tilde{\nu} = 1810\ cm^{-1}$ (s, C=O), 1580 (s, br, C=N), 1440 (s), 1360 (s), 1280 (s), 1250 (s), 1120 (s), 1100 (s). – ^1H NMR (CD_3NO_2): δ = 1.68 (t, 3H, ^3J = 6.9 Hz, CH_2CH_3), 3.19 (ddd, ^3J = 5.8, ^3J = 2.9, $^2J_{gem.}$ = 2.9 Hz, 2H, CH_2CO), 3.31 (t, ^5J = 1.1 Hz, 3H, NCH_3), 3.61 (m, 2H, CH_2CH_2CO), 5.10 (q, ^3J = 6.9 Hz, 2H, CH_2CH_3). – ^{13}C NMR (CD_3NO_2): δ = 14.62 (CH_2CH_3), 27.36 (CH_2CH_2CO), 28.39 (NCH_3), 29.20 (CH_2CO), 78.33 (CH_2CH_3), 175.6 (C=O), 193.9 (C=N). – FD-MSD, *m/z* (%): 127 [M^+ − CH_3] (40), 113 [M^+ − C_2H_5] (100). – $C_7H_{12}Cl_6NO_2Sb$ (476.6): calcd. C 17.68, H 2.33, N 2.94; found C 17.49, H 2.52, N 2.98.

5-Ethoxy-3,4-dihydro-1-methyl-2-oxo-2H-pyrrolium Tetrafluoroborate (**1ab**): From 1.90 g (10.0 mmol) of $Et_3O^+BF_4^-$ (**3b**) and 1.13 g (10.0 mmol) of *N*-methylsuccinimide (**5a**)[7] in dichloromethane (60 ml). After 68 h the reaction mixture is carefully covered with an upper layer of diethyl ether (20 ml) and very shortly cooled down to −40°C. Now crystallization commences. After 12 h at −5°C, then 48 h at −25°C, the precipitated needles (**1ab**) are collected by filtration and washed with ether (1.50 g, 66%); m.p. 105°C (dec.). – IR (paraffin): $\tilde{\nu} = 1800\ cm^{-1}$ (s, br, C=O), 1620 (s, br, C=N), 1440 (s, br), 1370 (s, br), 1100 (s, br, BF_4). – ^1H NMR (CD_3NO_2): δ = 1.64 (t, ^3J = 7.1 Hz, 3H, CH_2CH_3), 3.12 (ddd, ^3J = 5.9, ^3J = 3.0, $^2J_{gem.}$ = 3.0 Hz, 2H, CH_2CO), 3.26 (s, 3H, NCH_3), 3.52 (ddd, ^3J = 5.9, ^3J = 3.0, $^2J_{gem.}$ = 3.0 Hz, 2H, CH_2CH_2CO), 5.02 (q, ^3J = 7.19 Hz, 2H, CH_2CH_3). – ^{13}C NMR (CD_3NO_2): δ = 14.42 (CH_2CH_3), 27.17 (CH_2CH_2CO), 28.00 (NCH_3), 29.17 (CH_2CO), 77.71 (CH_2CH_3), 176.3 (C=O), 194.4 (C=N). – FD-MS, *m/z* (%): 142 [M^+] (64), 113 [M^+ − C_2H_5] (100). – $C_7H_{12}BF_4NO_2$ (229.0): calcd. C 36.72, H 5.28, N 6.12; found C 35.22, H 5.15, N 5.93. (Low carbon value because of tetrafluoroborate.)

5-Ethoxy-1-ethyl-3,4-dihydro-2-oxo-2H-pyrrolium Hexachloroantimonate (**1ba**): From 2.53 g (5.8 mmol) of $Et_3O^+SbCl_6^-$ (**3a**) and 0.74 g (5.8 mmol) of *N*-ethylsuccinimide (**5b**)[8] in dichloromethane (30 ml). After 24 h the reaction mixture is carefully covered with an upper layer of diethyl ether (5 ml) and kept at 5°C. The crystals formed are collected by filtration under reduced pressure, washed with ether and dried (1.80 g, 64%); m.p. 108°C. – IR (paraffin): $\tilde{\nu} = 1800\ cm^{-1}$ (s, C=O), 1590 (C=N), 1440 (s), 1370 (s), 1280 (s), 1250 (m), 1010 (m). – ^1H NMR (CD_3NO_2): δ = 1.26 (t, ^3J = 9.3 Hz, 3H, NCH_2CH_3), 1.69 (t, 3H, ^3J = 7.1 Hz, OCH_2CH_3), 3.17 (ddd, ^3J = 5.8, ^3J = 3.1, $^2J_{gem.}$ = 3.1 Hz, 2H, CH_2CO), 3.59 (ddd, ^3J = 5.8, ^3J = 3.1, $^2J_{gem.}$ = 3.1 Hz, 2H, CH_2CH_2CO), 3.87 (q, ^3J = 9.3 Hz, 2H, NCH_2CH_3), 5.02 (q, ^3J = 7.19 Hz, 2H, OCH_2CH_3). After warming up to 100°C the spectrum remains unchanged. – ^{13}C NMR (CD_3NO_2): δ = 12.07 (NCH_2CH_3), 14.42 (OCH_2CH_3), 27.39 (CH_2CH_2CO), 29.33 (CH_2CO), 38.68 (N–CH_2CH_3), 78.71 (O–CH_2CH_3), 175.7 (C=O), 193.0 (C=N). – MS (70 eV), *m/z* (%): 490 [M^+ of the cation + $SbCl_6^-$] (7), 191 [M^+ + Cl^-] (38), 127 [M^+ − C_2H_5] (60), 84 (62), 52 (100). – $C_8H_{14}Cl_6NO_2Sb$ (490.7): calcd. C 19.58, H 2.88, N 2.85; found C 19.41, H 2.88, N 2.85.

