The Reaction of Nitrilium Salts with Primary, Secondary, and Tertiary Carboxamides

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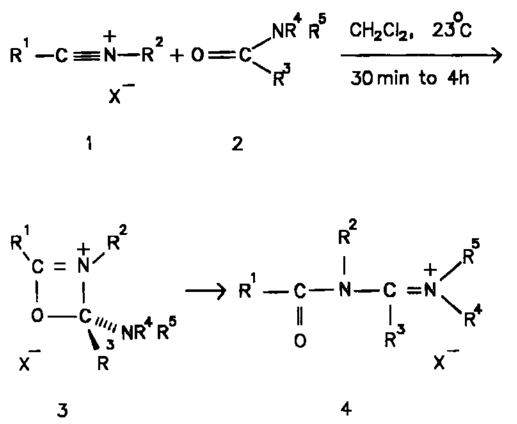
Nitrilium salts (**5a, b**) dehydrate primary carboxamides (**6a, b**) to give nitriles (**8a, b**) and *O*-protonated carboxamides (**7a, b**). Secondary carboxamides (**9a, b, e – g**) add to nitrilium salts (**5b – d**) to furnish mixtures of tautomeric *N*-acylamidinium salts (**10a – d**, **11a, c**). However, with the stable acetylcyanamidium salt **5d** the primarily formed amidinium salts **10** either cyclize with elimination of water to yield *s*-triazinium salts (**12f, g**) or react with a further carboxamide to afford the *N*-acylamidinium salts **14e, f**. At low temperatures formamides (**9g, h**) are dehydrated by **5d** to give isonitriles, which add to an excess of **5d** to furnish the oxazolidines **15g, h**. The triazinium salts **12** are characterized by 1,4-addition of alcohols giving the new triazinium salts **16a – c**. Tertiary carboxamides (**17a – k**) add to the nitrilium salts **5b – d** to give N^1-acyl-N^1,N^3,N^3-substituted amidinium salts **18a – k**. This reaction was extended to a vinylogous tertiary carboxamide (**19**) affording the cyanine dyes **20a, b**.

Stable nitrilium salts **1** have been isolated first by Klages[1] and Meerwein[2] et al. in the mid 1950s. Up to now, these salts have only moderately attracted the chemist's interest[3,4]. This is surprising because nitrilium salts have been shown or supposed to be key intermediates of a number of name reactions[5], some of which economically being most important[6]. For instance, nitrilium ions seem to play a crucial role in the Beckmann[5,6] and Schmidt rearrangement[5,7,8], in the Ritter[5,9], Bischler-Napieralski[5,8], von Braun[5], Gattermann[8], and Houben-Hoesch reaction[8].

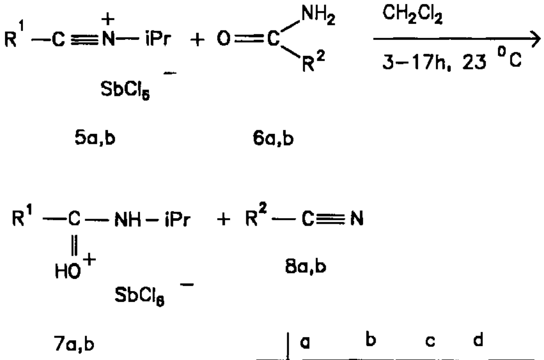
Recently, we have reported[10] on a new reaction of nitrilium salts with tertiary carboxamides **2** furnishing the hitherto almost unknown acylated persubstituted amidinium salts **4**[11–15]. The reaction is believed to proceed via an intermediate **3**.



In this communication we report on reactions of nitrilium salts with primary and secondary carboxamides as well as on new reactions with tertiary carboxamides and with a vinylogue.

Primary carboxamides **6** are dehydrated to nitriles **8** (e.g. **8b**: IR for $PhC\equiv N$ at 2230 cm^{-1} in CH_2Cl_2) by the nitrilium hexachloroantimonates **5**, which add the water to furnish the very moisture-sensitive protonated amides **7**.

