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Meerwein's Catalytic Beckmann Rearrangement [1])

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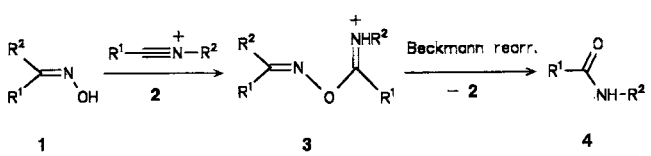
Abstract. Meerwein recommended nitrilium salts (**2**) as catalysts for the Beckmann rearrangement of oximes (**1**) under neutral and water-free conditions. For the first time, primary adducts (*Z*)–(**3**) of oximes to nitrilium salts have been isolated. Reported are activation energies for Beckmann rearrangements of these adducts, and an X-ray structural analysis of (*Z*)–**3a**. Rearrangement of **3** produces mixtures of up to four different *N*-acylamidinium salts **5**–**8**, which arise from fast reactions of primary-formed secondary amides (**4**) with nitrilium salts (**2**). Because of their ambident electrophilic character the *N*-acylamidinium salts react with excess of oxime not only to amides (**4**) but to mixtures of products. It is shown that nitrilium salts cannot be used as catalysts for the Beckmann rearrangement.

The economically important Beckmann rearrangement [1–3] of cyclohexanone oxime to a sulfate of ε-caprolactam requires large quantities of concentrated sulfuric acid or oleum [4, 5], which finally have to be neutralized with ammonia. In conventional processes, a total of 2.5 tons of ammonium sulfate per ton of ε-caprolactam is produced in oximation of cyclohexanone and in neutralization of the reaction mixture after the Beckmann rearrangement. Since the world capacity for the annual production of ε-caprolactam ranges around three million tons there are economical as well as ecological interests to find conditions, under which the Beckmann rearrangement can be carried out catalytically under neutral conditions. Procedures for catalytic rearrangements of cyclohexanone oxime in the gas phase are known since 1938, none of them having found application on an industrial scale till now. Recently, Mukayama and others reported catalytic Beckmann rearrangements in solution [6–9].



Scheme 1 Meerwein's catalytic Beckmann rearrangement

Years ago, Meerwein recommended nitrilium salts **2** as catalysts for the Beckmann rearrangement under neutral and water-free conditions (Scheme 1) [10]. Benzophenone oxime (**1a**) was rearranged to benzanilide in the presence of 2 mol percent of *N*-phenylbenzonitrilium hexachloroantimonate (**2f**).

While we were able to reproduce this experiment, attempts to rearrange acetone oxime or cyclohexanone oxime under Meerwein's conditions led to mixtures of compounds.

Meerwein's cycle starts with the formation of an adduct **3** of an oxime **1** to a nitrilium salt **2**. Recently, we

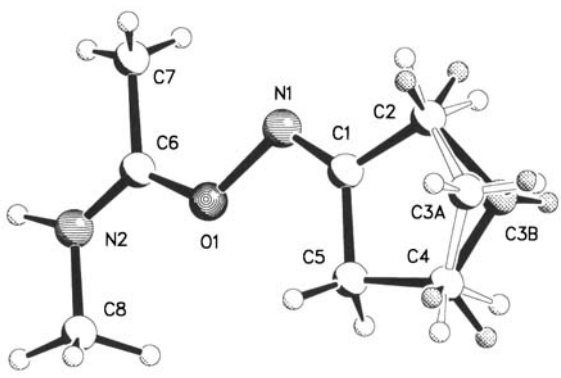


Fig. 1 X-Ray crystal structure of the cation (*Z*)-**3a**

[1]) Presented at the second conference on iminium salts, Stimpfach-Rechenberg, Germany, September 20–22, 1995

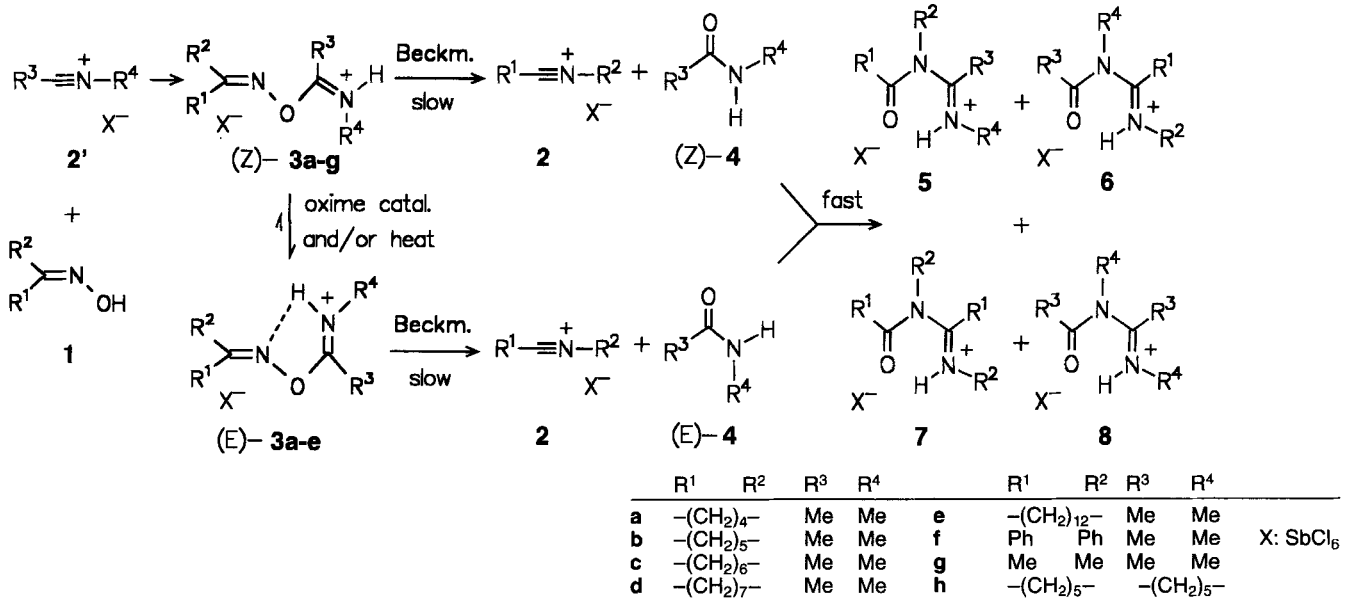
Table 1 Selected bond lengths [pm], bond angles, and torsional angles [°] for the cation (*Z*)-**3a** [15]