X-Ray Diffraction Analysis of **1ba**[14]: A colorless, white plate of $[C_8H_{14}NO_2]SbCl_6$ (from diethyl ether), crystal size 0.3 × 0.2 × 0.1 mm^3, was measured at room temp. at the Institute für Anorganische Chemie der Universität Münster by using an automatic CAD4 Turbo diffractometer (Enraf Nonius) with Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. 13664 reflexions were collected in the 2Θ range 4.0 ≤ 2Θ ≤ 60.0° (scan speed variable; 1.44 to 1.73°/min). Crystal system: Monoclinic, space group $P2_1/c$, $Z = 4$, $a = 10.858(2)$, $b = 9.876(2)$, $c = 16.383$ Å, β = 96.94(3)°, $V = 1743.9(6)$ $Å^3$, $d_{calc} = 1.869\ gcm^{-1}$. The structure

was solved by direct methods (SHELXTL-PLUS program[26]) using 4155 observed reflexions [$F > 3.9\sigma(F)$] for the non-hydrogen atoms. After the addition of the hydrogen atoms (coupled in position and temperature parameters to the corresponding carbon atoms), anisotropic refinement led to agreement factors $R_f = 0.0609$ and $R_w = 0.0671$ [weighting with $w^{-1} = \sigma^2(F) + 0.0002 \cdot F^2$]. The molecular shape is presented in Figure 1.

6-Ethoxy-1-ethyl-2,3,4,5-tetrahydro-2-oxopyridinium Hexachloroantimonate (**1ca**): From 3.02 g (6.9 mmol) of $Et_3O^+SbCl_6^-$ (**3a**) and 0.88 g (6.9 mmol) of **5d** in dichloromethane (40 ml). After stirring for 66 h the solution is concentrated to half its volume under reduced pressure. A colorless precipitate is formed, which dissolves again after some hours. Careful addition of an upper layer of diethyl ether (10 ml) leads to crystallization. The solid is filtered off, washed with ether and dried under reduced pressure (2.00 g, 59%); m.p. 137°C (dec.). – IR (paraffin): $\tilde{\nu} = 1770$ cm^{-1} (s, C=O), 1660 (C=N), 1440 (s), 1370 (s), 1300 (s), 1260 (m), 1170 (m), 1100 (m), 1050 (m). – ^{1}H NMR (CD_3NO_2): $\delta = 1.64$ (t, $^3J = 7.0$ Hz, 3H, CH_2CH_3), 2.28 (quint, $^3J = 6.4$ Hz, 2H, $CH_2CH_2CH_2$), 2.94 (t, $^3J = 6.4$ Hz, 2H, CH_2), 3.40 (m, 5H, CH_2, NCH_3), 5.01 (q, $^3J = 7.0$ Hz, 2H, CH_2CH_3). – ^{13}C NMR (CD_3NO_2): $\delta = 14.48$ (CH_2CH_3), 16.65 (CH_2), 28.24 (CH_2), 30.12 (NCH_3), 31.79 (CH_2), 78.56 (CH_2CH_3), 170.2 (C=O), 188.8 (C=N). – FD-MS, *m/z* (%): 156 [M^+] (100), 127 [$M^+ - C_2H_5$] (10). – $C_8H_{14}Cl_6NO_2Sb$ (490.7): calcd. C 19.58, H 2.88, N 2.85; found C 19.38, H 2.86, N 2.86.

6-Ethoxy-1-ethyl-2,3,4,5-tetrahydro-2-oxo-pyridinium Tetrafluoroborate (**1cb**): From 1.33 g (7.0 mmol) of $Et_3O^+BF_4^-$ (**3b**) and 0.89 g (7.0 mmol) of **5c** in dichloromethane (40 ml). After 44 h the reaction mixture is covered with an upper layer by careful addition of diethyl ether (30 ml), and the mixture is kept at −25°C for 2 d. The precipitated needles are filtered off, washed with ether and dried under reduced pressure (1.20 g, 70%); m.p. 88°C. – IR (CH_2ClCH_2Cl): $\tilde{\nu} = 1780$ cm^{-1} (s, C=O), 1580 (s, C=N), 1480 (m), 1380 (m), 1340 (m), 1100 (s, BF_4). – ^{1}H NMR (CD_3NO_2): $\delta = 1.65$ (t, $^3J = 6.9$ Hz, 3H, CH_2CH_3), 2.24 (quint, $^3J = 6.4$ Hz, 2H, $CH_2CH_2CH_2$), 2.91 (t, $^3J = 6.4$ Hz, 2H, CH_2), 3.36 (m, 5H, CH_2, NCH_3), 4.90 (q, $^3J = 7.0$ Hz, 2H, CH_2CH_3). – ^{13}C NMR (CD_3NO_2): $\delta = 14.33$ (CH_2CH_3), 16.55 (CH_2), 28.00 (CH_2), 29.82 (NCH_3), 31.66 (CH_2), 76.00 (CH_2CH_3), 170.7 (C=O), 189.0 (C=N). – FD-MS, *m/z* (%): 156 [M^+] (100), 127 [$M^+ - C_2H_5$] (12). – $C_8H_{14}BF_4NO_2$ (243.0): calcd. C 39.54, H 5.81, N 5.76; found C 37.72, H 5.81, N 5.24. (Low carbon value because of tetrafluoroborate.)

General Procedure for the Reaction of the Salts **1** *with C–H Acids* (**8**). *Method A:* To 5–6 mmol of **8** in dichloromethane (20 ml) an equimolar amount of ethyldiisopropylamine is added slowly at 0°C. At 0°C this mixture is transferred to an equimolar solution of **1** in dichloromethane (40 ml) by use of a syringe. After 1 h at 20°C, the reaction mixture is vigorously shacken with a satd. $NaHCO_3$ solution (50 ml); the phases are separated, and the aqueous layer is extracted several times with dichloromethane. The combined organic layers are dried with K_2CO_3, and the solvents are removed under reduced pressure. The crude product is purified by column chromatography.

Method B: From 5–6 mmol of the C–H acid **8** in diethyl ether (20 ml) and an equimolar amount of *n*-butyllithium in *n*-hexane a suspension of the lithium salt of the C–H acid is prepared. This mixture is added at −30°C to a suspension of an aliquot of **1** in diethyl ether (80 ml) by use of a syringe. After 24 h, precipitated $LiBF_4$ is removed by careful extraction with satd. $NaHCO_3$ solution. The layers are separated, the aqueous layer is extracted several times with diethyl ether, and the combined organic layers are dried with K_2CO_3. The crude product is purified by column chromatography.