The sites of protonation are inferred from the NMR spectra (Table 1), which show $^{13}C=O$ signals [e.g. **7a** (CD_3CN, 263 K): δ = 181.8] and signals for only one NH proton (**7a**: δ = 8.58) coupled to one isopropyl CH proton (**7a**: δ = 4.14) together with signals for an uncoupled OH proton (**7a**: δ = 10.53). Stable *O*-protonated carboxamidium salts have occasionally been isolated by Gompper[16] and others[17–19].



	a	b	c	d
R^1	iPr	Ph	Me	iPrNAc
R^2	Me	Ph	–	–

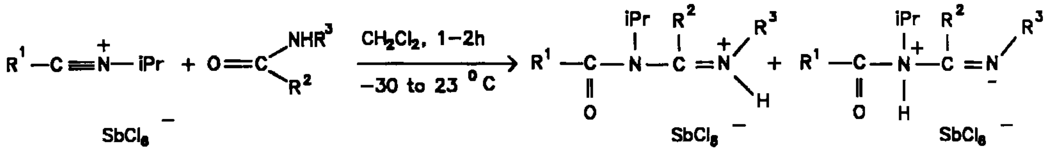
Interesting reactions are observed between nitrilium salts **5** and secondary carboxamides **9**. With 2-pyrrolidone (**9a**) and 2(1*H*)-pyridinone (**9b**) the *N*-isopropylnitrilium salts **5b, c** form mixtures of N^1-acylated N^1,N^3-disubstituted amidinium salts **10** and their tautomers **11**. From the 1:1 mixture of **10a** and **11a** pure **11a** is obtained by fractional crystallization. The salt **10c** is transformed into the tautomer **11c** by treatment with formic acid.

The stable crystalline, although moisture-sensitive *N*-acetylcyanamidium[23] hexachloroantimonate **5d**[20–23] reacts with 2-pyrrolidone (**9a**) to furnish the acylamidinium salt **10d**. However, with the *N*-methylamides **9e, f** the corresponding salts **10e, f** are formed as intermediates only, which either eliminate water to give the triazinium compound **12f** or react with a second molecule of the carboxamide **9** to afford the *N*-acylamidinium salts **14e, f**. Compounds **14** are not formed via **12** since under the experimental conditions no reactions are observed between **12f** and amides **9**. Nucleophilic substitutions of amidinium salts **10** have been reported[10].

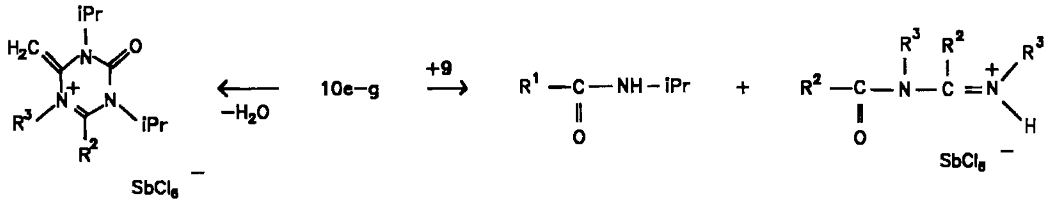
Different reactions are observed between **5d** and formamides. Depending on the reaction conditions, the formamides **9g, h** are dehydrated to isonitriles. From the reaction of two molecules of **5d** with one molecule of **9g** at −20°C a compound is obtained to which structure **15g** is tentatively assigned. On the other hand, if the reaction of **5d** with **9g** is carried out at +23°C a mixture of compounds is obtained containing some **15g**. As main component the triazinium salt **12g** is isolated. Experiments to transform the oxazolidine **15g** into the triazine **12g** have been unsuccessful.

From **5d** and *N*-methylformamide (**9h**) only **15h** is obtained. Attempts to prepare **15h** from **5d** and methyl isocyanide have failed. The reaction mixtures turn black. However, from **5d** and isopropyl isocyanide a small amount of **12g** is obtained together with much polymeric material.

