On the Reaction of Nitrilium and *N*-Acylamidinium Salts with Oximes and Other Hetero Nucleophiles

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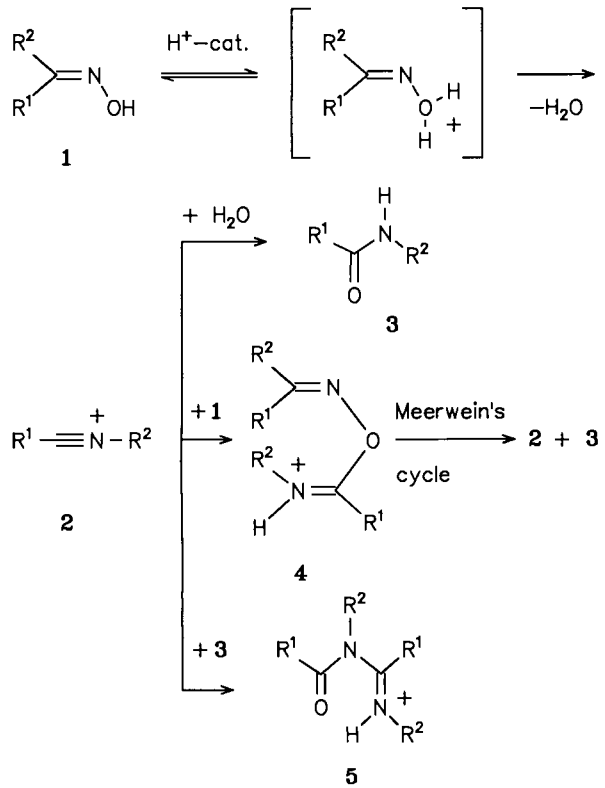
Nitrilium salts **2** add oximes **1** to form stable alkylideneaminooxy-substituted iminium salts **4**. Compounds **4** have been postulated by Meerwein as intermediates of the Beckmann rearrangement of oximes[1]. For (*E*)-**4c** an X-ray structural analysis is performed. Other intermediates of the Beckmann rearrangement are the *N*-acylamidinium salts **5**, which are produced by the reaction of nitrilium salts with amides. As models for the transformation of **5** into amides, the end products of the Beckmann rearrangement, reactions of *N*-acylamidinium salts with nucleophiles, e.g. oximes, alcohols, water, amines, thiols, and benzophenone imine are studied.

Nitrilium ions **2** are believed to be intermediates in the Beckmann rearrangement of oximes **1** to amides **3** (Scheme 1). The amides are formed from the nitrilium ions by addition of the water, which was eliminated from the oxime in the previous reaction step[2,3]. However, in the rearrangement of *free* oximes to *unmodified* (e.g. unprotonated) amides the intermediate nitrilium ions may not only react with water but competitively also with **1** and/or **3** to give adducts **4** and **5**, respectively.

Scheme 1



Meerwein proposed a mechanism for a nitrilium ion-catalyzed Beckmann rearrangement with compounds **4** as intermediates[1]. As far as we know adducts **4** have never been isolated[4].

In the beginnings of the Beckmann rearrangement the concentration of the oxime is high, while the stationary concentration of water is low. Thus, the reaction of the nitrilium ion with the oxime to give an adduct **4** could well be more important than the reaction with water.

In the course of the Beckmann rearrangement the concentration of the amide **3** increases, whereas the concentration of water remains negligible. Thus, as much as the amide **3** accumulates one may have to consider a reaction of the amide with the nitrilium ion to produce an *N*-acylamidinium ion **5**. Recently, we reported the reaction of nitrilium salts **2** with amides **3** to furnish salts **5**[5–14]. However, since not amidinium salts **5** are the end products of the Beckmann rearrangement there must be consecutive reactions, by which the ions **5** are transformed into amides **3**. Conceivable are reactions of **5** with nucleophiles like water or oximes **1**.

Here we describe the isolation of adducts **4**, the X-ray structural determination of (*E*)-**4c**, and reactions of *N*-acylamidinium salts **5** with several heteronucleophiles. Beckmann rearrangements of compounds **4** will be reported in a separate paper.

The nitrilium salts **2a–c** react with acetone oxime (**1a**) to furnish Meerwein's hypothetic adducts **4a–c** as temperature- and moisture-sensitive compounds. At low temperature and in the absence of excess of oxime the adducts **4** were produced stereochemically homogeneously (^{1}H NMR). However, heat (25°C) or traces of oxime catalyze a geometric isomerization to an equilibrium, in which a second isomer predominates (^{1}H NMR). Crystallization afforded the stereochemically pure second isomer. According to Hegarty and Johnson nitrilium ions add nucleophiles stereoelectronically controlled in such a way that the developing lone pair of electrons on the nitrilium nitrogen atom is *trans*-

oriented with respect to the intruding nucleophile[15–17]. Applied to compounds **4**, the primary adducts should be the (*Z*)-forms, which rearrange to the thermodynamically more stable (*E*)-forms (Scheme 2).

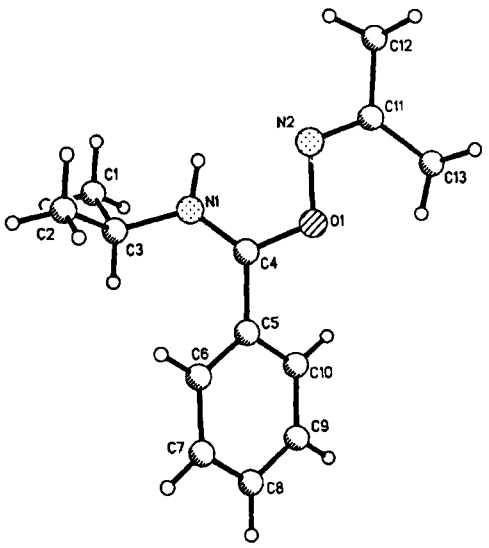


Figure 1. X-Ray crystal structure of the cation (*E*)-**4c**

The (*E*)-configuration of (*E*)-**4c** has been confirmed by an X-ray structural determination (Table 1, Figure 1)[18]. The site of *N*-protonation in **4c** has been inferred from the ^{1}H-NMR spectrum (CD_3CN, 273 K, Table 2), which showed an HN-CH coupling of 10.1 Hz. Similar couplings were observed for compounds **4a, b**. The position of the proton on N1 as shown in Figure 1 has been calculated. The enhanced stability of the (*E*)-isomer as compared to the (*Z*)-form may result from hydrogen bonding N1–H···N2 (distance N1···N2 = 251.6 pm).