5-(Dicyanomethylene)-1-methyl-2-pyrrolidinone (**9a**). From 1.33 g (5.8 mmol) of **1ab**, 0.34 g (5.8 mmol) of malononitrile (**8a**) and 0.75 g (5.8 mmol) of ethyl diisopropylamine (method A). The crude product is a yellow oil, giving solid **9a** after flash chromatography[27] [diethyl ether, R_f (DC) = 0.4] (0.65 g, 71%); m.p. 157°C. – IR (KBr): $\tilde{\nu} = 2940$ cm^{-1} (w, $CH_{aliph.}$), 2220 (s, C≡N), 1765 (s, C=O), 1580 (s, br, C=C), 1450 (s), 1420 (s), 1300 (s), 1260 (s), 1210 (s), 1120 (s). – ^{1}H NMR ($CDCl_3$): $\delta = 2.70-2.75$ (m, 2H, CH_2), 3.10–3.15 (m, 2H, CH_2), 3.50 (s, 3H, NCH_3). – ^{13}C NMR ($CDCl_3$): $\delta = 26.41$ (CH_2), 26.6 (CH_2), 30.77 (NCH_3), 58.10 (C=C(CN)$_2$), 112.0 (C≡N), 113.0 (C≡N), 171.7 (C=O), 175.8 (C=C(CN)$_2$). – MS (70 eV), *m/z* (%): 161 [M^+] (58), 159 [$M^+ - 2H$] (30), 134 (30), 133 (28), 119 (22), 106 (38), 105 (58), 104 (40), 79 (54), 77 (52), 67 (40), 55 (100). – $C_8H_7N_3O$ (161.2): calcd. C 59.62, H 4.38, N 26.07; found C 59.43, H 4.58, N 25.95.

5-[(Ethoxycarbonyl)cyanomethylene]-1-methyl-2-pyrrolidinone (**9b**): From 1.26 g (5.5 mmol) of **1ab**, 0.62 g (5.5 mol) of ethyl cyanoacetate (**8b**), and 0.71 g (5.5 mmol) of diethyldiisopropylamine (method A). The crude product is purified by flash chromatography[27] [diethyl ether/dichloromethane, 4:1, R_f(DC) = 0.8] giving **9b** as a colorless solid (only one isomer) (0.86 g, 75%); m.p. 121°C. – IR (KBr): $\tilde{\nu} = 2980$ cm^{-1} (w, $CH_{aliph.}$), 2940 (w, $CH_{aliph.}$), 2205 (m, C≡N), 1750 (s, C=O), 1700 (s, C=O), 1560 (s, C=C), 1480 (w), 1460 (m), 1410 (w), 1380 (w), 1360 (w), 1290 (s), 1220 (s), 1090 (s), 1030 (s). – ^{1}H NMR ($CDCl_3$): $\delta = 1.33$ (t, 3H, $^3J = 7.3$ Hz, CH_2CH_3), 2.60 (ddd, $^3J = 7.1$, $^3J = 4.5$, $^2J_{gem.} = 4.5$ Hz, 2H, CH_2CH_2), 3.38 (ddd, $^3J = 7.1$, $^3J = 4.5$, $^2J_{gem.} = 4.5$ Hz, 2H, CH_2CH_2), 3.54 (s, 3H, NCH_3), 4.25 (q, $^3J = 7.3$ Hz, 2H, CH_2CH_3). – ^{13}C NMR ($CDCl_3$): $\delta = 14.10$ (CH_2CH_3), 26.42 (CH_2), 27.28 (CH_2), 29.70 (NCH_3), 61.32 (CH_2CH_3), 78.92 (C–CN), 115.6 (C≡N), 163.7 (C=C–CN), 170.8 (C=O), 177.0 (C=O). – MS (70 eV), *m/z* (%): 208 [M^+] (40), 179 [$M^+ - C_2H_5$] (18), 163 [179 – O] (50), 162 (28), 136 (100), 134 (75), 125 (22), 107 (80), 106 (40), 80 (60), 79 (60), 55 (76). – $C_{10}H_{12}N_2O_3$ (208.2): calcd. C 57.71, H 5.81, N 13.46; found C 57.66, H 5.76, N 13.54.

5-[Bis(ethoxycarbonyl)methylene]-1-methyl-2-pyrrolidinone (**9c**): From 1.40 g (6.1 mmol) of **1ab**, 0.98 g (6.1 mmol) of diethyl malonate (**8c**), and 3.81 ml (6.1 mmol) of a 1.6 M *n*-butyllithium solution in *n*-hexane (method B). The oily, yellow residue is purified by column chromatography [diethyl ether, R_f(DC) = 0.5]. A colorless oil is obtained, which crystallizes in the refrigerator (0.87 g, 56%); m.p. 64°C. – IR (KBr): $\tilde{\nu} = 2980$ cm^{-1} (w, $CH_{aliph.}$), 2960 (w, $CH_{aliph.}$), 1745 (s, C=O), 1720 (s, C=O), 1700 (s, C=O), 1590 (s, C=C), 1460 (m), 1430 (m), 1380 (m), 1300 (m), 1240 (s), 1210 (m), 1140 (s), 1090 (s), 1040 (m), 1010 (m). – ^{1}H NMR ($CDCl_3$): $\delta = 1.27$ (t, $^3J = 7.2$ Hz, 3H, OCH_2CH_3), 1.35 (t, $^3J = 7.1$ Hz, 3H, OCH_2CH_3), 2.55 (ddd, $^3J = 7.5$, $^3J = 4.8$, $^2J_{gem.} = 4.8$ Hz, 2H, CH_2CH_2), 3.07 (s, 3H, NCH_3), 3.26 (ddd, $^3J = 7.5$, $^3J = 4.8$, $^2J_{gem.} = 4.8$ Hz, 2H, CH_2CH_2), 4.19 (q, $^3J = 7.2$ Hz, 2H, OCH_2CH_3), 4.29 (q, $^3J = 7.1$ Hz, 2H, OCH_2CH_3). – ^{13}C NMR ($CDCl_3$): $\delta = 13.74$ (CH_2CH_3), 13.95 (CH_2CH_3), 25.79 (CH_2), 26.96 (CH_2), 28.23 (NCH_3), 60.25 (O–CH_2CH_3), 61.35 (O–CH_2CH_3), 101.8 [C=C(CO$_2$Et)$_2$], 158.3 [C=C(CO$_2$Et)$_2$], 164.6 (C=O), 166.5 (C=O), 177.1 (C=O). – MS (70 eV), *m/z* (%): 255 [M^+] (20), 210 [$M^+ - OC_2H_5$] (40), 209 (42), 182 [$M^+ - CO_2Et$] (28), 151 (30), 137 (74), 111 (60), 109 [182 – CO_2Et] (70), 95 (38), 82 (68), 68 (78), 55 (100). – $C_{12}H_{17}NO_5$ (255.3): calcd. C 56.46, H 6.71, N 5.49; found C 56.75, H 6.89, N 5.43.