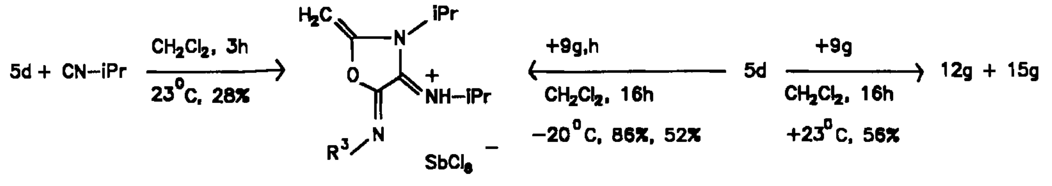
In conclusion, there are two independent reactions: At low temperatures the fast reaction is the dehydration of the formamide **9g** by the nitrilium salt **5d** followed by an ad-



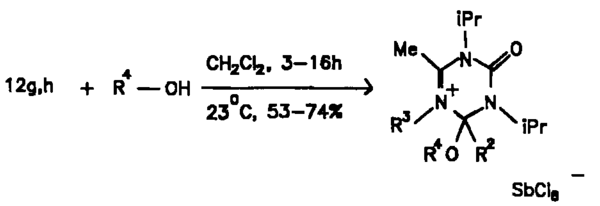
5b–d 9a,b,e–h 10a–d 11a,c



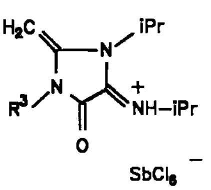
12f,g 10e–g 13d 14e,f



15g,h



16a–c



15'

9–15	R^1	R^2	R^3
a	Me	$(CH_2)_3$	
b	Me	$(CH)_4$	
c	Ph	$(CH)_4$	
d	iPrNAc	$(CH_2)_3$	
e	iPrNAc	Me	Me
f	iPrNAc	Ph	Me
g	iPrNAc	H	iPr
h	iPrNAc	H	Me

16	R^2	R^3	R^4
a	Ph	Me	$PhCH_2$
b	H	iPr	$PhCH_2$
c	H	iPr	Me

dition of the resulting isocyanide to an excess of **5d**. At higher temperatures the addition of the formamide **9g** to the nitrilium salt **5d** leading to the triazine **12g** via **10g** competes with the dehydration of **9g**.

The 1,4-addition of alcohols to compounds **12** furnishes the salts **16**.

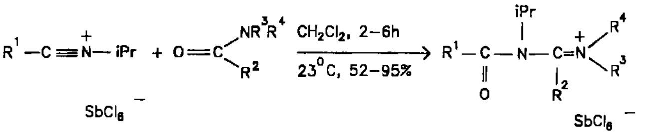
The structural assignments are based on elemental and spectroscopical analyses (Table 1). For instance, the site of protonation of the compounds **11** can be inferred from the vicinal coupling of the NH proton with the isopropyl CH proton. For the salts **10** protonation of the pyrrolidine or pyridine nitrogen atom is assumed, although no couplings of the NH protons are observed. Therefore, an alternative protonation of the carbonyl oxygen atom cannot be excluded. However, the NMR spectra of the salts **10** and **14** are very similar suggesting similar constitutions. Since the spectra of **14** show well resolved $NH-CH_3$ couplings we believe that compounds **10**, too, are *N*-protonated. The NH protons of **10** and **14**, which show signals at rather low fields (δ = 9.90 to 14.60) are probably involved in intramolecular hydrogen bonds to the carbonyl oxygen atoms. Compounds **12** and **15** show AB quartetts for the geminal CH_2 protons and four signals for sp^2-carbon atoms (Table 1). Salts **15g, h** both show sequences $HNCH(CH_3)_2$ and no sp^2-C−H couplings (gated decoupling and spin decoupling experiments), while for the salts **12f, g** no signals for NH protons are observed. A large sp^2-C−H coupling of 202 Hz is found for **12g**. The site of protonation in **15g** remains uncertain. Furthermore, an isomeric constitution **15′** resulting from a Dimroth rearrangement of **15** cannot be excluded presently. Unchanged **15h** was recovered after boiling in 1,2-dichloroethane for five hours. Large magnetic inequivalences are observed in the NMR spectra for the diastereotopic geminal methyl groups of compounds **16**.