C8-N2	146 (1)	C8-N2-C6	121.4(6)	C5-C1-C2	109.6 (5)
N2-C6	123.4 (8)	N2-C6-O1	119.1(7)	C8-N2-C6-C7	179.6 (6)
C6-01	127.9 (7)	N2-C6-C7	120.9(6)	C8-N2-C6-O1	–0.9 (9)
O1-N1	147.6 (6)	C7-C6-O1	120.0(6)	N2-C6-O1-N1	–179.8 (5)
N1-C1	126.7 (7)	C6-O1-N1	117.2(5)	C7-C6-O1-N1	–0.3 (7)
C1-C2	147.9 (9)	O1-N1-C1	109.2(5)	C6-O1-N1-C1	178.6 (5)
C1-C5	151.1 (9)	N1-C1-C5	127.6(6)	O1-N1-C1-C2	–178.4 (5)
C6-C7	155 (1)	N1-C1-C2	122.8(6)	O1-N1-C1-C5	1.7 (8)

reported the isolation of first salts **3**. Nitrilium salts reacted with acetone oxime to products sensitive to moisture and temperature, believed to be (*Z*)-**3**, which underwent isomerization to (*E*)-**3**. The structure of a compound (*E*)-**3** (R^1, R^2=Me, R^3=Ph, R^4=*i*Pr) was secured by X-ray crystallographic analysis [11]. Now we report the X-ray structural analysis of the primary adduct (*Z*)-**3a** formed from cyclopentanone oxime **1a** and the *N*-methylacetonitrilium salt **2'a** (Scheme 2, Fig.1, Table 1). The crystal contained cations with different conformations of the five-membered ring (ring puckerung disorder of C3). The (*Z*)-configuration is in accord with the well documented fact that nitrilium salts add nucleophiles stereoelectronically controlled in such a way that the lone pair of electrons on the nitrilium nitrogen atom developes *trans* with respect to the incoming nucleophile [12–14]. Note the antiperiplanar arrangement of N2 and N1 in (*Z*)-**3a** (N2-C6-O1-N1: –179.8°). The corresponding torsional angle in (*E*)-**3**(R^1,R^2=Me, R^3=Ph, R^4=*i*Pr) was found to be –1.6° (9) (synperiplanar conformation) indicating an intramolecular NH–N hydrogen bond [11], which cannot be formed in the (*Z*)-form **3**.

We observed that traces of oximes **1** catalyze the geometrical isomerization of the primary adducts (*Z*)-**3** to equilibria lying on the side of the (*E*)-forms. Therefore, one has to avoid any excess of oxime **1** during the preparation of compounds (*Z*)-**3**. The reaction temperature should be kept below 23 °C to prevent Beckmann rearrangement. Under these conditions it was possible to prepare both geometrical isomers of **3a–e**, (*Z*)-**3f** and (*Z*)-**3g**.

The second step of Meerwein's cycle, the Beckmann rearrangement of the adducts **3** was followed by ^{1}H NMR spectroscopy, integrating non-overlapping signals of **3** at a given temperature as a function of time (Table 2). For **3a–f** Beckmann rearrangement was faster than geometrical isomerization. In boiling dichloromethane (*Z*)-**3g** underwent geometrical isomerization leading to an equilibria of (*Z*)/(*E*)-**3g** (1:4). Beckmann rearrangement of **3g** required heating of the crystals just above their melting point (109–111°C). For the Beckmann rearrangement of **3a–e** first order kinetics were observed (Table 2). Probably due to a stabilizing intramolecular hydrogen bond the activation energies of (*E*)-isomers **3**

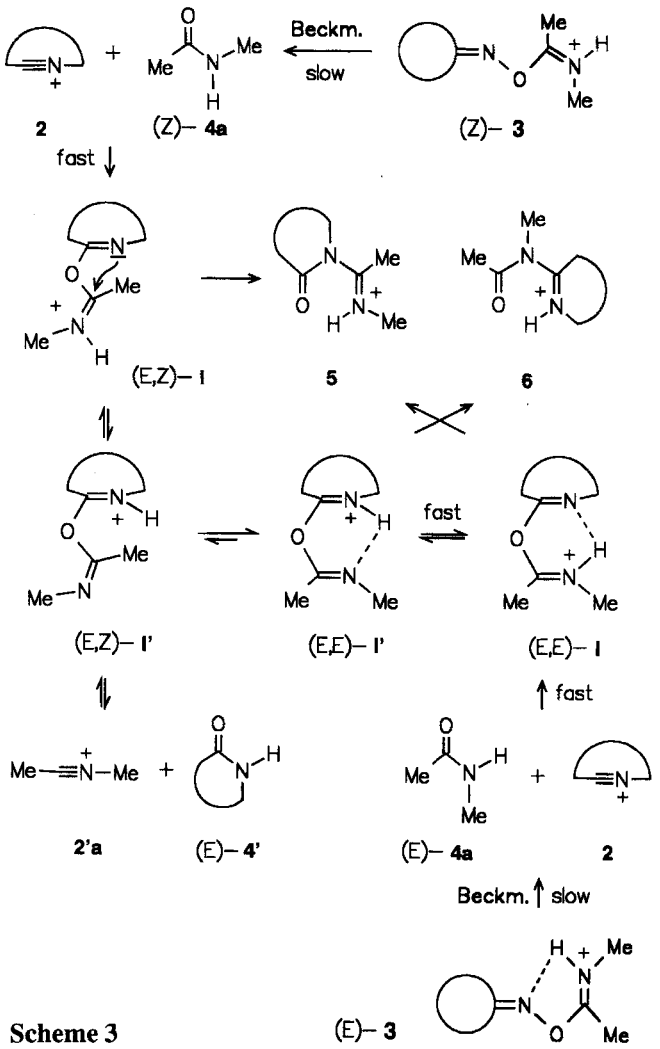


Scheme 2 Meerwein's Beckmann rearrangement complemented

Table 2 Rate constants k and activation energies $\Delta G^{\neq}$ for the Beckmann rearrangements of compounds **3**, and product distributions

	T [a] [K]	k×10⁴ [s⁻¹]	ΔG≠ [b] [kJ mol⁻¹]	products [%] [c] 5	6	7	8
(*Z*)-**3a**	316	1.28	101.1	38	40	– [d]	21
(*E*)-**3a**	335	0.44	110.3	+	+	–	+
	345	2.45	108.8	+	+	–	+
(*Z*)-**3b**	295	1.30	94.2	100	–	–	–
	295 [e]	1.56	93.7	100	–	–	–
(*E*)-**3b**	323	0.85	104.5	50	50	–	–
	338	6.13	103.9	52	48	–	–
(*Z*)-**3c**	303	0.77	98.1	50	5	32	12
	308	1.43	98.2	54	6	25	15
(*E*)-**3c**	342	2.59	107.6	52	6	32	10
(*Z*)-**3d**	298	0.70	96.7	69	1	24	6
(*E*)-**3d**	333	1.33	106.6	61	1	33	5
(*Z*)-**3e**	300	3.53	93.3	31	20	25	24
	298 [e]	3.46	92.7	+	+	+	+
(*E*)-**3e**	335	5.65	103.2	39	23	15	23
(*Z*)-**3f**	298	[f]		100	–	–	–
(*Z*)-**3g**	383	[g]		100			
(*E*)-**3h**	323	0.78	104.7	100			

[a]) In CD_3CN. [b]) ± 0.3 kJ mol⁻¹. [c]) ±8%. [d]) +: Product observed, –: product not observed. [e]) CD_2Cl_2. [f]) The rearrangement was complete after stirring (*Z*)-**3g** for 2 hours at 298 K in CH_2Cl_2. [g]) Rearrangement required melting of the compound (m. p. 109–111°C).