General Procedure for the Reactions of the Salt **1ab** *with Amines* (**10**): 5–10 mmol of **1ab** is dissolved in dichloromethane (30–60 ml) and treated with equimolar amounts of the respective amine. A slightly turbid solution is formed, which is vigorously shaken with a satd. $NaHCO_3$ solution (50 ml) after 3 h. The organic layer

becomes clear. After separation of the layers, the aqueous layer is extracted several times with dichloromethane. The combined organic extracts are dried with K_2CO_3. The solvent is removed under reduced pressure, and the crude products are purified as indicated.

5-(Isopropylimino)-1-methyl-2-pyrrolidinone (**11a**): From 1.45 g (6.4 mmol) of **1ab** and 0.38 g (6.4 mmol) of isopropylamine (**10a**) in dichloromethane (30 ml). The crude product is a yellow oil, which is purified by kugelrohr distillation (0.70 g, 70%); b.p. 70°C/0.1 mbar. – IR (neat): $\tilde{\nu} = 2960\ cm^{-1}$ (s, $CH_{aliph.}$), 2940 (s, sh, $CH_{aliph.}$), 2880 (m, $CH_{aliph.}$), 1740 (s, C=O), 1660 (s, br, C=N), 1430 (s), 1390 (s), 1300 (s), 1250 (m), 1150 (s), 1120 (m). – ^{1}H NMR ($CDCl_3$): $\delta = 1.15$ (d, $^3J = 6.2$ Hz, 6H, CH_3), 2.56–2.61 (m, 2H, CH_2), 2.68–2.73 (m, 2H, CH_2), 3.00 (s, 3H, NCH_3), 3.60 (quint, $^3J = 6.2$ Hz, 1H, CH). – ^{13}C NMR ($CDCl_3$): $\delta = 14.98$ [$C(CH_3)_2$], 21.49 (CH_2), 23.99 (NCH_3), 28.03 (CH_2), 49.59 (CH), 157.3 (C=N), 176.2 (C=O). – MS (70 eV), *m/z* (%): 154 [M^+] (20), 139 [$M^+ - CH_3$] (100), 68 (30), 55 (20). – $C_8H_{14}N_2O$ (154.2): calcd. C 62.31, H 9.15, N 18.17; found C 62.08, H 9.29, N 18.66.

5-(Butylimino)-1-methyl-2-pyrrolidinone (**11b**): From 2.20 g (9.6 mmol) of **1ab** and 0.70 g (9.6 mmol) of *n*-butylamine (**10b**) in dichloromethane (60 ml). The pure product is obtained after kugelrohr distillation as a colorless oil (1.05 g, 65%); b.p. 75°C/0.01 mbar. – IR (neat): $\tilde{\nu} = 2940\ cm^{-1}$ (s, $CH_{aliph.}$), 2920 (s, $CH_{aliph.}$), 2850 (s, $CH_{aliph.}$), 1730 (s, C=O), 1660 (s, C=N), 1430 (s), 1380 (s), 1300 (s), 1250 (m), 1180 (w), 1140 (s), 1120 (s), 1060 (m), 1000 (w), 960 (w), 910 (m), 820 (m), 660 (m). – ^{1}H NMR ($CDCl_3$): $\delta = 0.68$ (t, $^3J = 7.2$ Hz, 3H, CH_3), 1.12 (sext., $^3J = 7.2$ Hz, 2H, CH_2CH_3), 1.32 (quint, $^3J = 7.2$ Hz, 2H, $CH_2CH_2CH_2$), 2.29–2.34 (m, 2H, CH_2CH_2CO), 2.40–2.46 (m, 2H, CH_2CH_2CO), 2.73 (s, 3H, NCH_3), 3.20 (t, $^3J = 7.2$ Hz, 2H, $=NCH_2$). – ^{13}C NMR ($CDCl_3$): $\delta = 13.71$ (CH_2CH_3), 20.30 (CH_2), 21.73 (CH_2), 25.49 (NCH_3), 28.17 (CH_2), 33.10 (CH_2), 49.31 (CH_2), 159.2 (C=N), 176.2 (C=O). – MS (70 eV), *m/z* (%): 168 [M^+] (30), 139 [$M^+ - C_2H_5$] (10), 126 (62), 125 [$M^+ - C_3H_7$] (100), 97 (38), 68 (33), 55 (22). – $C_9H_{16}N_2O$ (168.2): calcd. C 64.25, H 9.59, N 16.65; found C 64.02, H 9.66, N 17.23.