Reactions of tertiary carboxamides with nitrilium salts give access to N^1-acylated N^1,N^3,N^3-trisubstituted amidinium salts **4** ($R^2,R^4,R^5 \neq H$)[10]. Little seems to be known about such salts[11,12], although recently some interesting synthetic applications have been reported[10,13,14]. N^1,N^3-Diacylated N^1,N^3-disubstituted amidinium salts are likely to be intermediates of the long-known Bamberger ring cleavage reaction[24−26].

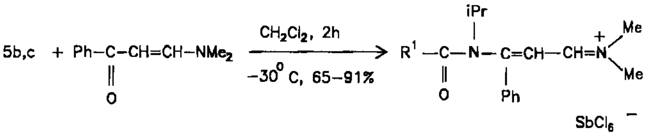
The nitrilium salts **5b−d** react smoothly with the tertiary amides **17a−k** to furnish the acylamidinium salts **18a−k** in high yields. In these reactions the *N*-acylcyanamidium salt **5d** behaves like other nitrilium salts, e.g. **5b, c**. *N*-Alkylidene carboxamides (**17c, d**) react to give *N*-acylamino substituted 2-azoniaallene salts (**18c, d**).

The scope of this reaction may be extended to the vinylogous tertiary carboxamide **19**, which reacts with the nitrilium salts **5b, c** to afford the trimethine salts **20a, b**.

The following limitations of the reaction are observed: 1) A mixture of the nitrilium salt **5b** and (benzoylazo)benzene [PhC(=O)N=NPh] in dichloromethane evolves nitrogen. Other well-defined products have not been isolated. 2) No reactions are observed between the nitrilium salts **5b, c** and 1,3-dimethylisocyanuric acid in boiling 1,2-dichloroethane. 3) Occasionally unstable products are formed, e.g. $PhC(=O)C\equiv CNMe_2$ reacts with the nitrilium salts **5** to give tarry mixtures of unstable compounds. Similarly, from the reaction mixture of 1,3-bis(diphenylmethylene)urea [$(Ph_2C=N)_2C=O$] with nitrilium salts **5** pure products have not been isolated.



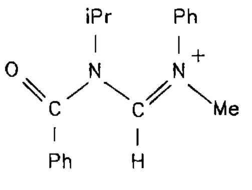
5b–d 17a–k 18a–k



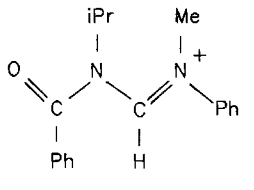
19 20a,b

17–20	R^1	R^2	R^3	R^4
a	Me	H	Ph	Me
b	Ph	H	Ph	Me
c	Me	Ph	$=CPh_2$	
d	Ph	Ph	$=CPh_2$	
e	Me	$C\equiv CPh$	Me	Me
f	Ph	$C\equiv CPh$	Me	Me
g	iPrNAc	H	Me	Me
h	iPrNAc	$(CH_2)_3$		Me
i	iPrNAc	H	Ph	Me
j	iPrNAc	Ph	Me	Me
k	iPrNAc	$C\equiv CPh$	Me	Me

The NMR spectra of compounds **18** and **20** are in some cases complicated by geometrical isomerism of the cations (Table 1, **18a, b, f, i, 20b**). For instance, in the ^1H- and ^{13}C-NMR spectra of **18b** all signals appear twice indicating a mixture of two geometrical isomers in the ratio of about 7:1. The minor component shows a ^4J-long-range $H_3C-N=C-H$ coupling of 0.6 Hz suggesting *trans* substitution **18b″** at the N=C partial double bond. The main component, for which a long-range coupling is not observed, accordingly should be the *cis* form **18b′**. The conformation of the benzamide group in **18b** is not known. Barriers to rotation about the C−N bonds of amidinium salts are known to be quite high ($\geq$ 80 kJmol^{-1})[27].