Table 1. Selected bond lengths [pm], bond angles, and torsional angles [°] for the cation (*E*)-**4c**

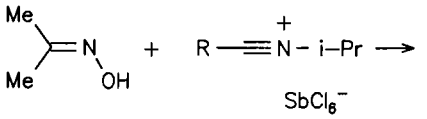
C11-N2	127.7(7)	N1-C3	147.3(8)
N2-O1	146.7(7)	C11-C12	148.1(9)
O1-C4	133.1(7)	C11-C13	149.2(9)
C4-N1	128.0(8)	C11-N2-O1	109.4(5)
C4-C5	146.8(8)	N2-O1-C4	110.3(4)
O1-C4-N1	121.0(5)	C3-N1-C4-C5	-9(1)
C4-N1-C3	128.3(5)	C12-C11-N2-O1	-179.4(7)
C12-C11-N2	114.4(6)	C13-C11-N2-O1	2(1)
C13-C11-N2	125.9(6)	C11-N2-O1-C4	-162.4(7)
O1-C4-C5	112.4(5)	N2-O1-C4-N1	-1.6(9)
N1-C4-C5	126.6(5)	N2-O1-C4-C5	177.5(6)
N1-C3-C1	108.2(5)	O1-C4-N1-C3	169.6(7)
C4-C5-C6	121.4(5)	O1-C4-C5-C6	138.1(7)
C6-C5-C10	119.5(5)	C4-N1-C3-C1	-118.5(8)
N1-C4-C5-C6	-43(1)	C4-N1-C3-C2	119.1(8)

Noteworthy is the large N2–O1 distance [146.7(7) pm] in (*E*)-**4c**. For the N–O bond in benzaldehyde oxime a length of 140 pm has been reported[19,20].

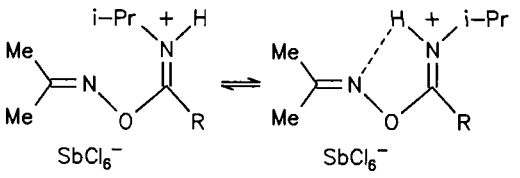
The *N*-acylamidinium salts **6d–n** were prepared by the reaction of nitrilium salts **2** with secondary and tertiary amides (Scheme 2)[5,6]. The reaction cannot be applied to *N*-*tert*-alkylnitrilium salts[21]. For secondary amides clean products were obtained only for $R^1 = R^3$ and $R^2 = R^4$. Otherwise mixtures of compounds were formed. Alternatively, the salts **6** (e.g. **6e, i**) were obtained by acylation of amidines, e.g. **7**[22,23]. Recently, cyclic *N*-tosyl- and *N*-acylamidinium salts have found interesting synthetic applications[14,24].

N-Acylamidinium salts **6** are attacked by nucleophiles Nu–H competitively at both electrophilic centers (Scheme

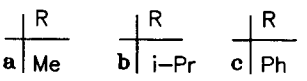
Scheme 2

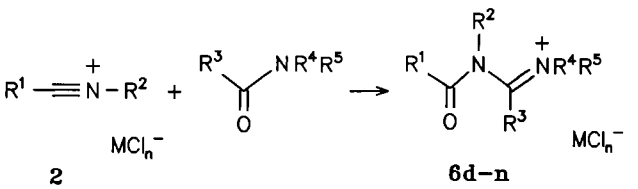


1a **2a–c**

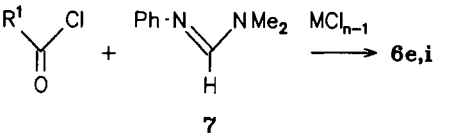


(Z)-4 **(E)-4a–c**





2 **6d–n**



7

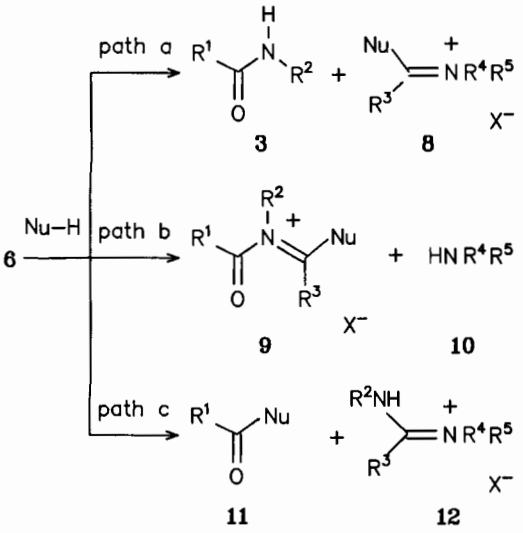
	R^1	R^2	R^3	R^4	R^5
d	Me	Me	H	Me	Me
e	Me	Ph	H	Me	Me
f	Me	Ph	Me	Me	Me
g	Ph	i–Pr	Me	Me	Me
h	Me	Me	Me	Me	Me
i	Ph	Ph	H	Me	Me

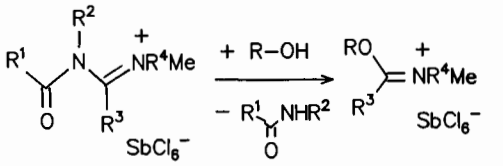
	R^1	R^2	R^3	R^4	R^5
j	Me	Me	Me	Me	H
k	Me	Ph	Me	Ph	H
l	Ph	i–Pr	H	Me	Me
m	Ph	i–Pr	H	Ph	Me
n	i–PrNAc	i–Pr	H	Me	Me

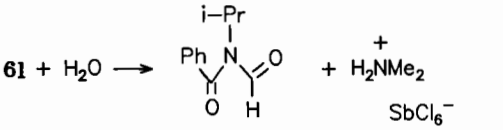
MCl_n=$SbCl_6$ **6i**: MCl_n=$AlCl_4$

3). For $R^3 = H$ nucleophilic attack occurs preferentially on the amidinium carbon atom to produce either an amide **3** plus an iminium salts **8** (path a), or an *N*-acyliminium salt **9** together with an amine **10** (path b). In many cases reactions predominatly occur along path a. Alternatively, nucleophilic attack on the carbonyl carbon atom gives compounds **11** and the amidinium salts **12** (path c). The formamidinium salts **6** ($R^3 = H$) are preparatively useful since they react with nucleophiles in much the same way as do (chloromethylene) ammonium salts (Vilsmeier-Arnold salts)[25,26], however with the advantage that instead of HCl a neutral amide **3** is eliminated[27]. Especially reactive is the carbamoyl derivative **6n**[7], which reacts with heteronucleophiles exclusively along path a.