5-(Cyclohexylimino)-1-methyl-2-pyrrolidinone (**11c**): From 1.72 g (7.5 mmol) of **1ab** and 0.74 g (7.5 mmol) of cyclohexylamine (**10c**) in dichloromethane (50 ml). The crude product is recrystallized from diethyl ether/petroleum ether (1:1) and separated from *N*-methylsuccinimide by HPLC [t_R value: 8–9 min; diethyl ether; flow: 15 ml/min] (1.20 g, 84%); m.p. 78°C. – IR (KBr): $\tilde{\nu} = 2920\ cm^{-1}$ (m, $CH_{aliph.}$), 2850 (m, $CH_{aliph.}$), 1730 (m, C=O), 1660 (s, C=N), 1430 (m), 1300 (m), 1290 (m), 1150 (w), 1130 (w), 920 (w). – ^{1}H NMR ($CDCl_3$): $\delta = 1.21–1.43$ [m, 5H, $CH_{2(cyclohexyl)}$], 1.56–1.62 [m, 3H, $CH_{2(cyclohexyl)}$], 1.74–1.78 [m, 2H, $CH_{2(cyclohexyl)}$], 2.51–2.56 (m, 2H, CH_2CH_2), 2.63–2.68 (m, 2H, CH_2CH_2), 2.91 (s, 3H, NCH_3), 3.16 (tt, $^3J = 10.0$, $^3J = 4.1$ Hz, CH). – ^{13}C NMR ($CDCl_3$): $\delta = 21.75$ (CH_2), 24.35 (CH_2), 25.64 (CH_2), 25.88 (NCH_3), 28.43 (CH_2), 34.26 (CH_2), 58.19 (CH_2), 157.5 (C=N), 176.4 (C=O). – MS (70 eV), *m/z* (%): 194 [$M^+ + H$] (40), 193 [M^+] (10), 165 (28), 152 (22), 151 (100), 113 (98), 69 (38), 68 (40), 55 (40), 41 (22). – $C_{11}H_{17}N_2O$ (193.3): calcd. C 68.01, H 9.34, N 14.42; found C 67.79, H 9.43, N 14.13.

General Procedure for the Reactions of the Salt **1ab** *with the Amidines* **12**: 5–10 mmol of **1ab** is dissolved in dichloromethane (30–60 ml) and treated with an equimolar amount of amidine **12** in dichloromethane (80–120 ml). After the addition of one aliquot of the tertiary base the solution is stirred for 30–60 min. The precipitated ammonium salt is removed by extraction with a satd. $NaHCO_3$ solution (50 ml). The layers are separated, and the aqueous phase is extracted several times with dichloromethane. The combined organic layers are dried with K_2CO_3, and the solvent is removed under reduced pressure.

N¹-(1-Methyl-5-oxo-2-pyrrolidinylidene)-N²-phenylbenzamidine (**13a**): From 1.53 g (6.7 mmol) of **1ab**, 1.31 g (6.7 mmol) of *N*-phenylbenzamidine (**12a**)[28], and 0.68 g (6.7 mmol) of triethylamine. After 30 min a yellow oil is formed, from which a pure white solid is obtained after recrystallization from diethyl ether/dichloromethane (15:4) (1.39 g, 72%); m.p. 148°C. – IR (KBr): $\tilde{\nu} = 3060\ cm^{-1}$ (w, $CH_{arom.}$), 3020 (w, $CH_{arom.}$), 2920 (w, $CH_{aliph.}$), 1750 (m, C=O), 1660 (s, br, C=N), 1590 (s, C=$C_{arom.}$), 1580 (s, C=$C_{arom.}$), 1560 (s), 1480 (w), 1440 (m), 1430 (s), 1390 (m), 1340 (m), 1310 (m), 1290 (m), 1260 (s), 1210 (s), 1170 (w), 1120 (s). – ^{1}H NMR ($CDCl_3$): $\delta = 2.27–2.32$ (m, 2H, CH_2), 2.37–2.42 (m, 2H, CH_2), 3.05 (s, 3H, CH_3), 6.98–7.03 (m, 3H, $CH_{arom.}$), 7.23–7.29 (m, 2H, $CH_{arom.}$), 7.42–7.46 (m, 3H, $CH_{arom.}$), 7.95–7.98 (m, 2H, $CH_{arom.}$). – ^{13}C NMR ($CDCl_3$): $\delta = 25.11$ (CH_2), 25.86 (NCH_3), 28.14 (CH_2), 121.4 ($CH_{arom.}$), 123.3 ($CH_{arom.}$), 127.8 ($CH_{arom.}$), 128.3 ($CH_{arom.}$), 128.6 ($CH_{arom.}$), 130.9 ($CH_{arom.}$), 135.3 (C_{ipso}), 149.1 (C_{ipso}), 159.1 (C=N), 159.3 (C=N), 176.1 (C=O). – MS (70 eV), *m/z* (%): 291 [M^+] (38), 290 [$M^+ - H$] (48), 181 (20), 180 [PhC=NPh$^+$] (62), 93 (22), 86 (78), 84 (98), 77 [Ph^+] (96), 68 (38), 57 (38), 51 (100). – $C_{18}H_{17}N_3O$ (291.4): calcd. C 74.21, H 5.88, N 14.42; found C 74.24, H 5.89, N 14.53.

N¹-(1-Methyl-5-oxo-2-pyrrolidinylidene)-2,2-dimethyl-N²-phenylpropanamidine (**13b**): From 1.35 g (5.9 mmol) of **1ab**, 1.04 g (5.9 mmol) of 2,2-dimethyl-*N*-phenylpropanamidine (**12b**)[28], and 0.76 g (5.9 mmol) of ethyldiisopropylamine. After 45 min, a yellow oil is obtained, which is purified by flash chromatography[27] [diethyl ether, R_f(DC) = 0.8]. **13b** forms a slightly yellow oil, which solidifies slowly (0.74 g, 46%); m.p. 55°C. – IR (KBr): $\tilde{\nu} = 2920\ cm^{-1}$ (s, $CH_{aliph.}$), 1750 (s, C=O), 1660 (s, br, C=N), 1610 (s, br, C=N), 1580 (s), 1470 (m), 1420 (s), 1380 (m), 1320 (m), 1290 (m), 1260 (m), 1240 (w), 1190 (w), 1120 (s), 1060 (w). – ^{1}H NMR ($CDCl_3$): $\delta = 1.27$ [s, 9H, $C(CH_3)_3$], 2.26–2.29 (m, 4H, CH_2CH_2), 2.93 (s, 3H, NCH_3), 6.82–6.85 (m, 2H, $CH_{arom.}$), 6.91–6.94 (m, 1H, $CH_{arom.}$), 7.15–7.18 (m, 2H, $CH_{arom.}$). – ^{13}C NMR ($CDCl_3$): $\delta = 25.65$ (NCH_3), 26.05 (CH_2), 28.09 [$C(CH_3)_3$], 28.19 (CH_2), 39.11 [$C(CH_3)_3$], 121.1 ($CH_{arom.}$), 122.7 ($CH_{arom.}$), 128.5 ($CH_{arom.}$), 149.6 (C_{ipso}), 156.4 (C=N), 170.3 (C=N), 176.0 (C=O). – MS (70 eV), *m/z* (%): 271 [M^+] (30), 256 [$M^+ - CH_3$] (10), 215 (20), 214 [$M^+ - C_4H_9$] (100), 160 (10), 123 (10), 104 (22), 93 (31), 77 [Ph^+] (22), 68 (58), 55 (20). – $C_{16}H_{21}N_3O$ (271.4): calcd. C 70.82, H 7.80, N 15.49; found C 70.65, H 7.77, N 15.45.