Scheme 3

are about 10 kJ mol⁻¹ higher than those of the (*Z*)-forms **3**. The $\Delta G^{\neq}$ values for **3a–e** are comparable to barriers reported for Beckmann rearrangements of the corresponding O-tosyloximes [16] and of the free oximes in concentrated sufuric acid [17].

According to *ab initio* calculation the Beckmann rearrangement of protonated formaldehyde oxime is a concerted reaction with a transition structure possessing C_s symmetry, in which the migrating H atom and the leaving group H_2O are situated trans with respect to each other, in accord with the experimental results [18–20].

Beckmann rearrangement of compounds **3** should give nitrilium salts **2** plus secondary amides **4** (Scheme 1). However, we never observed even a trace of these products in the ^1H NMR spectra of rearranging **3**. Instead, mixtures of up to four different *N*-acylamidinium salts **5–8** were formed (Table 2). For instance, from both geometrical isomers of the eight- and thirteen-membered oxime adducts **3d,e** mixtures of **5–8d,e** were formed. The ratios **5/6/7/8** were found to be independent of the configuration of **3d,e**. Mixtures of **5–8d,e** with similar compositions were produced by reactions of the cyclic nitrilium salts **2d,e** with *N*-methylacetamide **4a** [21]. A single compound **5f** was isolated after Beckmann rearrangement of (*Z*)-**3f** as well as from the reaction of the *N*-phenylbenzonitrilium salt **2f** with **4a**. These coincidences speak for nitrilium salts **2** and secondary amides **4** as the primary products of the Beckmann rearrangement of **3**, in agreement with the literature [2, 3]. The *N*-acylamidinium salts **5–8** are formed by fast subsequent reactions of **2** with **4** according to the mechanism reported previously [21]. The formation of **5** and **6** is shown in Scheme 3 for the cyclic oximes **1a–e**.

The configuration of the activated oxime **3** is retained in the amide **4a**. This is concluded from the observation that the cyclohexanone derivative (*Z*)-**3b** gave a single product **5b**, while from (*E*)-**3b** a 1:1 mixture of **5b** and **6b** was obtained. Open-chain secondary amides such as **4a** exist in solution mainly in the (*Z*)-configuration [22]. For **4a** barriers to geometrical isomerization $\Delta G^{\neq}_{E\to Z}$ = 75 kJ mol⁻¹ and $\Delta G^{\neq}_{Z\to E}$ = 87 kJ mol⁻¹ (in 1,2-dichloro-ethane) have been reported [23, 24]. Provided the reaction of **2b** with **4a** is faster than the

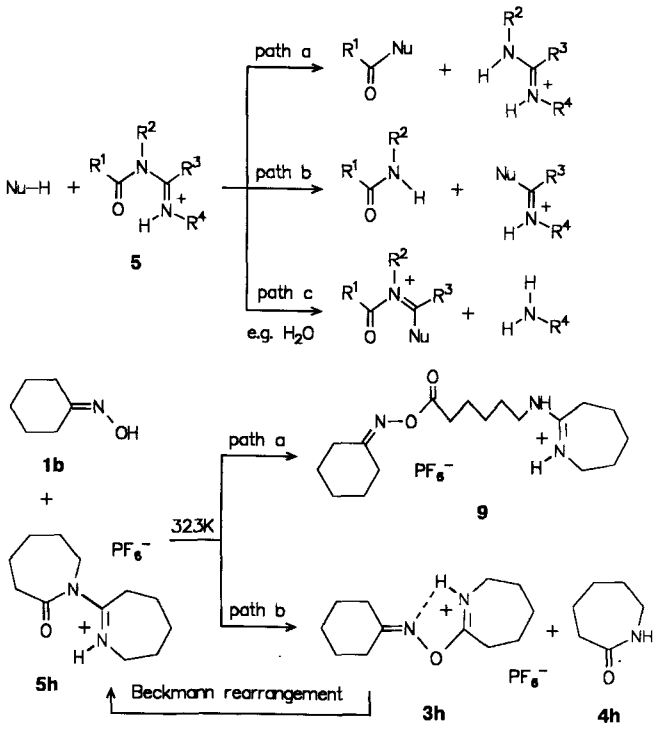
geometrical isomerization of **4a**, and the steady state concentrations of these components are low, the formation of only **5b** from (*Z*)-**4a** and the cyclic nitrilium salt **2b**, and of both **5b** and **6b** from (*E*)-**4a** and **2b** can be understood. These assumptions are fulfilled for the strained seven-membered nitrilium salt **2b**, while for the less strained eight-, nine- and thirteen-membered salts **2c,d,e** geometrical isomerization of **4a** is faster than its reaction with **2c,d,e**. The cyclic nitrilium salts **2d,e** are stable enough for isolation [21].

It has been pointed out earlier that the prototropic rearrangement (*E,Z*)-**I** → (*E,Z*)-**I'** (and vice versa) is an *inter*molecular autocatalyzed reaction, which is slowed down with increasing dilution of **2** [21]. The steady state concentration of **2** in Beckmann rearrangements is low. For the Beckmann rearrangement of (*Z*)-**3b** the rate of the product formation (*E,Z*)-**Ib** → **5b** must be much faster than the competing prototropy (*E,Z*)-**Ib** → (*E,Z*)-**I'b**.

The question why this does not apply for the even more strained six-membered nitrilium salt **2a** remains open. The production of **8a** as well as of **6a** by Beckmann rearrangement of (Z)-**3a** requires the intermediacy of (*E,Z*)-**I'a**. From (*E,Z*)-**I'a** the *N*-methylacetonitrilium salt **2'a** is formed, which reacts with *N*-methylacetamide **4a** to afford **8a**. Competing with this reaction is the rearrangement of (*E,Z*)-**I'a** to **6a** via (*E,E*)-**I'a**.