Scheme 3





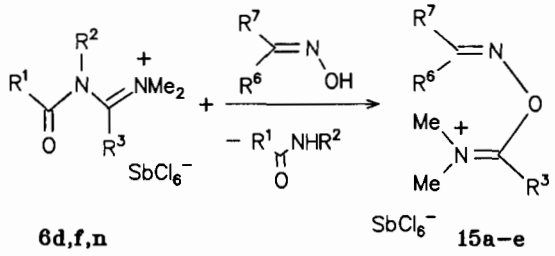


	R		R		R
a	Me	**e**	L–menthyl	**i**	i–Pr
b	Me	**f**	Bn	**j**	L–menthyl
c	Et	**g**	Me		
d	i–Pr	**h**	Et		

Primary and secondary alcohols are acylated by **6** to alkoxyiminium salts **13** (Scheme 3)[28]. No reactions were observed between **6l**, **m** and *tert*-butyl alkohol or phenol.

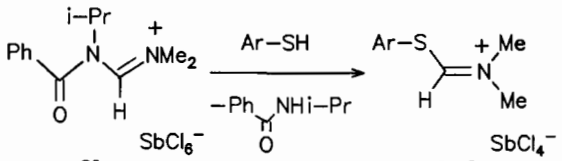
Water gave mixtures of compounds. From **6l** the imide **14** was isolated (Scheme 3, below; according to path b). Hydrolyses of *N*-acylamidinium salts according to path a and b have been reported[22,28–33].

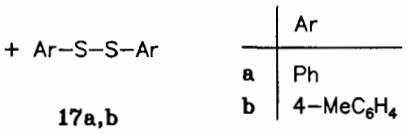
Scheme 4



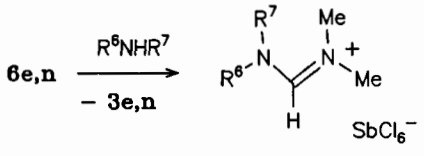
	R^3	R^6	R^7
a	Me	Me	Me
b	H	Me	Me
c	H	2–C_6H_4–C_6H_4–2	

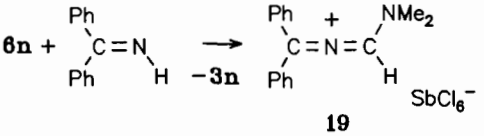
	R^3	R^6	R^7
d	H	H	Ph
e	Me	H	Ph





	Ar
a	Ph
b	4–MeC_6H_4





	R^6	R^7
a	Me	i–Pr
b	H	Ph
c	H	Bn

	R^6	R^7
d	$(CH_2)_5$	
e	Et	Et
f	$(CH_2)_2O(CH_2)_2$	

The reaction of **6** with oximes **1** provided salts **15**, which are closely related to compounds **4** (Scheme 4). In contrast to phenols, thiophenols reacted with **6** to afford the *tetra*-chloroantimonates **16**. The mother liquors of compounds **16** contained the disulfides **17**.

With primary and secondary amines and **6** the amidinium salts **18** were formed (Scheme 4). With benzophenone imine the 2-azoniaallene salt **19** was isolated.

Considering these results it seems doubtful that the intermediate *N*-acylamidinium salts **5** of the Beckmann rearrangement (Scheme 1) are transformed into the secondary amides **3** by hydrolysis with water. More likely, the starting oximes **1** react with **5** to give Meerwein's intermediates **4** plus amides **3**.

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Experimental

Melting points: uncorrected. – IR: Mattson Polaris FT-IR spectrometer. – ^1H and ^{13}C NMR: Bruker AC 250 spectrometer (Table 2). – All experiments were carried out with exclusion of moisture in solvents dried by standard methods.

(E)-Isopropyl[1-(isopropylideneaminooxy)ethylidene]ammonium Hexachloroantimonate [(*E*)-**4a**]: A solution of **1a**[34] (0.73 g, 10 mmol) in CH_2Cl_2 (15 ml) was added dropwise to a suspension of **2a**[35] (4.19 g, 10 mmol) in CH_2Cl_2 (15 ml). After stirring at 23°C for 4 h and cooling to −50°C, ether (80 ml) was added dropwise. Filtration afforded a colorless powder, which was reprecipitated from CH_2Cl_2 (20 ml)/ether (80 ml). Yield: 3.72 g (76%), m.p. 126−130°C (dec.). – $C_8H_{17}Cl_6N_2OSb$ (491.7): calcd. C 19.54, H 3.94, N 5.70; found C 19.70, H 3.74, N 5.68.

(E)-Isopropyl[1-(isopropylideneaminooxy)isobutylidene]ammonium Hexachloroantimonate [(*E*)-**4b**]: From **1a** (0.73 g, 10 mmol) and **2b**[35] (4.47 g, 10 mmol) as described for (*E*)-**4a**. Yield: 4.42 g (85%) of a colorless powder, m.p. 127−129°C (dec.). – $C_{10}H_{21}Cl_6N_2OSb$ (519.8): calcd. C 23.11, H 4.07, N 5.39; found C 23.07, H 4.13, N 5.37.

(E)-Isopropyl[(isopropylideneaminooxy)phenylmethylene]ammonium Hexachloroantimonate [(*E*)-**4c**]: From **1a** (0.73 g, 10 mmol) and **2c**[35] (4.81 g, 10 mmol) as described for (*E*)-**4a**. Yield: 4.82 g (87%) of a colorless powder, m.p. 98−100°C (dec.). Crystals for the X-ray structural analysis were obtained from a cold (−30°C) solution of 1.00 g (*E*)-**4c** in CH_2Cl_2 (3 ml)/ether (5 ml). – $C_{13}H_{19}Cl_6N_2OSb$ (553.8): calcd. C 28.19, H 3.46, N 5.06; found C 28.00, H 3.54, N 5.13.

X-Ray Diffraction Analysis of (*E*)-**4c**[18]: $[C_{13}H_{19}N_2O]SbCl_6$, Crystal size 0.3 × 0.3 × 0.3 mm³, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 983.2(2)$, $b = 2490.5(4)$, $c = 1026.2(2)$ pm, $\beta = 118.12(2)°$, $V = 2216.1 \cdot 10^6$ pm³, $d_{calc} = 1.66$ Mgm^{-3}, $T = 271$ K, $\mu_{Mo\text{-}K\alpha} = 12.5$ cm^{-1}, ω scan, $1.5 \leq \omega \leq 29.3°$ min^{-1}, $4.0 \leq 2\Theta \leq 52°$, 4718 collected reflections, 4344 independent reflections ($I > 5\sigma$). 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 by direct methods using the program Siemens SHELXTL PLUS. Hydrogen atoms were fixed on calculated geometrically ideal positions (riding model, fixed isotropic *U*). The anisotropic refinement led to agreement factors $R_1 = 0.047$ and $R_2 = 0.061$.