N²-tert-Butyl-N¹-(1-methyl-5-oxo-2-pyrrolidinylidene)benzamidine (**13c**): From 1.33 g (5.8 mmol) of **1ab**, 1.02 g (5.8 mmol) of *N-tert*-butylbenzamidine (**12c**)[28], and 0.59 g (5.8 mmol) of triethylamine. After 45 min a yellow solid is obtained, from which after recrystallization from diethyl ether/petroleum ether (1:1) **13c** (colorless needles) is isolated (0.83 g, 53%); m.p. 88°C. – IR (KBr): $\tilde{\nu} = 2960\ cm^{-1}$ (m, $CH_{aliph.}$), 1740 (s, C=O), 1650 (s, C=N), 1610 (s, br, C=N), 1440 (m), 1420 (m), 1380 (m), 1350 (m), 1310 (s), 1290 (m), 1250 (s), 1210 (m), 1120 (s), 1090 (w), 1070 (w), 1020 (w), 1000 (w). – ^{1}H NMR ($CDCl_3$): $\delta = 1.33$ [s, 9H, $C(CH_3)_3$], 2.18–2.33 (m, 2H, CH_2), 2.48–2.54 (m, 2H, CH_2), 3.20 (s, 3H, NCH_3), 7.31–7.33 (m, 3H, $CH_{arom.}$), 7.66–7.68 (m, 2H, $CH_{arom.}$). – ^{13}C NMR ($CDCl_3$): $\delta = 24.35$ (CH_2), 25.85 (NCH_3), 28.20 (CH_2), 29.67 [$C(CH_3)_3$], 54.31 [$C(CH_3)_3$], 127.0 ($CH_{arom.}$), 128.2 ($CH_{arom.}$), 129.4 ($CH_{arom.}$), 137.8 (C_{ipso}), 156.1 (C=N), 159.3 (C=N), 176.0 (C=O). – MS (70 eV), *m/z* (%): 271 [M^+] (22), 256 [$M^+ - CH_3$] (40), 144 (60), 105 (20), 104 (100), 103 (20), 86 (38), 84 (52), 77 [Ph^+] (40), 69 (24), 68 (62), 57 [$C_4H_9^+$] (88). – $C_{16}H_{21}N_3O$ (271.4): calcd. C 70.82, H 7.80, N 15.49; found C 70.74, H 7.92, N 15.49.

N-(1-Methyl-5-oxo-2-pyrrolidinylidene)benzamide (**15**): 1.65 g (7.2 mmol) of **1ab** is dissolved in dichloromethane (40 ml) and

treated with a suspension of 0.87 g (7.2 mmol) of benzamide (**14**) in dichloromethane (40 ml). Then 0.73 g (7.2 mmol) of triethylamine is added, and the mixture is stirred for 24 h at 20°C. The resulting yellow solution is washed with a satd. $NaHCO_3$ solution. The layers are separated, and the aqueous layer is extracted several times with dichloromethane; the combined organic extracts are dried with K_2CO_3. After removal of the solvent under reduced pressure, the grayish residue is recrystallized from diethyl ether/dichloromethane (3:1). It is not possible to remove benzamide thoroughly either by recrystallization or by chromatographic methods. Yield: 0.28 g (18%); m.p. 106°C. – IR (KBr): $\tilde{\nu} = 3040$ cm^{-1} (w, $CH_{arom.}$), 2980 (w, $CH_{aliph.}$), 2920 (w, $CH_{aliph.}$), 1740 (s, br, C=O), 1650 (s, br, C=O), 1580 (s, br, C=N), 1420 (m), 1240 (s), 1120 (m), 1050 (m). – ^{1}H NMR ($CDCl_3$): $\delta = 2.66-2.70$ (m, 2H, CH_2), 3.06–3.10 (m, 2H, CH_2), 3.20 (s, 3H, NCH_3), 7.43–7.49 (m, 2H, $CH_{arom.}$), 7.55–7.58 (m, 1H, $CH_{arom.}$), 8.11–8.14 (m, 2H, $CH_{arom.}$). – ^{13}C NMR ($CDCl_3$): $\delta = 24.79$ (CH_2), 26.33 (NCH_3), 28.12 (CH_2), 128.3 ($CH_{arom.}$), 129.8 ($CH_{arom.}$), 133.1 ($CH_{arom.}$), 134.6 (C_{ipso}), 167.5 (C=N), 177.0 (C=O), 178.2 (C=O). – MS (70 eV), *m/z* (%): 216 [M^+] (20), 188 (20), 187 (22), 149 (30), 139 [M^+ – Ph] (40), 111 [M^+ – PhCO], (34), 105 [$PhCO^+$] (100), 83 (38), 77 [Ph^+] (90), 57 (66). – High resolution MS: $C_{12}H_{12}N_2O_2$: *calcd.* 216.089878, found 216.090038.

General Procedure for the Reaction fo the Salts **1ab** *with N-Acylamidines* (**16**): 3–6 mmol of **1ab** is dissolved in dichloromethane (20–40 ml) and treated with an equimolar amount of **16**, dissolved in dichloromethane (40–60 ml). After the addition of one aliquot of triethylamine the mixture is stirred for 10 h at room temp. Then the mixture is washed with 50 ml of a satd. $NaHCO_3$ solution. After separation of the layers and extraction of the organic layer with dichloromethane, the combined organic extracts are dried with K_2CO_3. Evaporation of the solvent under reduced pressure yields oily residues.