We are still left with the question why Meerwein's catalytic Beckmann rearrangement works with benzophenone oxime but not with other oximes. In the beginning of the cycle there is a large excess of oxime **1** while the steady state concentration of the nitrilium salt **2** is low during the whole reaction. Meerwein's cycle should still work if the nitrilium salt **2** would react much faster with the oxime **1** than with the amide **4**. Apparently, this is not generally the case. Even under Meerwein's catalytic conditions *N*-acylamidinium salts **5–8** are formed, which undergo consecutive reactions, for instance, with excess of oxime. Nucleophiles NuH are known to react with *N*-acylamidinium ions (e.g. **5**) at both nucleophilic centers to furnish either an acylated nucleophile (path a) or an amide (path b, Scheme 4). Hydrolysis of N-acylamidinium salts often proceeds along path c [11].

The *N*-acylamidinium salt **5h** was prepared by independent methods. Reaction with cyclohexanone oxime **1b** afforded mixtures of **3–5h** and **9**. For instance, reaction of one equivalent of **5h** with one equivalent of cyclohexanone oxime **1b** afforded a mixture of **9**, ε-caprolactam **4h**, and **5h** (1.00:0.54:1.38). Starting with **5h** and **1b** (1:10) at a temperature, at which **3h** undergoes Beckmann rearrangement, a mixture **9/4h** (1.35:1.00) containing no **5h** was obtained. Compound **9** is the product of the reaction of the *N*-acylamidinium salt with a nucleophile along path a.



Scheme 4

In conclusion, the problem of Meerwein's catalytic Beckmann rearrangement is the fact that *N*-acylamidinium salts are attacked by oximes on both electrophilic centers. Hence, side products such as **9** accumulate. If only path b would be operative Meerwein's proposal should still work.

These results lead to the conclusion that catalytic Beckmann rearrangements of unprotected oximes to unprotected secondary amides are not feasable. A catalyzed Beckmann rearrangement requires protected oximes, e.g. sulfonic esters, which are formed in concentrated sulfuric acid, or O-silylated oximes, the starting materials of Mukaiyama's catalytic Beckmann rearrangement [7, 8]. The amides should accumulate in a form, e.g. as salts or O-silylated isoamides, which does not react with nitrilium salts.

This work was supported by the *Fonds der Chemischen Industrie* and by the *Deutscher Akademischer Austauschdienst* (P. B. Shrestha-Dawadi). We would like to thank Prof. Dr. H. Fischer, *Universität Konstanz*, for his help with the X-ray structural analysis, and Mr. S. Herzberger for technical assistance.

Experimental

The melting points are uncorrected. All solvents were dried by standard methods. All experiments were carried out with exclusion of moisture. NMR: Bruker WM-250 and AC-250

spectrometers; CD_3CN; TMS as internal standard; δ-scale; J: Hz. IR: Perkin-Elmer, FTIR 1600 and 1320 spectrometers; CH_2Cl_2; cm^{-1}; m: multiplet; dq: doublet of quartets; b: broad; sh: shoulder.

(Z)-[1-(Cyclopentylideneaminooxy)ethylidene]methylammonium Hexachloroantimonate ((Z)-**3a**)

A solution of **1a** [25] (0.99 g, 10 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a cold (–50 °C) suspension of **2'a** [26] (4.69 g, 12 mmol) in CH_2Cl_2 (30 ml). Slow (2h) warming to 0 °C, cooling again to –20 °C and slow addition of pentane (50 ml) afforded a yellow precipitate (4.60 g, 94%), which was first reprecipitated at –30 °C from CH_2Cl_2 (20 ml)/Et_2O (80 ml) and then at 23 °C from CH_2Cl_2 (30 ml)/pentane (50 ml) to furnish a moisture and temperature sensitive colorless powder (3.33 g, 68%); m.p. 78–79 °C (dec). Crystallization at –20 °C from MeCN/Et_2O afforded a few crystals suitable for the X-ray structural analysis. – IR: 1516, 1652, 1675. – ^{1}H NMR: 1.87 (m, 4H), 2.58 (m, 2H), 2.74 (m, 2H) (CH_2), 2.51 (quint,J=0.9), 3.05 (dq,J=5.3 and 0.9) (CH_3), 9.18 (NH, b, coupl. to 3.05). – ^{13}C NMR: 19.5, 25.1, 26.0, 30.0, 31.0, 32.1 (CH_3, CH_2), 179.5 (b), 181.7 (C=N). – $C_8H_{15}Cl_6N_2OSb$ (489.7): calcd. C 19.62, H 3.09, N 5.72; found C 19.45, H 3.09, N 5.73.

X-Ray Diffraction Analysis of *(Z)-3a* [15]

$[C_8H_{15}N_2O]SbCl_6 \cdot (C_2H_5)_2O$, crystal size 0.5 × 0.5 × 0.5 mm^3, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 965.8(3)$, $b = 1633.8(5)$, $c = 1482.8(6)$ pm, $\beta = 97.17(3)°$, $V = 23214(1) \cdot 10^6$ pm^3, $d_{calc} = 1.61$ Mgm^{-3}, $T = 250$ K, $\mu_{Mo\text{-}K\alpha} = 18.86$ cm^{-1}, Wyckoff-scan, speed variable 200 to 29.30° min^{-1} in ω, $2.39 \leq \vartheta \leq 27.00°$, 5344 collected reflections, 5053 independent reflections, 4177 observed reflections [$I > 2\sigma(I)$]. The cell constants and the intensities of the reflections were measured on a Siemens R3m/V diffractometer with a graphite monochromator, $\lambda_{Mo\text{-}K\alpha} = 71.073$ pm. The structure was solved using the program DIRDIF [27]. Refinement was done with the program SHELXL-93. The positions of nine hydrogen atoms were obtained from a difference Fourier analysis. The strongly disordered carbon atoms of Et_2O were refined isotropically. Atom C3 had to be split into two positions, C3A and C3B, which were refined isotropically. The non-hydrogen atoms were refined anisotropically leading to agreement factors $R(F) = 0.049$, $wR(F^2) = 0.131$ (observed reflections).

(E)-[1-(Cyclopentylideneaminooxy)ethylidene]methylammonium Hexachloroantimonate ((E)-**3a**)

A mixture of **1a** (1.19 g, 12 mmol) and **2'a** (3.91 g, 10 mmol) in CH_2Cl_2 (40 ml) was stirred at 10 °C for 1h. Slow addition of pentane (50 ml) afforded a yellow precipitate (4.26 g, 87%), which was reprecipitated from CH_2Cl_2 (40 ml)/pentane (40 ml) to furnish a moisture sensitive colorless powder (4.11 g, 84%); m.p. 117–119 °C (dec). – IR: 1484, 1659(sh), 1682. – ^{1}H NMR: 1.87 (m, 4H), 2.60 (m, 2H), 2.71 (m, 2H) (CH_2), 2.42, 3.16 (d, J=4.9) (CH_3), 9.50 (NH, b, coupl. to 3.16). – ^{13}C NMR: 16.8, 25.2, 25.9, 31.3, 32.1, 32.4 (CH_3, CH_2), 177.1, 183.1(C=N). – $C_8H_{15}Cl_6N_2OSb$ (489.7): calcd. C 19.62, H 3.09, N 5.72; found C 19.57, H 3.25, N 5.72.