18b′



18b″

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Experimental

IR: Mattson Polaris FT-IR spectrometer; solutions in dichloromethane. − ^1H and ^{13}C NMR: Bruker WM-250 and AC 250 spec-

Table 1. Selected NMR and IR data for the prepared new compounds

Product	^1H NMR (CD_3CN, 300 K) δ, J [Hz]	^{13}C NMR (CD_3CN, 300 K) δ	IR (CH_2Cl_2) [cm^{-1}]
5d	1.53 (d, J = 6.7), 1.77 (d, J = 6.7), 2.66 (CH_3), 4.63 (sept, J = 6.7), 5.03 (sept, J = 6.7) (CH)[a]	21.2 (2 CH_3), 22.3 (2 CH_3), 24.2 (CH_3), 55.0, 56.6 (CH), 104.4 (C≡N), 165.5 (C=O)[a,c]	1711[b], 1744[b] 1787, 2336
7a	1.25 (d, J = 6.7), 1.27 (d, J = 6.7) (CH_3), 2.85 (sept, J = 6.7), 4.14 (m, J = 6.7 and ca 8, coupled to 8.58) (CH), 8.58 (NH), 10.53 (OH)[c]	18.7, 21.2 (CH_3), 34.6, 47.1 (CH), 181.8 (C=O)[c]	1671, 1609[b]
7b	1.38 (d, J = 6.7) (CH_3), 4.37 (m) (CH), 9.23 (NH), 12.35 (OH)	21.5 (CH_3), 47.3 (CH), 128.8 (i-C), 129.3, 130.0 (o,m-C), 135.2 (p-C), 172.6 (C=O)[d]	1562, 1605, 1655
10a[e]	1.51 (d, J = 6.9), 2.50 (CH_3), 4.48 (sept, J = 6.9) (CH), 10.82 (NH[f])	19.8, 21.0, 26.6, 35.5, 50.5, 54.9 (CH_3, CH_2, CH), 172.8, 177.4 (C=O, C=N)[c]	1630, 1720
10b	1.46 (d, J = 6.3), 2.80 (CH_3), 4.40 (sept, J = 6.3) (CH), 14.60 (NH[f])	18.2 (CH_3), 22.0 (2 CH_3), 52.3 (CH), 111.7, 123.4, 132.6, 143.8, 167.9, 170.6 (C=C, C=O, C=N)[d]	1551, 1612, 1663
10c	1.39 (d, J = 6.4) (CH_3), 3.78 (sept, J = 6.4) (CH), 14.53 (NH[f])	22.2 (CH_3), 54.3 (CH), 168.2, 168.7 (C=N, C=O)[d]	1551, 1609, 1648, 1690
10d	1.38 (d, J = 6.5), 2.24 (broad) (CH_3), 2.22 (m), 2.81 (t), 3.91 (m, broad) (CH_2), 4.24 (2 H, m, broad) (CH), 11.17 (broad) (NH[f])	18.2, 21.6, 22.5, 23.0, 33.6, 50.0, 51.8, 54.2 (CH_3, CH_2, CH), 157.1, 171.0, 180.4 (C=N, C=O)	1640, 1690, 1750
11a	1.35 (d, J = 6.3), 2.44 (CH_3), 2.16 (m), 2.72 (t), 3.95 (t) (CH_2), 4.17 (m, J = 6.3 and ca 8.5) (CH), 11.34 (coupled to 4.17) (NH)	17.9, 18.1, 22.2, 33.5, 49.7, 50.2 (CH_3, CH_2, CH), 167.9, 182.6 (C=O, C=N)	1512, 1640, 1744
11c	1.26 (d, J = 6.6) (CH_3), 4.22 (m, J = 6.6 and ca 7.1, coupled to 7.42) (CH), 7.42 (NH)	22.5 (CH_3), 43.8 (CH), 169.5 (C=O)	1540, 1563[b], 1605, 1652[b]