N¹-Acetyl-N¹,N³,N³-trimethylformamidinium Hexachloroantimonate (**6d**): A solution of DMF (0.73 g, 10 mmol) in CH_2Cl_2 (10 ml) was added dropwise under stirring to a cold (−50°C) suspension of **2d**[36] (3.91 g, 10 mmol) in CH_2Cl_2 (20 ml). The reaction mixture was stirred at 23°C for 4 h. Ether (80 ml) was added, and a pale yellow powder (3.25 g, 70%) was filtered off. Crystallization at −20°C from CH_2Cl_2 (30 ml)/CH_3CN (5 ml)/CCl_4 (15 ml) afforded a colorless powder, m.p. 114−118°C (dec.). – $C_6H_{13}Cl_6N_2OSb$ (463.7): calcd. C 15.54, H 2.83, N 6.04; found C 15.49, H 2.84, N 5.95.

N¹-Acetyl-N³,N³-dimethyl-N¹-phenylformamidinium Hexachloroantimonate (**6e**)

a) From DMF (0.73 g, 10 mmol) and **2e**[37] (4.53 g, 10 mmol) as described for **6d**. However, the reaction mixture was stirred at −30°C for 1 h. Yield: 4.26 g (81%) of a colorless powder. Crystallization at −20°C from CH_2Cl_2 (15 ml)/ether (2 ml) afforded a colorless powder, m.p. 166−168°C (dec.). – $C_{11}H_{15}Cl_6N_2OSb$ (525.7): calcd. C 25.13, H 2.88, N 5.33; found C 25.15, H 2.90, N 5.36.

b) A solution of acetyl chloride (1.18 g, 15 mmol) in ether (10 ml) was added dropwise to a solution of **7**[38] (1.48 g, 10 mmol) in ether (10 ml). After stirring for 10 min the solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (20 ml). The solution was cooled to −50°C, and a solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 ml) was added dropwise. After stirring at −50°C for 30 min, ether (80 ml) was added dropwise. A pale yellow powder (4.78 g, 91%) was filtered off. Crystallization afforded the pure product; m.p. 165−167°C (dec.).

N¹-Acetyl-N³,N³-dimethyl-N¹-phenylacetamidinium Hexachloroantimonate (**6f**): From *N,N*-dimethylacetamide (0.91 g, 10.5 mmol) and **2e** (4.53 g, 10 mmol) as described for **6d**. However, the reaction mixture was stirred at 23°C for 1 h. Yield: 4.59 g (85%) of a pale yellow powder. Purification by stirring at 23°C under CH_2Cl_2 (20 ml) for 15 min afforded a pale yellow powder, m.p. 151−153°C (dec.). – $C_{12}H_{17}Cl_6N_2OSb$ (539.7): calcd. C 26.70, H 3.18, N 5.19; found C 26.69, H 3.21, N 5.22.

N¹-Benzoyl-N¹-isopropyl-N³,N³-dimethylacetamidinium Hexachloroantimonate (**6g**): From *N,N*-dimethylacetamide (0.91 g, 10.5 mmol) and **2c** (4.81 g, 10 mmol) as described for **6f**. Yield: 5.11 g (90%) of a pale yellow powder. Crystallization at −20°C from CH_2Cl_2 (15 ml)/CCl_4 (5 ml) afforded a pale yellow powder, m.p. 108−110°C (dec.). – $C_{14}H_{21}Cl_6N_2OSb$ (567.8): calcd. C 29.61, H 3.73, N 4.94; found C 29.68, H 3.69, N 4.98.

N¹-Acetyl-N¹,N³,N³-trimethylacetamidinium Hexachloroantimonate (**6h**): From *N,N*-dimethylacetamide (0.91 g, 10.5 mmol) and **2d** (3.91 g, 10 mmol) as described for **6f**. Yield: 4.40 g (92%) of a colorless powder. Crystallization at −20°C from CH_2Cl_2 (25 ml)/CH_3CN (5 ml)/ether (12 ml) afforded fine colorless needles, m.p. 84−86°C. – $C_7H_{15}Cl_6N_2OSb$ (477.7): calcd. C 17.60, H 3.17, N 5.87; found C 17.59, H 3.68, N 5.88.

N¹-Benzoyl-N³,N³-dimethyl-N¹-phenylformamidinium Tetrachloroaluminate (**6i**): From benzoyl chloride (1.41 g, 10 mmol) and **7** (1.48 g, 10 mmol) as described for **6e** b). However, solid $AlCl_3$ (1.33 g, 10 mmol) was added to the reaction mixture. The oily precipitate (2.95 g, 70%) solidified on drying. Crystallization at −20°C from CH_2Cl_2 (10 ml) afforded moisture-sensitive pale yellow leaflets; m.p. 95−99°C. – $C_{16}H_{17}AlCl_4N_2O$ (422.1): calcd. C 45.52, H 4.06, N 6.64; found C 44.80, H 4.58, N 6.61.

N¹-Acetyl-N¹,N³-dimethylacetamidinium Hexachloroantimonate (**6j**): From *N*-methylacetamide (0.73 g, 10 mmol) and **2d** (3.91 g, 10 mmol) as described for **6f**. Yield: 3.25 g (70%) of a pale yellow powder. Crystallization at −20°C from CH_2Cl_2 (30 ml)/CH_3CN (3 ml)/ether (10 ml) afforded fine colorless prisms, m.p. 196−198°C (dec.). – $C_6H_{13}Cl_6N_2OSb$ (463.7): calcd. C 15.54, H 2.83, N 6.04; found C 15.80, H 2.84, N 6.30.