(Z)-[1-(Cyclohexylideneaminooxy)ethylidene]methylammonium Hexachloroantimonate ((Z)-**3b**)

From **1b** [28] (1.13 g, 10 mmol) and **2'a** (4.69 g, 12 mmol) as described for (Z)-**3a**. Precipitation by slow addition of CCl_4 (100 ml) at –50 °C afforded a temperature and moisture sensitive colorless powder (3.98 g, 79%); m.p. 58–60 °C (dec). – IR: 1520, 1648 (sh), 1675. – ^{1}H NMR: 1.71 (m, 6H), 2.38 (m, 2H), 2.67 (m, 2H) (CH_2), 2.52 (quint, J=0.9), 3.05 (dq, J=5.2 and 0.9) (CH_3), 9.26 (NH, b, coupl. to 3.05). – ^{13}C NMR (263 K): 27.6, 27.8, 30.0, 31.8 (CH_3, CH_2), 174.3, 179.5 (C=N). – $C_9H_{17}Cl_6N_2OSb$ (503.7): calcd. C 21.46, H 3.40, N 5.56; found C 21.44, H 3.50, N 5.41.

(E)-[1-(Cyclohexylideneaminooxy)ethylidene]methylammonium Hexachloroantimonate ((E)-**3b**)

From **1b** (1.36 g, 12 mmol) and **2'a** (3.91 g, 10 mmol) as described for (E)-**3a**. However, the mixture was stirred at 10 °C for only 15 min. Yield: 4.79 g (95%) of a temperature and moisture sensitive pale yellow powder; m.p. 108–110 °C (dec). – IR: 1486, 1648(sh), 1683. – ^{1}H NMR (263 K): 1.72 (m, 6H), 2.42 (m, 2H), 2.68 (m, 2H) (CH_2), 2.43, 3.17 (d, J= 5.1) (CH_3), 9.56 (NH, b, coupl. to 3.17). – ^{13}C NMR (263 K): 16.9, 25.5, 26.6, 27.6, 28.1, 31.9, 32.2 (CH_3, CH_2), 175.7, 177.0 (C=N). – $C_9H_{17}Cl_6N_2OSb$ (503.7): calcd. C 21.46, H 3.40, N 5.56; found C 21.37, H 3.51, N 5.53.

(Z)-[1-(Cycloheptylideneaminooxy)ethylidene]methylammonium Hexachloroantimonate ((Z)-**3c**)

From **1c** [29] (1.27 g, 10 mmol) and **2'a** (4.69 g, 12 mmol) as described for (Z)-**3b**. Precipitation by slow addition of CCl_4 (80 ml) afforded a temperature and moisture sensitive colorless powder (4.38 g, 87%); m.p. 76–79 °C (dec). – IR: 1517, 1623, 1673. – ^{1}H NMR(273 K): 1.58–1.80 (m, 8H), 2.54 (m, 2H), 2.79 (m, 2H) (CH_2), 2.50 (quint, J=0.9), 3.05 (dq, J=5.2 and 0.9) (CH_3), 9.25 (NH, b, coupl. to 3.05). – ^{13}C NMR (273 K): 19.5, 24.7, 27.7, 30.0, 30.5, 30.6, 31.3, 33.3 (CH_3, CH_2), 178.1, 179.4(C=N). – $C_{10}H_{19}Cl_6N_2OSb$ (517.7): calcd. C 23.20, H 3.70, N 5.41; found C 23.22, H 3.87, N 5.58.

(E)-[1-(Cycloheptylideneaminooxy)ethylidene]methylammonium Hexachloroantimonate ((E)-**3c**)

From **1c** (1.53 g, 12 mmol) and **2'a** (3.91 g, 10 mmol) as described for (E)-**3b**. Yield: 4.92 g (95%) of a colorless moisture sensitive powder; m.p. 99–101 °C (dec). – IR: 1489, 1631, 1681. – ^{1}H NMR (273 K): 1.61–1.77(m, 8H), 2.58 (m, 2H), 2.78 (m, 2H) (CH_2), 2.43, 3.16 (d, J=5.3) (CH_3), 9.60 (NH, b, coupl. to 3.16). – ^{13}C NMR (273 K): 16.9, 24.8, 27.4, 30.4, 30.6, 31.4, 32.0, 33.8 (CH_3, CH_2), 176.9, 179.3 (C=N). – $C_{10}H_{19}Cl_6N_2OSb$ (517.7): calcd. C 23.20, H 3.70, N 5.41; found C 23.28, H 4.00, N 5.43.

(Z)-[1-(Cyclooctylideneaminooxy)ethylidene]methylammonium Hexachloroantimonate ((Z)-**3d**)

From **1d** [29] (1.41 g, 10 mmol) and **2'a** (3.91 g, 10 mmol) as described for (Z)-**3b**. Precipitation by slow addition of CCl_4 (50 ml) afforded a temperature and moisture sensitive colorless powder (3.14 g, 59%); m.p. 73–75 °C (dec). – IR: 1517,

1625(sh), 1672. – ^{1}H NMR (273 K): 1.42–1.92 (m, 10H), 2.46 (m, 2H), 2.64 (m, 2H) (CH_2), 2.50 (quint, J=0.8), 3.06 (dq, J=5.2 and 0.9) (CH_3), 9.34 (NH, b, coupl.to 3.06). – ^{13}C NMR (273 K): 19.5, 23.4, 25.7, 26.2, 26.6, 28.0, 29.3, 30.0, 33.2 (CH_3, CH_2), 178.8, 179.4 (C=N). – $C_{11}H_{21}Cl_6N_2OSb$ (531.8): calcd. C 24.85, H 3.98, N 5.27; found C 24.67, H 3.95, N 5.27.

(E)-[1-(Cyclooctylideneaminooxy)ethylidene]methylammonium Hexachloroantimonate ((*E*)-**3d**)

From **1d** (1.70 g, 12 mmol) and **2'a** (3.91 g, 10 mmol) as described for (*E*)-**3b**. Yield after reprecipitation from CH_2Cl_2 (40 ml)/pentane (40 ml): 4.34 g (82%) of a colorless moisture sensitive powder; m.p. 107–108 °C (dec). – IR: 1485, 1628, 1680. – ^{1}H NMR (273 K): 1.39–1.62 (m, 6H), 1.76-1.93 (m, 4H), 2.50(m,2H), 2.64(m, 2H) (CH_2), 2.45, 3.17 (d, J=5.2) (CH_3), 9.56 (NH, b, coupl. to 3.17). – ^{13}C NMR (273 K): 17.0, 23.5, 25.6, 26.2, 26.8, 28.0, 29.4, 31.9, 33.6 (CH_3, CH_2), 176.1, 180.3 (C=N). – $C_{11}H_{21}Cl_6N_2OSb$ (531.8): calcd. C 24.85, H 3.98, N 5.27; found C 24.69, H 3.95, N 5.21.