12f	1.39 (d, J = 6.4), 1.51 (d, J = 6.6), 3.19 (CH_3), 4.80 (AB q, J = 5.9) (CH_2), 3.73 (sept, J = 6.7), 4.39 (sept, J = 6.7) (CH)	19.0, 20.5, 42.7 (CH_3), 53.9, 58.4 (CH), 88.9 (CH_2), 139.9, 145.4, 164.8 (NC(=)N, C=O, C=N)[d]	1580, 1660, 1750
12g	1.42 (d, J = 6.7), 1.44 (d, J = 6.7), 1.51 (d, J = 6.7) (CH_3), 4.31 (sept, J = 6.7), 4.44 sept, J = 6.7), 4.59 (sept, J = 6.7) (CH), 4.75, 4.79 (AB q, J = 6.4) (CH_2), 8.04 (CH)	19.0, 21.1, 21.2 (CH_3), 87.8 (CH_2), 138.1, 145.7 (C=N), C=O), 151.1 (J_{CH} = 202) (HC=)[c]	1682, 1748
14e	2.43, 2.44 (CH_3), 3.23 (d, J = 5.2), 3.40 (NCH_3), 11.96 (NH)	18.3, 26.4, 33.5, 37.8 (CH_3), 172.0, 179.3 (C=N, C=O)[d]	1505, 1644, 1725
14f	3.05 (d, J = 4.9), 3.41 (CH_3), 9.90 (NH)	34.6, 39.9 (CH_3), 169.8, 174.3 (C=O, C=N)	1630, 1700
15g	1.21 (d, J = 6.1), 1.34 (d, J = 6.7), 1.51 (d, J = 7.0) (CH_3), 4.06 (sept, J = 6.1), 4.41 (sept, J = 7.0), 5.46 (m, J = 6.7 and 8.5) (CH), 7.89 (broad, NH)[c]	18.6, 22.2, 23.2 (CH_3), 48.9, 49.9, 50.9 (CH), 76.3 (CH_2), 141.4 (q, J = 8.0 and 10.8) (OCN), 147.4(m, J = 4), 148.3 (C=N)[c],	1675, 1721
15h	1.34 (d, J = 6.4), 1.51 (d, J = 7.0), 3.30 (CH_3), 4.59 (AB q, J = 5.8) (CH_2), 4.42 (sept, J = 7.0), 5.44 (m, J = 6.4 and 8.9) (CH), 7.89 (d, J = 8.9, broad) (NH)	18.7, 22.4, 36.4 (CH_3), 49.1, 50.1 (CH), 76.7 (CH_2), 144.3, 147.4, 148.1 (OCN, C=N)[d]	1670, 1730
16a	1.43 (d, J = 6.4), 1.44 (d, J = 6.7), 1.54 (d, J = 6.7), 1.55 (d, J = 6.7), 2.03, 2.98 (CH_3), 3.83 (sept, J = 6.7), 4.03 (sept, J = 6.7) (CH), 4.62 (AB q, J = 11.4) (CH_2)	20.5, 20.6, 25.9, 37.9 (CH_3), 50.8, 58.5, 66.8 (CH_2, CH), 102.1 (C), 145.2, 165.7 (C=N, C=O)[d]	1598, 1740
16b	1.36 (d, J = 6.9), 1.38 (d, J = 6.9), 1.42 (d, J = 6.7), 1.48 (d, J = 6.6, 6H), 1.57 (d, J = 6.8), 2.62 (CH_3), 4.35 (sept, J = 6.7), 4.40 (sept, J = 6.9), 4.54 (sept, J = 6.7), 6.08 (CH), 4.57 (CH_2)[d]	18.1, 20.2, 20.3, 20.4, 20.7, 20.9, 21.1 (CH_3), 50.8, 55.2, 55.9, 68.2 (CH), 86.1 (CH_2), 148.0, 167.3 (C=N, C=O)[d]	1590, 1737
16c	1.31 (d, J = 6.6), 1.34 (d, J = 6.6), 1.38 (d, J = 6.7), 1.42 (d, J = 6.7), 1.48 (d, J = 6.7), 1.54 (d, J = 6.8), 2.60, 3.32 (CH_3), 4.34 (sept, J = 6.8, 2 H), 4.50 (sept, J = 6.7), 5.87 (CH)[d]	18.1, 20.1, 20.2, 20.4, 20.6, 20.7, 20.9 (CH_3), 50.7, 53.4, 55.1, 55.8, 86.8 (OCH_3, CH), 147.9, 167.1 (C=N, C=O)[d]	1590, 1737