N^2-Benzoyl-N^1-(1-methyl-5-oxo-2-pyrrolidinylidene)benzamidine (**17a**): From 1.31 g (5.7 mmol) of **1ab**, 1.28 g of *N*-benzoylbenzamidine (**16a**)[29], and 0.58 g (5.7 mmol) of triethylamine. The crude product is a viscous, brown oil, which is purified by column chromatography [ethyl acetate/petroleum ether, 1:3, R_f(DC) = 0.6]. The product **17a** is a colorless oil, which solidifies slowly (0.80 g, 44%); m.p. 102°C. – IR (KBr): $\tilde{\nu} = 3050$ cm^{-1} (w, $CH_{arom.}$), 2980 (w, $CH_{aliph.}$), 2940 (w, $CH_{aliph.}$), 1750 (s, C=O), 1620 (s, br, C=N, C=O), 1460 (s), 1440 (s), 1430 (s, sh), 1380 (m), 1320 (s), 1250 (s, br), 1170 (s), 1120 (s), 1070 (m), 1040 (m), 1020 (m), 1000 (m). – ^{1}H NMR ($CDCl_3$): $\delta = 2.58-2.63$ (m, 2H, CH_2), 2.83–2.88 (m, 2H, CH_2), 2.93 (s, 3H, NCH_3), 7.40–7.55 (m, 6H, $CH_{arom.}$), 7.95–8.01 (m, 4H, $CH_{arom.}$). – ^{13}C NMR ($CDCl_3$): $\delta = 24.29$ (CH_2), 25.84 (NCH_3), 28.22 (CH_2), 128.3 ($CH_{arom.}$), 128.6 ($CH_{arom.}$), 129.2 ($CH_{arom.}$), 132.1 ($CH_{arom.}$), 132.8 ($CH_{arom.}$), 133.0 (C_{ipso}), 133.2 (C_{ipso}), 159.8 (C=N), 152.1 (C=N), 176.2 (C=O), 180.4 (C=O). – MS (70 cV), *m/z* (%): 319 [M^+] (20), 301 (48), 272 (22), 242 [M^+ – Ph] (20), 139 (22), 105 [$PhCO^+$] (100), 103 (50), 77 [Ph^+] (92), 76 (42), 67 (28), 51 (58). – $C_{19}H_{17}N_3O_2$ (319.4): calcd. C 71.46, H 5.37, N 13.16; found C 71.23, H 5.39, N 12.91.

N^1-(1-Methyl-5-oxo-2-pyrrolidinylidene)-N^2-pivaloylbenzamidine (**17b**): From 0.75 g (3.3 mmol) of **1ab**, 0.67 g (3.3 mmol) of *N*-pivaloylbenzamidine (**16b**)[30], and 0.33 g (3.3 mmol) of triethylamine. The crude oil is purified by flash chromatography[27] [ethyl acetate/petroleum ether, 3:1; R_f(DC) = 0.8]. **17b** is obtained as a colorless oil, which solidifies slowly (0.50 g, 52%); m.p. 106°C; it is not stable even at –25°C, but decomposes within two weeks to form a black oil. – IR (KBr): $\tilde{\nu} = 3060$ cm^{-1} (w, $CH_{arom.}$), 2960 (m, $CH_{aliph.}$), 2860 (w, $CH_{aliph.}$), 1740 (s, C=O), 1670 (s, br, C=O, C=N), 1610 (C=N), 1570 (m), 1480 (m), 1440 (m), 1430 (m), 1380 (w), 1330 (w), 1310 (w), 1290 (w), 1250 (s), 1150 (s), 1130 (s), 1070 (m), 1050 (m), 1020 (w). – ^{1}H NMR ($CDCl_3$): $\delta = 1.23$ [s, 9H, $C(CH_3)_3$], 2.57–2.62 (m, 2H, CH_2), 2.78–2.83 (m, 2H, CH_2), 3.08 (s, 3H, NCH_3), 7.26–7.50 (m, 3H, $CH_{arom.}$), 7.82–7.85 (m, 2H, $CH_{arom.}$). – ^{13}C NMR ($CDCl_3$): $\delta = 24.16$ (CH_2), 25.81 (NCH_3), 27.11 [$C(CH_3)_3$], 28.25 (CH_2), 41.56 [$C(CH_3)_3$], 128.1 ($CH_{arom.}$), 128.5 ($CH_{arom.}$), 131.7 ($CH_{arom.}$), 133.2 (C_{ipso}), 157.0 (C=N), 162.4 (C=N), 176.4 (C=O), 195.0 (C=O). – MS (70 eV), *m/z* (%): 299 [M^+] (8), 243 (60), 242 [M^+ – C_4H_9] (100), 214 [M^+ – C_4H_9CO] (20), 201 (20), 171 (22), 139 (90), 130 (28), 111 (28), 104 (40), 96 (24), 83 (34), 77 [Ph^+] (40), 69 (60), 68 (80), 57 [$C_4H_9^+$] (70), 55 (82). – $C_{17}H_{21}N_3O_2$ (299.4): calcd. C 68.21, H 7.07, N 14.04; found C 68.23, H 7.18, N 13.89.

N^2-Benzoyl-N^1-(1-methyl-5-oxo-2-pyrrolidinylidene)acetamidine (**17c**): From 1.26 g (5.5 mmol) of **1ab**, 0.89 g of *N*-benzoylacetamidine (**16c**)[31], and 0.56 g (5.7 mmol) of triethylamine. The crude **17c** is a reddish solid, which forms a colorless powder after recrystallization from dichloromethane/petroleum ether (1:1) (0.30 g, 22%); m.p. 152°C. At –25°C **17c** decomposes within two weeks to give a black oil. – IR (KBr): $\tilde{\nu} = 3040$ cm^{-1} (w, $CH_{arom.}$), 2940 (w, $CH_{aliph.}$), 1740 (s, C=O), 1640 (s, br, C=N, C=O), 1440 (m), 1430 (s), 1340 (m), 1310 (m), 1290 (s), 1270 (m), 1250 (s), 1220 (s), 1170 (m), 1130 (s), 1090 (s), 1060 (m). – ^{1}H NMR ($CDCl_3$): $\delta = 2.21$ (s, 3H, C–CH_3), 2.65–2.69 (m, 2H, CH_2), 2.93 (s, 3H, NCH_3), 3.03–3.05 (m, 2H, CH_2), 7.45–7.50 (m, 2H, $CH_{arom.}$), 7.47 (m, 1H, $CH_{arom.}$), 7.94–7.97 (m, 2H, $CH_{arom.}$). – ^{13}C NMR ($CDCl_3$): $\delta = 22.75$ (C–CH_3), 23.80 (CH_2), 25.83 (NCH_3), 28.12 (CH_2), 128.3 ($CH_{arom.}$), 129.2 ($CH_{arom.}$), 132.9 ($CH_{arom.}$), 133.1 (C_{ipso}), 161.1 (C=N), 164.2 (C=N), 176.3 (C=O), 179.1 (C=O). – MS (70 eV), *m/z* (%): 257 [M^+] (60), 239 (36), 180 [M^+ – Ph] (60), 152 [M^+ – PhCO] (72), 138 [M^+ – ONCPh] (68), 119 [M^+ – 138] (58), 111 (70), 105 [$PhCO^+$] (100), 95 (70), 85 (64), 83 (90), 69 (90). – $C_{14}H_{15}N_3O_2$ (257.3): calcd. C 65.36, H 5.88, N 16.33; found C 65.53, H 6.03, N 16.58.