(Z)-[1-Cyclododecylideneaminooxy)ethylidene]methylammonium Hexachloroantimonate ((Z)-**3e**)

From **1d** [29] (1.97 g, 10 mmol) and **2'a** (3.91 g, 10 mmol) as described for (Z)-**3a**. However, the mixture was stirred at –50 °C for 1h. Precipitation by slow addition of pentane (60 ml) and reprecipitation at –30 °C from CH_2Cl_2 (20 ml)/MeCN (10 ml)/Et_2O (100 ml) afforded a temperature and moisture sensitive colorless powder (2.86 g, 49%); m.p. 71–74 °C (dec). – IR: 1517, 1637(sh), 1674. – ^{1}H NMR (273 K): 1.33, 1.37, 1.71 (m's, 18H), 2.54 (m, 2H), 2.60 (m, 2H) (CH_2), 2.53 (b), 3.08 (dq, J=5.2, 0.8) (CH_3), 9.36 (NH, b, coupl. to 3.08). – ^{13}C NMR (273 K): 19.8, 22.7, 23.1, 23.2, 23.7, 23.8, 24.1, 25.0, 26.3, 26.4, 30.2, 30.3, 30.9 (CH_3, CH_2), 174.0, 179.7 (C=N). – $C_{15}H_{29}Cl_6N_2OSb$ (587.9): calcd. C 30.65, H 4.97, N 4.77; found C 30.61, H 4.97, N 4.75.

(E)-[1-(Cyclododecylideneaminooxy)ethylidene]methylammonium Hexachloroantimonate ((E)-**3e**)

From **1e** (2.37 g, 12 mmol) and **2'a** (3.91 g, 10 mmol) as described for (*E*)-**3a**. However, the mixture was stirred at 0 °C for 15 min. Yield after reprecipitation from CH_2Cl_2 (40 ml)/pentane (40 ml): 4.84 g (82%) of a temperature and moisture sensitive colorless powder; m.p. 101–102 °C (dec). – IR: 1633, 1681. – ^{1}H NMR: 1.33, 1.38, 1.69, 1.80 (m's,18H), 2.56 (m, 2H), 2.62 (m, 2H) (CH_2), 2.44, 3.19 (d, J= 5.4) (CH_3), 9.46 (NH, b, coupl. to 3.19). – ^{13}C NMR: 17.0, 23.2, 23.3, 23.6, 24.0, 24.1, 24.8, 25.3, 26.0, 26.3, 30.4, 31.7, 32.2 (CH_3 ,CH_2), 176.3, 177.0 (C=N). – $C_{15}H_{29}Cl_6N_2OSb$ (587.9): calcd. C 30.65, H 4.97, N 4.77; found C 30.74, H 4.95, N 4.76.

(Z)-[1-(Diphenylmethyleneaminooxy)ethylidene]methylammonium Hexachloroantimonate ((*Z*)-**3f**)

From **1f** [30] (1.97 g, 10 mmol) and **2'a** (3.91 g, 10 mmol) as described for (Z)-**3e**. However, the product was precipitated at –50 °C by slow addition of CCl_4 (50 ml). Yield: 5.00 g (85%) of a pale yellow powder; m.p. 82–86 °C (dec). – IR: 1513, 1679. – ^{1}H NMR (263 K): 2.72, 2.77 (d, J=5.2) (CH_3), 7.44–7.66 (m, phenyl), 9.46 (NH, b, coupl. to 2.77). – ^{13}C NMR (263 K): 19.6, 30.2 (CH_3), 168.7, 179.7 (C=N). – $C_{16}H_{17}Cl_6N_2OSb$ (587.8): calcd. C 32.69, H 2.92, N 4.77; found C 32.45, H 3.13, N 4.81.

(Z)- and *(E)-[1-(Isopropylideneaminooxy)ethylidene]methylammonium Hexachloroantimonate* ((Z)-**3g**)

From **1g** [29] (0.73 g, 10 mmol) and **2'a** (3.91 g, 10 mmol). After stirring at –50 °C for 2h the product was precipitated by slow addition of CCl_4 (50 ml). Yield: 3.71 g (80%) of the pure (Z)-form; m.p. 109–111 °C (dec). – IR: 1520, 1679. – ^{1}H NMR (263 K): 2.08, 2.15, 2.52 (quint, J=0.9), 3.08 (dq, J=5.1 and 0.5) (CH_3), 9.34 (NH, b, coupl. to 3.08). – ^{13}C NMR (263 K): 17.8, 19.6, 21.5, 30.1 (CH_3), 170.4, 179.3 (C=N). – $C_6H_{13}Cl_6N_2OSb$(463.7): calcd. C 15.54, H 2.83, N 6.04; found C 15.38, H 2.90, N 5.95.
At 25 °C in the course of 12h isomerization to an (Z)/(E)-equilibrium (1:4) took place. The pure (*E*)-form could not be obtained. – ^{1}H NMR: 2.11, 2.16, 2.44 (b), 3.17 (d, 5.2) (CH_3), 9.55 (NH, b, coupl. to 3.17). – ^{13}C NMR: 16.8, 18.0, 21.8, 32.1 (CH_3), 172.0, 177.1 (C=N).

7-(Cyclohexylideneaminooxy)-3,4,5,6-tetrahydro-2H-azepinium Hexachloroantimonate (**3h**)

Crude **10** (X = $OPCl_4$) was prepared from **4h** (1.13 g, 10 mmol). The yellow product was dissolved in CH_2Cl_2 (10 ml). A solution of **1b** (1.13 g, 10 mmol) in CH_2Cl_2 (10 ml) was added dropwise. After stirring at 20 °C for 1h and cooling to 0 °C a solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 ml) was added dropwise. Stirring at 20 °C for 2h, filtration from a turbidity, cooling to 0 °C, and slow addition of pentane (40 ml) afforded a temperature sensitive colorless powder (5.33 g, 98%), which was crystallized at –18 °C from CH_2Cl_2 (25 ml)/CCl_4 (5 ml) to furnish colorless leaflets; m.p. 102–104 °C (dec). – IR: 1630, 1710. – ^{1}H NMR (273 K): 1.81 (m, 12H), 2.90 (m, 4H), 3.74 (m, 2H), 3.90 (m, 2H), 11.92 (NH, b). – ^{13}C NMR (273 K): 21.8, 23.7, 26.2, 28.3, 28.7, 29.7, 31.0, 39.9, 46.8, 50.4 (CH_2), 176.4, 182.9 (C=N). – $C_{12}H_{21}Cl_6N_2OSb$ (543.8): calcd. C 26.50, H 3.89, N 5.15; found C 26.60, H 4.02, N 5.16.