Table 1 (*Continued*)

Product	^1H NMR (CD_3CN, 300 K) δ, J [Hz]	^{13}C NMR (CD_3CN, 300 K) δ	IR (CH_2Cl_2) [cm^{-1}]
18a	1.23 (d, J = 6.7), 2.32, 3.81 (CH_3), 3.91 (sept, J = 6.7), 8.31 (CH)[g]; 1.49 (d, J = 6.7), 2.49, 3.56 (d, J = 0.9) (CH_3), 4.54 (sept, J = 6.7), 8.19 (CH)[h]		1640, 1680[b], 1760
18b	1.55 (d, J = 7.0), 3.67 (CH_3), 4.34 (sept, J = 7.0), 8.40 (CH)[i]; 1.52 (d), 3.24 (d, J = 0.6) (CH_3), 8.36 (CH)[j]	22.2, 49.0 (CH_3), 59.4, 156.8 (CH), 170.5 (C=O)[d,i], 22.2, 44.8 (CH_3), 59.0, 158.2 (CH), 170.8 (C=O)[d,j]	1590, 1640, 1730
18c	1.40 (d, J = 6.7), 2.52 (broad) (CH_3), 4.70 (sept, J = 6.7) (CH)	20.7, 22.3 (broad) (CH_3), 56.8 (CH), 170.5, 172.8, 174.4 (C=O, C=N)[c]	1590, 1620 (broad), 1730
18d	1.49 (d, J = 6.7) (CH_3), 4.93 (sept, J = 6.7) (CH)	21.2 (CH_3), 57.1 (CH), 170.0, 170.8 (C=N), 177.5 (C=O)[c]	1560, 1590, 1670, 1730
18e	1.52 (d, J = 6.7), 2.32, 3.50, 3.91 (CH_3), 4.50 (sept, J = 6.7) (CH)	21.3, 23.7, 45.1, 46.7, 54.4 (CH_3, CH), 81.8, 116.6 (C), 152.5 (C=N), 170.4 (C=O)[c]	1590, 1600, 1700, 2210
18f	1.62 (d, J = 6.7), 3.22, 3.54 (CH_3), 4.75 (sept, J = 6.7) (CH)	20.9, 45.0, 46.0, 57.3 (CH_3, CH), 80.9, 115.9 (C), 153.7 (C=N), 169.8 (C=O)[d]	1590, 1600[b], 1705, 2200
18g	1.38 (d, J = 6.7), 1.40 (d, J = 6.7), 2.34, 3.08 (d, J = 0.9), 3.53 (CH_3), 4.23 (2 H, m), 7.93 (CH)	20.7 (broad), 22.4, 24.8 (CH_3), 44.1, 47.7, 52.7, 57.3 (NCH_3, CH), 152.9, 157.2, 174.2 (C=N, C=O)[c]	1660, 1710[b], 1730
18h	1.37 (d, J = 6.7), 1.43 (d, J = 6.7), 2.34, 3.15 (broad) (CH_3), 2.24 (m), 3.21 (t), 3.99 (t) (CH_2), 4.21 (sept), 4.26 (sept) (CH)	19.0, 20.5, 21.5, 25.1, 36.1, 39.2, 53.1, 57.2, 59.9 (CH_3, CH_2, CH), 152.3, 172.8, 174.6 (C=N, C=O)[d]	1635, 1710
18i	1.13 (d, J = 6.7), 1.33 (d, J = 6.7), 1.43 (d, J = 7.0), 1.48 (d, J = 6.7), 2.29, 2.42, 3.49, 3.76 (CH_3), 3.88 (sept, J = 6.7), 4.09 (sept, J = 6.7), 4.32 (m), 8.10 (CH)[m]	19.9, 20.3, 21.4, 22.4, 25.2, 25.3 (CH_3), 45.0, 49.8, 53.0, 53.2, 57.0, 58.9 (NCH_3, CH), 151.0, 152.0, 155.9, 156.7, 173.5, 174.6 (C=N, C=O)[d,m]	1644, 1721
18j	1.02 (broad), 1.46 (d, J = 6.7), 2.14, 3.38, 3.70 (CH_3), 3.76 (sept, J = 6.7), 4.24 (sept, J = 6.7) (CH)	20.5 (broad), 21.5 (broad), 24.8 (CH_3), 46.9, 47.2, 52.7, 58.7 (NCH_3, CH), 153.8 (C=N), 172.7, 174.6 (C=O)[d]	1605, 1700
18k	1.41 (d, J = 6.7), 1.52 (d, J = 7.0), 2.27, 3.61, 3.85 (CH_3), 4.22 (2 H, m) (CH)	21.4, 21.5, 24.0 (CH_3), 46.1, 47.1, 52.7, 57.4 (NCH_3, CH), 81.8, 115.5 (C), 151.9, 154.4, 174.3 (C=N, C=O)[c]	1590, 1600, 1690 (broad), 2190
20a	1.58 (d, J = 6.7) (CH_3), 3.33, 3.36 (d, J = 0.6) (NCH_3), 4.70 (sept, J = 6.7), 6.38 (d, J = 11.0) (CH)[k]; 1.43 (d, J = 6.7), 3.08, 3.59 (CH_3), 4.38 (sept, J = 6.7), 6.47 (d, J = 10.4) (CH)[l]	20.8, 41.4, 49.2, 57.0 (CH_3, CH), 107.1 (C=), 167.2, 170.7, 174.0 (C=O, C=N, C=)[k]; 20.8, 42.4, 49.9, 56.3 (CH_3, CH), 114.6 (C=), 164.6, 166.6, 171.8 (C=O, C=N, C=)[c,l]	1525, 1630, 1700
20b	1.24 (d, J = 6.7), 2.05, 3.46, 3.50 (CH_3), 4.22 (sept, J = 6.7), 6.48 (d, J = 10.7) (CH)[g]; 1.09 (d, J = 7.0), 2.04 (broad), 3.59, 3.69 (CH_3), 4.55 (sept, J = 7.0), 7.11 (d, J = 10.7) (CH)[h]	20.8, 21.3 (broad), 23.7, 25.5 (CH_3), 42.3, 43.3, 49.9, 50.7, 51.3 (broad), 54.0 (NCH_3, CH), 164.5, 165.0, 167.5, 168.5, 171.7 (C=, C=N, C=O)[c]	1563, 1582, 1648, 1767