Table 2. Selected NMR- and IR-Data for the prepared new compounds

Product	^{1}H NMR (CD_3CN, 295 K)[a] δ, *J*[Hz]	^{13}C NMR (CD_3CN, 295 K)[a] δ	IR (CH_2Cl_2) [cm^{-1}]
(E)-4a	1.36 (d, J=6.8, 6H), 2.12, 2.15, 2.46 (CH_3), 4.12 (m, J_{NH}=9.5, J_{CH}=6.8, CH), 9.37 (NH)	16.8, 18.0, 21.6 (2C), 21.7 (CH_3), 50.9 (CH), 171.7, 175.1 (C=N)	1648, 1660[b]
(E)-4b	1.32 (d, J=6.7, 6H), 1.38 (d, J=6.4, 6H), 2.14, 2.16 (CH_3), 3.28 (sept, J=6.7), 4.23 (m, J_{NH}=9.8, J_{CH}=6.4, CH), 9.33 (NH)	17.9, 18.8 (2C), 21.8, 22.2 (2C)(CH_3), 30.3, 50.4 (CH), 172.8, 179.8 (C=N)	1640[c]
(E)-4c	1.42 (d, J=6.6, 6H), 2.18, 2.22 (CH_3), 4.17 (m, J_{NH}=10.1, J_{CH}=6.6, CH), 9.86 (NH)[d]	18.3, 22.0, 22.2 (2C) (CH_3), 52.3 (CH), 124.4, 135.6 (i, p-C), 130.1, 130.5 (o,m-C), 171.8, 172.2 (C=N)[d]	1578,[b] 1632[c]
6d	2.41, 3.40, 3.43 (d, J= 0.7), 3.48 (CH_3), 8.42 (CH)[e]	23.3, 35.1, 42.6, 48.4 (CH_3), 159.3, 172.8 (C=O,C=N)[e]	1679, 1760
6e	2.11, 2.57 (d, J=1.0), 3.52 (d, J=0.8) (CH_3), 8.76 (m, CH)	23.6, 41.4, 49.8 (CH_3), 130.0 131.6 (o,m-C), 132.3, 135.7 (i,p-C), 154.3, 172.4 (C=O,C=N)	1679, 1763
6f	2.09, 2.34 (m, J=0.9), 3.42 (q, J=1.2), 3.61 (q, J=0.6) (CH_3),	22.1, 24.4, 45.5, 47.3 (CH_3), 130.0, 131.5, 131.6, 138.0 (aryl), 170.3, 171.7 (C=O,C=N)	1640, 1733
6g	1.56 (d, J=6.8, 6H), 2.70, 3.22 (q, J=1.0), 3.26 (CH_3), 4.30 (sept, J=6.8, CH)	20.7 (2C), 24.3, 44.5, 46.1 (CH_3), 56.2 (CH), 128.5, 130.2 (o,m-C), 134.1, 135.1 (i,p-C), 169.6, 176.0 (C=O, C=N)[d]	1628, 1710
6h	2.26, 2.53[c], 3.27, 3.32 (q, J=1.0[f], 3.54[c](CH_3)	21.3, 23.3, 37.1, 44.8, 46.6 (CH_3), 170.9, 174.9 (C=O,C=N)	1644, 1725
6i	2.74, 3.57 (CH_3), 8.71 (CH)[g]	41.5, 48.8 (CH_3), 156.0, 170.0 (C=O,C=N)[g]	1679, 1725
6j	2.44, 2.45, 3.24 (d, J= 5.1), 3.41 (CH_3), 12.00 (NH)[d]	18.3, 26.3, 33.5, 37.8 (CH_3) 172.0, 179.2 (C=O,C=N)[d]	1644, 1725
6k	1.99, 2.10 (CH_3), 13.48 (NH)	21.6, 27.3 (CH_3), 126.9, 129.5, 131.0, 131.1, 132.1, 132.3, 135.3, 138.4 (aryl), 172.2, 179.1 (C=O,C=N)	1590, 1625, 1721
13a	2.45[c], 3.21 (q, J=0.8), 3.33, 4.18 (CH_3)	15.7, 39.7, 42.2, 61.7 (CH_3), 177.4 (C=N)	1663
13b	3.16 (d, J=1.0), 3.33, 4.32 (CH_3), 8.19 (CH)	37.2, 42.3, 65.8 (CH_3), 168.4 (C=N)	1705
13c	1.45 (t, J=7.3), 3.16, 3.32 (CH_3), 4.66 (q, J= 7.3, CH_2), 8.25 (CH)	15.3, 37.1, 42.2 (CH_3), 76.7 (CH_2), 167.3 (C=N)	1695
13d	1.47 (d, J=6.4, 6H), 3.15 (d, J=0.9), 3.32 (CH_3), 5.01 (sept, J= 6.2), 8.29 (CH)	22.5 (2C), 37.0, 42.2 (CH_3), 86.6 (CH), 166.3 (C=N)	1695
13e	0.82 (d, J=6.7), 0.95 (d, J=7.0), 0.97 (d, J=6.6), 3.14 (d, J=0.9), 3.30 (CH_3), 4.57 (m, J=4.4 and 10.7), 8.26 (CH)	16.7, 20.8, 22.0, 24.2, 27.0, 32.2, 34.1, 37.3, 42.2, 42.4, 47.9, 92.3 (CH_3, CH_2, CH), 166.2 (C=N)	1690
13f	3.15 (d, J=0.9), 3.33 (CH_3), 5.60 (CH_2), 7.49 (phenyl, 5H), 8.38 (CH)[c,e]	37.2, 42.3 (CH_3), 80.6 (CH_2), 129.9, 130.1, 130.9, 133.3 (aryl), 167.0 (C=N)[e]	1695
13g	3.60, 4.50 (CH_3), 8.51 (CH)	38.9, 66.7 (CH_3), 124.4, 131.1 (o,m-C), 131.4, 139.7 (i,p-C), 169.9 (C=N)[e]	1590, 1670
13h	1.54 (t, J=7.1), 3.59 (d, J=0.9) (CH_3), 4.84 (q, J=7.1, CH_2), 8.57 (CH)	15.3, 38.8 (CH_3), 78.0 (CH_2), 168.9 (C=N)[e]	1585, 1660
13i	1.57 (d, J=6.4, 6H), 3.59 (d, J=0.9) (CH_3), 5.22 (sept, J=6.4), 8.61 (CH)[e]	22.6 (2C), 38.8 (CH_3), 88.5 124.5, 131.0, (o,m-C), 1655 131.2, 139.9 (i,p-C), 167.7 (C=N)[e]	1585,
13j	0.86 (d, J=7.0), 0.98 (d, J=6.6), 0.99 (d, J=7.0) 3.60 (d, J=0.9) (CH_3), 4.79 (m, J=4.6 and 10.7), 8.63 (q, J=0.9) (CH)	16.4, 21.0, 22.1, 23.5, 26.5, 32.1, 33.9, 39.1, 42.2, 47.7, 93.3 (CH_3,CH_2,CH), 124.6, 131.0 (o,m-C), 131.3, 140.0 (i,p-C), 167.4 (C=N)[e]	1585, 1655
14	1.48 (d, J=6.9, CH_3), 4.79 (sept, J=6.9), 8.79 (CH)[g]	19.6 (CH_3), 46.1 (CH), 170.8, 173.1 (C=O)[g]	1663, 1721
15a	2.07, 2.13, 2.59[c], 3.29 (d, J=0.9), 3.38 (CH_3)	16.7, 17.9, 21.4, 40.2, 42.4 (CH_3), 169.9, 177.8 (C=N)	1663[c]
15b	2.06, 2.15, 3.25 (d, J= 1.1), 3.39 (d, J=0.9) (CH_3), 8.71 (m, CH)	17.8, 21.1, 38.3, 43.0 (CH_3) 167.9, 171.0 (C=N)	1702
15c	3.50 (d, J=1.2), 3.56 (d, J=0.6) (CH_3), 9.03 ($CH^{[h]}$)	39.3, 43.8 (CH_3), 162.5, 168.8 (C=N)[h]	1605, 1640, 1764
15d	3.40 (d, J=0.6), 3.54 (CH_3), 8.81, 8.97[c] (CH)[i]	38.4, 43.2 (CH_3), 127.7, 133.9 (i,p-C), 129.3, 129.9 (o,m-C), 160.9, 167.5 (C=N)[i]	1605, 1706
15e	2.74, 3.39 (d, J=0.8), 3.45 (CH_3), 8.79 (CH)	16.8, 40.2, 42.5 (CH_3), 128.5 133.7 (i,p-C), 129.4, 129.9 (o,m-C), 160.0, 177.7 (C=N)[d]	1605, 1667
16a	3.46, 3.62 (CH_3), 9.20 (CH)	44.0, 50.3 (CH_3), 126.1 (i-C), 132.6 (p-C), 131.4, 134.4 (o,m-C), 182.7 (C=N)[h]	
16b	2.42, 3.43, 3.58 (CH_3), 9.15 (CH)	21.4, 43.8, 50.0 (CH_3), 122.5, 132.0, 134.4, 143.6 (aryl), 182.9 (C=N)	1600, 1630[b] 1705
17a		126.9, 136.6 (i,p-C), 127.0, 128.9 (o,m-C)[e,g]	
18a	1.27 (d, J=6.7, 6H), 3.16, 3.18, 3.28 (CH_3), 3.79 (sept, J=6.7), 7.49 (CH)[d]	20.2 (2C), 32.7, 40.0, 46.8 (CH_3), 60.5 (CH), 156.0 (C=N)[d]	1690[j]
18b	3.22, 3.39 (CH_3), 8.17 (d, J=13.4, CH), 9.07[c] (NH)	38.2, 44.9 (CH_3), 120.7, 130.7 (o,m-C), 128.0, 137.2 (i,p-C), 154.2 (C=N)	1601, 1694[c]
18c	2.99, 3.22 (CH_3), 4.56 (d, J=6.7, CH_2), 7.59[c] (NH), 7.78 (d, J=13.6, CH)	37.3, 44.2, 51.3 (CH_3, CH_2), 128.9, 129.8 (o,m-C), 129.3, 136.8 (i,p-C), 157.1 (C=N)	1605, 1710
18d	3.19, 3.21 (CH_3), 1.71 (6H), 3.50[c], 3.74[c] (CH_2), 7.43 (CH)	23.7 (2C), 26.7, 48.8[c], 56.2[c] (CH_2), 40.6, 46.6 (CH_3), 155.2 (C=N)	1520, 1694
18e	1.28 (t, J=7.1), 3.21, 3.23 (CH_3), 3.45[c], 3.59[c] (CH_2), 7.43 (CH)	14.8 (2C), 39.5, 43.7[c], 47.3[c], 52.2[c] (CH_3, CH_2), 156.1 (C=N)[e]	1694
18f	3.21, 3.22 (CH_3), 3.64[c] (4H), 3.77[c] (4H) (CH_2), 7.54 (CH)	40.9[c], 46.7[c], 51.4[c], 66.5, 66.8 (CH_3, CH_2), 155.9 (C=N)	1694