[1-(Hexahydro-2-oxo-2H-azepin-1-yl)ethylidene]methylammonium Hexachloroantimonate (**5b**)

A solution of (Z)-**3b** (5.04 g, 10 mmol) in CH_2Cl_2 (20 ml) was boiled under reflux for 60 min. After addition of pentane (80 ml) the mixture was kept at –20 °C for 12h. Filtration afforded a pale yellow powder (4.37 g, 87%), which was crystallized at –20 °C from CH_2Cl_2 (20 ml)/CCl_4 (10 ml) to give a colorless crystalline powder (3.60 g); m.p. 132–134 °C. – IR: 1644, 1710. – ^{1}H NMR: 2.43, 3.22 (d, J=5.0) (CH_3), 1.81 (m, 6H), 2.87(m, 2H), 3.91(m, 2H) (CH_2), 11.94 (NH, b, coupl. to 3.22). – ^{13}C NMR: 18.1, 23.7, 27.8, 28.7, 33.5, 39.9, 50.3 (CH_3, CH_2), 171.9, 183.4 (CO, NCN). – $C_9H_{17}Cl_6N_2OSb$ (503.7): calcd. C 21.46, H 3.40, N 5.56; found C 21.45, H 3.51, N 5.51.

N^1-Benzoyl-N^2-methyl-N^1-phenylacetamidinium Hexachloroantimonate (**5f**)

A suspension of (Z)-**3f** (5.88 g, 10 mmol) in CH_2Cl_2 (20 ml) was stirred at 23 °C for 2 h. After cooling to –20 °C pentane

(160 ml) was added to the clear solution. A pale yellow powder (5.29 g, 90%) was filtered off. Crystallization at –20°C from CH_2Cl_2 (60 ml)/CCl_4 (10 ml) gave colorless leaflets (3.00 g, 51%); m.p. 168–170 °C (dec). – IR: 1648, 1706. – ^{1}H NMR: 2.41, 3.27(d, J=5.2) (CH_3), 7.29–7.54 (phenyl), 10.26 (NH, b, coupl. to 3.27). – ^{13}C NMR: 19.9, 33.5 (CH_3), 129.4, 129.8, 130.2, 131.6, 131.7, 133.5, 133.6, 137.5 (phenyl), 172.4, 173.7(CO, CN). – $C_{16}H_{17}Cl_6N_2OSb$ (587.8): calcd. C 32.69, H 2.92, N 4.77; found C 32.62, H 2.97, N 4.95.

N^1-Acetyl-N^1,N^2-dimethylacetamidinium Hexachloroantimonate (**5g**)

A mixture of (*E*),(Z)-**3g** or (*Z*)-**3g** (4.64 g, 10 mmol) was kept at 115 °C for 15 min. According to the ^{1}H NMR spectrum the resulting brown product consisted of **5g** [11] (80%) and unidentified products of decomposition (20%). – ^{1}H NMR: 2.43, 2.44, 3.24 (d, J=5.1), 3.40 (CH_3), 11.96 (NH, b, coupl. to 3.24). – ^{13}C NMR: 18.3, 26.4, 33.6, 37.8 (CH_3), 172.2, 179.5(CO, CN).

[1-(Hexahydro-2-oxo-2H-azepin-1-yl)ethylidene]methylammonium Hexachloroantimonate (**5b**) and *3,4,5,6-Tetrahydro-7-(N-methylacetamido)-2H-azepinium Hexachloroantimonate* (**6b**)

A mixture of **4h** (1.13 g, 10 mmol) and **2'a** (3.91 g, 10 mmol) was stirred at 23 °C in CH_2Cl_2 (40 ml) for 30 min. Cooling to –20 °C and slow addition of pentane (100 ml) afforded a colorless powder (4.79 g, 95%; ^{1}H NMR: **5b/6b** (1:1)), which was purified by stirring in boiling CH_2Cl_2 (25 ml) for 15 min. Cooling and slow addition of pentane (80 ml) afforded a colorless powder (^{1}H NMR: **5b/6b** (2:1)); m.p. 123–125 °C. – ^{1}H NMR: **6b**: 2.43, 3.42 (CH_3), 2.99 (m), 3.75 (m) (CH_2), 11.95 (NH, b, coupl. to 3.75). – ^{13}C NMR: **6b**: 21.4, 26.3, 26.4, 29.7, 31.1, 38.0, 46.7(CH_3, CH_2), 176.6, 178.9 (C=N). – $C_9H_{17}Cl_6N_2OSb$ (503.7): calcd. C 21.46, H 3.40, N 5.56; found C 21.38, H 3.43, N 5.49.

7-(Hexahydro-2-oxo-2H-azepin-1-yl)-3,4,5,6-tetrahydro-2H-azepinium Hexachloroantimonate (**5h**)

a) A mixture of crude **10** (X = $OPCl_4$) (10 mmol) and **4h** (1.13 g, 10 mmol) in CH_2Cl_2 (20 ml) was stirred for 2h. After cooling to –40 °C a solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 ml) was added dropwise. After stirring for 1h pentane (80 ml) was added and the mixture was left at –20 °C for 12h. A pale yellow powder (3.87 g, 71%) was filtered off. Crystallization at –20 °C from CH_2Cl_2 (30 ml)/CCl_4 (10 ml) afforded colorless prisms; m.p. 148–151°C (dec). – IR: 1635, 1710. – ^{1}H NMR: 1.81 (m, 12H), 2.90 (m, 4H), 3.74(m,2H), 3.90 (m, 2H) (CH_2), 11.92 (NH, b). – ^{13}C NMR: 21.8, 23.7, 26.2, 28.3, 28.7, 29.7, 31.0, 39.9, 46.8, 50.4 (CH_2), 176.4, 182.9 (CO, CN). – $C_{12}H_{21}Cl_6N_2OSb$ (543.8): calcd. C 26.50, H 3.89, N 5.16; found C 26.23, H 3.99, N 5.16.

b) A solution of **3h** (5.44 g, 10 mmol) in $ClCH_2CH_2Cl$ (20 ml) was boiled under reflux for 1h. Evaporation of the solvent afforded a powder (5.40 g, 99%), which was crystallized at –20 °C from CH_2Cl_2 (40 ml)/CCl_4 (20 ml) to furnish a colorless powder; m.p. 147–150 °C (dec).