☆ Dedicated to Prof. Dr. *Alan R. Katritzky* FRS on the occasion of his 65th birthday.

[1] S. M. Weinreb, P. M. Scola, *Chem. Rev.* **1989**, *89*, 1525–1534; W. N. Speckamp, H. Hiemstra, *Tetrahedron* **1985**, *41*, 4367–4416; H. E. Zaugg, *Synthesis* **1984**, 85–110; H. E. Zaugg, *ibid.* **1984**, 181–212; T. R. Govindachari, P. Chinnasamy, S. Rajeswari, S. Chandrasekaran, M. S. Premila, S. Natarajan, K. Nagarajan, B. R. Pai, *Heterocycles* **1984**, *22*, 585–655; W. N. Speckamp, *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 345–354; H. E. Zaugg, *Synthesis* **1970**, 49–73; H. E. Zaugg, W. B. Martin, *Org. React.* **1965**, *14*, 52–269; R. Merten, G. Müller, *Angew. Chem.* **1962**, *74*, 866–871.

[2] H. Hiemstra, W. N. Speckamp in *The Alkaloids*, vol. 32 (Ed.: A. Brossi), Academic Press, New York, **1988**, p. 271–339.

[3] J. V. Paukstelis, A. G. Cook in *Enamines* (Ed.: A. G. Cook), Marcel Dekker, New York, **1988**, p. 275–345; *Iminium-Salts in Organic Chemistry*, vol. 1 (Eds.: H. Böhme, H. G. Viehe), Wiley, New York, **1976**.

[4] J. C. Jochims, M. O. Glocker, J. Hofmann, H. Fischer, *Tetrahedron* **1991**, *47*, 205–218.

[5] K. Th. Wanner, I. Praschak, U. Nagel, *Arch. Pharm. (Weinheim)* **1990**, *323*, 335–350.

[6] B. Lamatsch, D. Seebach, T.-K. Ha, *Helv. Chim. Acta* **1992**, *75*, 1095–1110.

[7] A. E.-H. Ismail, A. Hamed, M. T. Abdel-Aal, I. Zeid, M. Al-Talib, Q. Wang, J. C. Jochims, *J. Prakt. Chem.* **1992**, *334*, 661–668.

[8] W. Funke, E.-U. Würthwein, *Chem. Ber.* **1992**, *125*, 1967–1968.

[9] E.-U. Würthwein, R. Kupfer, *Chem. Ber.* **1986**, *119*, 1557–1568; E.-U. Würthwein, R. Kupfer, R. Allmann, M. Nagel, *ibid.* **1985**, *118*, 3632–3642.

[10] W. Funke, Dissertation, Universität Münster, **1992**.

[11] W. Flitsch, *Chem. Ber.* **1964**, *97*, 1542–1547.

[12] N. Menschutkin, *Liebigs Ann. Chem.* **1876**, *182*, 90–93.

[13] G. R. Krow, C. Pyun, C. Leitz, J. Marakowski, *J. Org. Chem.* **1974**, *39*, 2449–2451; Y. Yamamoto, T. Nakada, H. Nemoto, *J. Am. Chem. Soc.* **1992**, *114*, 121–125.

[14] Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Federal Republic of Germany, on quoting the depository number CSD-57037, the names of the authors, and the journal citation.
[15] P. C. Hariharan, J. A. Pople, *Theoret. Chim. Acta (Berlin)* **1973**, *28*, 213.
[16] *GAUSSIAN 92*, Revision B, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. DeFrees, J.Baker, J. J. P. Stewart, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1992**.
[17] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618; M. J. Frisch, R. Krishnan, J. A. Pople, *Chem. Phys. Lett.* **1980**, *75*, 66.
[18] R. Kupfer, E.-U. Würthwein, M. Nagel, R. Allmann, *Chem. Ber.* **1985**, *118*, 643–652.
[19] E.-U. Würthwein, MP2/6–31G*//6–31G* ab initio calculations, unpublished.
[20] R. Kupfer, M. Nagel, E.-U. Würthwein, R. Allmann, *Chem. Ber.* **1985**, *118*, 3089–3104.
[21] K. B. Wiberg, P. R. Rablen, M. Marquez, *J. Am. Chem. Soc.* **1992**, *114*, 8654–8668.
[22] S. Hünig, M. Kiesel, *Chem. Ber.* **1958**, *91*, 380–392.
[23] Y. Yamazaki, K. Matoba, S. Imoto, M. Terashima, *Chem. Pharm. Bull.* **1976**, *24*, 3011–3018.
[24] W. Flitsch, S. R. Schindler, *Synthesis* **1975**, 685–700.
[25] M. Buhmann, M. H. Möller, E.-U. Würthwein, *Chem. Ber.* **1993**, *126*, 957–967.
[26] G. Sheldrick, *SHELXTL-plus, Programmsystem zur Kristallstrukturbestimmung*, Siemens AG, **1989**.
[27] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.
[28] P. Luthardt, Dissertation, Universität Münster, **1989**.
[29] T. Fuchigami, K. Odo, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3607–3610.
[30] M. Buhmann, Diplomarbeit, Universität Münster, **1989**.
[31] S.-O. Chua, M. J. Cook, A. R. Katritzky, *J. Chem. Soc., Perkin Trans 2*, **1974**, 546–552.

[92/93]