[a] TMS as internal standard. — [b] Shoulder. — [c] Broad. — [d] At 273 K. — [e] At 263 K. — [f] Coupled to δ = 2.53. — [g] In $CDCl_3$. — [h] At 333 K. — [i] At 263 K in CD_3CN/CD_2Cl_2 (1:1). — [j] KBr disk.

N^1-Acetyl-N^1,N^3-diphenylacetamidinium Hexachloroantimonate (**6k**): From acetanilide (1.35 g, 10 mmol) and **2e** (4.53 g, 10 mmol) as described for **6f**. Yield: 4.47 g (76%). Crystallization at −20°C from CH_2Cl_2 (7 ml)/ether (15 ml) afforded fine colorless needles, m.p. 163−165°C (dec.). — $C_{16}H_{17}Cl_6N_2OSb$ (587.8): calcd. C 32.69, H 2.92, N 4.77; found C 32.70, H 2.94, N 4.72.

(1-Methoxyethylidene)dimethylammonium Hexachloroantimonate (**13a**): A mixture of **6h** (4.78 g, 10 mmol) and methanol (8.01 g, 250 mmol) in CH_2Cl_2 (25 ml) was stirred at 23°C for 4 h. After cooling to −50°C ether (80 ml) was added. Filtration furnished a colorless powder (3.23 g, 74%), which crystallized at −20°C from CH_3CN (10 ml)/CH_2Cl_2 (25 ml) to give a colorless powder, m.p.

230–232°C (dec.) (ref.[39] 225–226°C). – $C_5H_{12}Cl_6NOSb$ (436.6): calcd. C 13.75, H 2.77, N 3.21; found C 13.82, H 3.03, N 3.33.

(Methoxymethylene)dimethylammonium Hexachloroantimonate (**13b**): From **6l**[5] (5.54 g, 10 mmol) and methanol (8.01 g, 250 mmol) as described for **13a**. The crude product was washed with ether to furnish colorless fine needles (3.65 g, 87%), m.p. 100°C (ref.[5] 102–104°C).

(Ethoxymethylene)dimethylammonium Hexachloroantimonate (**13c**): From **6l** (5.54 g, 10 mmol) and ethanol (3.92 g, 85 mmol) as described for **13a**. The crude product (3.40 g, 78%) crystallized at 5°C from $ClCH_2CH_2Cl$ (50 ml)/benzene (150 ml) to afford pale yellow leaflets, m.p. 142–146°C (ref.[40] 156–158°C).

(Isopropoxymethylene)dimethylammonium Hexachloroantimonate (**13d**): From **5l** (5.54 g, 10 mmol) and 2-propanol (5.11 g, 85 mmol) as described for **13a**. However, the stirring time was 26 h. The crude product (3.43 g, 76%) crystallized at –20°C from CH_2Cl_2 (20 ml)/$CHCl_3$ (100 ml) to afford colorless needles, m.p. 110–112°C. – $C_6H_{14}Cl_6NOSb$ (450.7): calcd. C 15.99, H 3.13, N 3.11; found C 15.99, H 3.33, N 2.90.

[(Menthyloxy)methylene]dimethylammonium Hexachloroantimonate (**13e**)[28]: From **6l** (5.54 g, 10 mmol) and menthol (13.82 g, 85 mmol) as described for **13a**. However, the mixture was stirred at 23°C for 110 h. The crude product (3.70 g, 68%) crystallized at –20°C from CH_2Cl_2 (250 ml)/$CHCl_3$ (120 ml) to afford colorless needles, m.p. 162–164°C (dec.). – $C_{13}H_{26}Cl_6NOSb$ (546.8): calcd. C 28.55, H 4.79, N 2.56; found C 28.32, H 4.88, N 2.60.