7-(Hexahydro-2-oxo-2H-azepin-1-yl)-3,4,5,6-tetrahydro-2H-azepinium Hexafluorophosphate (**5h**, X = PF_6)

A mixture of crude **10** (X = $OPCl_4$) (100 mmol) and **4h** (11.32 g, 100 mmol) in acetonitrile (100 ml) was stirred for 2h. KPF_6 (18.41 g, 100 mmol) was added. After stirring for 24h the suspension was filtered, and the solvent of the filtrate was evaporated. The remaining oil was stirred in CH_2Cl_2 (100 ml) for 30 min. After filtration CCl_4 (50 ml) was added. At –20 °C a pale yellow powder crystallized (21.00 g, 59%), which was dissolved in CH_2Cl_2 (100 ml). After filtration CCl_4 (30 ml) was added. At –20 °C a colorless powder (15.78 g, 45%) crystallized; m.p. 145–147 °C. – IR: 1635, 1710. – ^{1}H NMR: 1.79 (m, 12H), 2.89 (m, 4H), 3.70 (m, 2H), 3.89 (m, 2H) (CH_2), 11.89 (NH, b). – ^{13}C NMR: 21.6, 23.5, 26.1, 28.1, 28.7, 29.7, 30.8, 39.8, 46.6, 50.2 (CH_2), 176.4, 182.9 (CO, CN). – $C_{12}H_{21}F_6N_2OP$ (354.3): calcd. C 40.68, H 5.98, N 7.91; found C 40.74, H 6.03, N 7.79.

7-(Cyclohexylideneaminooxycarbonylpentamethyleneamino)-3,4,5,6-tetrahydro-2H-azepinium Hexafluorophosphate (**9**)

a) A solution of **5h** (X = PF_6) (3.54 g, 10 mmol) and **1b** (2.26 g, 20 mmol) in $ClCH_2CH_2Cl$ (40 ml) was boiled under reflux for 1h. Evaporation of the solvent afforded a brown oil, which was crystallized at –20 °C from CH_2Cl_2 (40 ml)/$CHCl_3$ (20 ml)/Et_2O (20 ml). Yield: 2.88 g (62%) of a colorless powder; m.p. 90–92 °C. – IR: 1655, 1740. – ^{1}H NMR (273 K): 1.40 (m, 2H), 1.64 (m, 16H), 2.29 (m, 2H), 2.41 (t, J=7.4, 2H), 2.53 (m, 2H), 2.63 (m, 2H), 3.13 (m, 2H), 3.44 (m, 2H) (CH_2), 7.61 (2H, NH, b). – ^{13}C NMR (273 K): 24.1, 24.9, 25.9, 26.7, 27.3, 27.4, 27.8, 28.4 (2C), 30.0, 32.6, 33.0, 33.1, 42.9, 44.8 (CH_2), 170.3, 170.4, 172.3 (CO, CN). – $C_{18}H_{32}F_6N_3O_2P$ (467.4): calcd. C 46.25, H 6.90, N 8.99; found C 46.05, H 6.85, N 9.02.

b) A mixture of crude **11** (3.37 g, 12 mmol), **1b** (1.13 g, 10 mmol) and pyridine (1.42 g, 18 mmol) in CH_2Cl_2 (20 ml) was stirred at 5 °C for 24h. The solvent was evaporated and the residue was dissolved in $CHCl_3$ (30 ml). The solution was shaken with 1 M aqueous HCl (30 ml) and then with H_2O (30 ml). Drying over Na_2SO_4 and evaporation of the solvent afforded 2.85 g (80%) of the oily chloride **9**. The product (3.58 g, 10 mmol) was dissolved in MeCN (25 ml) containing KPF_6 (1.84 g, 10 mmol). The mixture was stirred at 25 °C for 24h. Filtration from KCl and evaporation of the solvent afforded pure **9** (3.69 g, 79%).

7-Chloro-3,4,5,6-tetrahydro-2H-azepinium Hexachloroantimonate (**10**, X = $SbCl_6$)

A solution of **4h** (1.13 g, 10 mmol) in toluene (10 ml) was added dropwise to a solution of PCl_5 (2.08 g, 10 mmol) in toluene (10 ml). After stirring at 23 °C for 3h the solvent was evaporated under reduced pressure. The yellow residue (**10**, X = $OPCl_4$) was dissolved in CH_2Cl_2 (15 ml). At –40 °C a solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (15 ml) was added dropwise. Stirring was continued at –40 °C for 30 min. Slow addition of CCl_4 (40 ml) at –20 °C afforded a yellow powder (4.40 g, 94%), which was precipitated at –20 °C from CH_2Cl_2 (25 ml)/CCl_4 (5 ml)/MeCN (0.1 ml) to give a colorless powder; m.p. 162–164 °C (dec). – IR: 1655. – ^{1}H NMR: 1.81–

1.97 (m, 6H), 3.27 (m, 2H), 3.86 (m, 2H) (CH_2), 11.75 (NH, b). – ^{13}C NMR: 22.0, 24.7, 29.3, 41.6, 41.6, 51.5(CH_2), 186.6 (C=N, b). – $C_6H_{11}Cl_7NSb$ (467.1): calcd. C 15.43, H 2.37, N 3.00; found C 15.42, H 2.41, N 3.03.

7-(Chlorocarbonylpentamethyleneamino)-3,4,5,6-tetrahydro-2H-azepinium Chloride (**11**)

N-(3,4,5,6-tetrahydro-2*H*-azepinyl-7)-5-aminohexanoic acid [31, 32] (10 mmol) prepared *in situ* from *O*-methyl ε-caprolactim and 6-aminohexanoic acid [33] was dissolved in 2 M aqueous HCl (10 ml). After evaporation of most of the water the residue was dissolved in $SOCl_2$ (20 ml). The mixture was stirred at 25 °C for 12h. Evaporation of excess of $SOCl_2$ afforded a pale brown solid (2.67 g, 95%); m.p. 100–102 °C. – IR (nujol): 1655, 1785, 1796. – ^{1}H NMR ($CDCl_3$): 1.51 (m, 2H), 1.75 (m, 10H), 2.87–2.96 (m, 4H), 3.43–3.51 (m, 4H) (CH_2), 9.57 (t, J=5,b), 9.89 (t, J=5, b) (NH). – ^{13}C NMR ($CDCl_3$): 23.9, 24.6, 25.6, 27.2, 28.3, 29.8, 31.9, 42.8, 43.9, 46.9 (CH_2), 168.4, 173.7 (C=O, C=N). – $C_{12}H_{22}Cl_2N_2O$ (281.2): calcd. C 51.25, H 7.89, N 9.96; found C 51.06, H 8.01, N 10.07.

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