[(Benzyloxy)methylene]dimethylammonium Hexachloroantimonate (**13f**)[41]: From **6l** (5.54 g, 10 mmol) and benzyl alcohol (9.19 g, 85 mmol) as described for **13a**. However, the mixture was stirred at 0°C for 90 h. The crude product (2.00 g, 40%) crystallized at 5°C from $ClCH_2CH_2Cl$ (10 ml)/benzene (50 ml) to afford a temperature- and moisture-sensitive pale yellow powder, m.p. 117–119°C (dec.). – $C_6H_{14}Cl_6NOSb$ (450.7): calcd. C 15.99, H 3.13, N 3.11; found C 15.99, H 3.33, N 2.90.

(Methoxymethylene)methylphenylammonium Hexachloroantimonate (**13g**): From **6m**[6] (6.16 g, 10 mmol) and methanol (0.35 g, 11 mmol) as described for **13a**. However, the mixture was stirred at 23°C for 22 h. The crude product (2.70 g, 56%) crystallized at –20°C from CH_2Cl_2 (50 ml)/ether (15 ml) to afford pale green leaflets, m.p. 125–128°C (dec.). – $C_9H_{12}Cl_6NOSb$ (484.7): calcd. C 22.30, H 2.50, N 2.89; found C 22.39, H 2.47, N 2.79.

(Ethoxymethylene)methylphenylammonium Hexachloroantimonate (**13h**): From **6m** (6.16 g, 10 mmol) and ethanol (0.51 g, 11 mmol) as described for **13g**. However, the mixture was stirred at 23°C for 22 h. The crude product (3.20 g, 64%) crystallized at –20°C from CH_2Cl_2 (25 ml)/ether (15 ml) to afford a pale green powder, m.p. 145–147°C (dec.). – $C_{10}H_{14}Cl_6NOSb$ (498.7): calcd. C 24.08, H 2.83, N 2.81; found C 23.81, H 2.95, N 2.72.

(Isopropoxymethylene)methylphenylammonium Hexachloroantimonate (**13i**): From **6m** (6.16 g, 10 mmol) and 2-propanol (0.67 g, 11 mmol) as described for **13g**. However, the mixture was stirred at 23°C for 22 h. The crude product (4.20 g, 82%) crystallized at –20°C from CH_2Cl_2 (150 ml)/$CHCl_3$ (70 ml) to afford a colorless powder, m.p. 170–172°C (dec.). – $C_{11}H_{16}Cl_6NOSb$ (512.7): calcd. C 25.77, H 3.15, N 2.73; found C 25.76, H 3.39, N 2.68.

[(Menthyloxy)methylene]methylphenylammonium Hexachloroantimonate (**13j**): From **6m** (6.16 g, 10 mmol) and menthol (1.72 g, 11 mmol) as described for **13g**. However, the mixture was stirred at 23°C for 120 h. The crude product (3.70 g, 61%) was reprecipitated from CH_2Cl_2 (60 ml)/ether (80 ml) to afford a pale green powder, m.p. 131–133°C (dec.). – $C_{18}H_{28}Cl_6NOSb$ (608.9): calcd. C 35.50, H 4.64, N 2.30; found C 35.25, H 4.32, N 2.26.

N-Formyl-N-isopropylbenzamide (**14**): Water (2.5 ml) was added to a solution of **6l** (5.54 g, 10 mmol) in CH_3CN (12 ml). The mixture was stirred at 23°C for 2 h. After evaporation of the solvent the residue was extracted with CH_2Cl_2 (2 × 30 ml). Evaporation of the solvent and column chromatography on silica gel (25 g) with CH_2Cl_2 as eluent gave an oil (1.57 g, 82%), which crystallized at –20°C, m.p. 65–67°C. – $C_{11}H_{13}NO_2$ (191.2): calcd. C 69.09, H 6.85, N 7.33; found C 69.42, H 7.06, N 7.07.

[1-(Isopropylideneaminooxy)ethylidene]dimethylammonium Hexachloroantimonate (**15a**): A mixture of **6f** (5.40 g, 10 mmol) and **1a** (0.80 g, 11 mmol) in CH_2Cl_2 (40 ml) was stirred at 23°C for 2 h. After cooling to –50°C ether (80 ml) was added. Filtration furnished a colorless powder (4.40 g, 92%), which crystallized at –20°C from CH_3CN (3 ml)/ether (80 ml) to afford a colorless powder, m.p. 130–132°C (dec.). – $C_7H_{15}Cl_6N_2OSb$ (477.7): calcd. C 17.60, H 3.17, N 5.87; found C 17.87, H 3.26, N 5.86.

[(Isopropylideneaminooxy)methylene]dimethylammonium Hexachloroantimonate (**15b**): From **6n** (5.77 g, 10 mmol) and **1a** (0.80 g, 10 mmol) as described for **15a**. Reprecipitation of the product from CH_2Cl_2 (20 ml)/ether (100 ml) afforded a colorless powder (4.41 g, 95%), m.p. 63–67°C (dec.). – $C_6H_{13}Cl_6N_2OSb$ (463.7): calcd. C 15.54, H 2.83, N 6.04; found C 15.83, H 2.92, N 6.16.

[(9-Fluorenylidene)aminooxymethylene]dimethylammonium Hexachloroantimonate (**15c**): A mixture of **6d** (4.64 g, 10 mmol) and fluorenone oxime[42] (1.95 g, 10 mmol) in CH_2Cl_2 (40 ml) was stirred at 23°C for 3 h. Addition of ether (40 ml) to the suspension and filtration afforded a yellow powder (5.45 g, 93%), which was stirred under CH_2Cl_2 (50 ml) for 30 min. Yield: 5.00 g (85%) of a yellow powder, m.p. 215–218°C (dec.). – $C_{16}H_{15}Cl_6N_2OSb$ (585.8): calcd. C 32.81, H 2.58, N 4.78; found C 32.80, H 2.76, N 4.97.

(Benzylideneaminooxymethylene)dimethylammonium Hexachloroantimonate (**15d**): A mixture of **6d** (4.64 g, 10 mmol) and benzaldehyde oxime (1.33 g, 11 mmol) in CH_2Cl_2 (40 ml) was stirred at 23°C for 8 h. After cooling to –50°C ether (80 ml) was added dropwise. Filtration afforded a colorless powder (2.00 g, 39%). The mother liquor contained inter alia benzonitrile, *N*-methylacetamide, and the complex DMF · $SbCl_5$ (^{1}H NMR). Crystallization at –20°C from CH_3CN (7 ml)/CCl_4 (35 ml) afforded a colorless powder (1.67 g, 33%), m.p. 136–138°C (dec.). – $C_{10}H_{13}Cl_6N_2OSb$ (511.7): calcd. C 23.47, H 2.56, N 5.48; found C 23.20, H 2.62, N 5.43.

[1-(Benzylideneaminooxy)ethylidene]dimethylammonium Hexachloroantimonate (**15e**): A mixture of **6f** (5.40 g, 10 mmol) and benzaldehyde oxime (1.33 g, 11 mmol) in CH_2Cl_2 (40 ml) was stirred at 23°C for 24 h. Filtration and stirring of the residue for 10 min under CH_2Cl_2 (20 ml) afforded a colorless powder (3.15 g, 60%), m.p. 162–164°C (dec.). – $C_{11}H_{15}Cl_6N_2OSb$ (525.7): calcd. C 25.13, H 2.88, N 5.33; found C 25.17, H 2.95, N 5.35.

Dimethyl[(phenylthio)methylene]ammonium Tetrachloroantimonate (**16a**)[42] *and Diphenyl Disulfide* (**17a**): From **6l** (5.54 g, 10 mmol) and thiophenol (9.37 g, 85 mmol) as described for **13g**. The crude product (3.91 g, 91%) crystallized at –20°C from CH_3CN (200 ml) to afford colorless needles of **16a**, m.p. 149–151°C. – $C_9H_{12}Cl_4NSSb$ (429.8): calcd. C 25.15, H 2.81, N 3.26; found C 25.18, H 2.93, N 3.18.

The solvent of the combined filtrates was evaporated and the residue suspended in $CHCl_3$ (30 ml). After addition of H_2O (50 ml) the mixture was filtered. The organic phase was extracted with H_2O (3 × 30 ml) and dried with Na_2SO_4. Evaporation of the solvent

afforded an oil, which crystallized at 0°C from CH_3OH (30 ml) to give colorless needles of **17a** (1.55 g, 71%), m.p. 58–59°C (ref.[43] 61.5°C).

Dimethyl[(4-methylphenylthio)methylene]ammonium Tetrachloroantimonate (**16b**): From **6l** (5.54 g, 10 mmol) and *p*-thiocresol (10.56 g, 85 mmol) as described for **16a**. Yield: 4.15 g (94%) of colorless needles, m.p. 183–184°C. – $C_{10}H_{14}Cl_4NSSb$ (443.9): calcd. C 27.06, H 3.18, N 3.16; found C 26.95, H 2.98, N 3.08.

N^1-Isopropyl-N^1,N^3,N^3-trimethylformamidinium Hexachloroantimonate (**18a**): A solution of isopropylmethylamine (0.81 g, 11 mmol) in CH_2Cl_2 (10 ml) was added dropwise to a cold (–20°C) solution of **6e** (5.26 g, 10 mmol) in CH_2Cl_2 (40 ml). The mixture was stirred at –20°C for 1 h. Ether (100 ml) was added dropwise. After stirring for another 30 min at –20°C a pale yellow powder (4.54 g, 98%) was filtered off, m.p. 147–149°C (dec.). – $C_7H_{17}Cl_6N_2Sb$ (463.7): calcd. C 18.13, H 3.70, N 6.04; found C 18.24, H 3.93, N 5.99.

N^3,N^3-Dimethyl-N^1-phenylformamidinium Hexachloroantimonate (**18b**): From aniline (0.93 g, 10 mmol) and **6e** (5.26 g, 10 mmol) as described for **18a**. The product precipitates from the reaction mixture without addition of ether. Filtration afforded a yellow-green powder (3.87 g, 80%), which crystallizes at –20°C from CH_3CN (5 ml)/CCl_4 (40 ml), m.p. 234–237°C (dec.). – $C_9H_{13}Cl_6N_2Sb$ (483.7): calcd. C 22.35, H 2.71, N 5.79; found C 22.40, H 2.72, N 5.80.

N^1-Benzyl-N^3,N^3-dimethylformamidinium Hexachloroantimonate (**18c**): From benzylamine (1.07 g, 10 mmol) and **6e** (5.26 g, 10 mmol) as described for **18a**. Yield: 3.73 g (75%) of a pale yellow powder, which crystallizes at –20°C from CH_3CN (30 ml)/ether (300 ml), m.p. 184–187°C (dec.). – $C_{10}H_{15}Cl_6N_2Sb$ (497.7): calcd. C 24.13, H 3.04, N 5.63; found C 23.83, H 3.22, N 5.54.

Dimethyl(piperidinomethylene)ammonium Hexachloroantimonate (**18d**): From piperidine (0.86 g, 10 mmol) and **6e** (5.26 g, 10 mmol) as described for **18a**. However, the mixture was stirred at 23°C for 15 min. The crude product was washed with CH_2Cl_2. Yield: 4.47 g (94%) of a colorless powder, m.p. 225–230°C (dec.). – $C_8H_{17}Cl_6N_2Sb$ (475.7): calcd. C 20.20, H 3.60, N 5.89; found C 20.33, H 3.74, N 5.88.

N^1,N^1-Diethyl-N^3,N^3-dimethylformamidinium Hexachloroantimonate (**18e**): From diethylamine (0.88 g, 12 mmol) and **6n** (5.77 g, 10 mmol) as described for **18a**. However, the reaction mixture was stirred at –20°C for 2 h. Crystallization at –20°C from CH_2Cl_2 (40 ml)/ether (20 ml) afforded pale yellow prisms (3.62 g, 78%), m.p. 121–125°C (dec.). – $C_7H_{17}Cl_6N_2Sb$ (463.7): calcd. C 18.13, H 3.70, N 6.04; found C 18.18, H 3.87, N 5.95.

Dimethyl(morpholinomethylene)ammonium Hexachloroantimonate (**18f**): From morpholine (1.05 g, 12 mmol) and **6n** (5.77 g, 10 mmol) as described for **18e**. The crude product was crystyallized at –20°C from CH_3CN (120 ml)/ether (40 ml) to give pale yellow prisms (2.15 g, 45%), m.p. 233–236°C (dec.). – $C_7H_{15}Cl_6N_2OSb$ (477.7): calcd. C 17.60, H 3.17, N 5.87; found C 17.98, H 3.40, N 5.80.

3-(Dimethylamino)-1,1-diphenyl-2-azoniaallene Hexachloroantimonate (**19**): From benzophenone imine (1.81 g, 10 mmol) and **6n** (5.77 g, 10 mmol) as described for **18e**. The crude product was washed with pentane to give a colorless powder (5.43 g, 95%), m.p. 171–173°C (ref.[5] 173–175°C).

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