[a] In CD_2Cl_2. — [b] Shoulder. — [c] At 263 K. — [d] At 273 K. — [e] Spectra of an 1:1 mixture of **10a** and **11a**. — [f] Or OH. — [g] About 2:1 mixture of the geometric isomers: main component. — [h] About 2:1, minor component. — [i] About 7:1, main component. — [j] About 7:1, minor component. — [k] About 10:1, main component. — [l] About 10:1, minor component. — [m] About 1:1 mixture.

trometers; internal reference tetramethylsilane. – All experiments are carried out with exclusion of moisture. – Antimony pentachloride is distilled before use. – All solvents are dried by standard methods. – The melting points are uncorrected.

1-Acetyl-1,3-diisopropylcyanamidium Hexachloroantimonate (**5d**): Acetyl chloride (3.93 g, 50 mmol) in dichloromethane (20 ml) is added dropwise to a cold (0°C) stirred solution of diisopropylcarbodiimide (6.31 g, 50 mmol) in dichloromethane (20 ml). Stirring is continued at 0°C for 15 min and then at 23°C for 4 h. The reaction mixture is added dropwise to a cold (–40°C) solution of antimony pentachloride (14.95 g, 50 mmol) in dichloromethane (40 ml). Slow addition of ether (150 ml) at –40°C affords a colourless precipitate, which is suspended in ether (50 ml) at 23°C. Filtration furnishes a colourless moisture-sensitive powder (24.01 g, 95%); dec. 87–90°C.

$[C_9H_{17}N_2O]SbCl_6$ (503.7) Calcd. C 21.46 H 3.43 N 5.56
Found C 21.20 H 3.73 N 5.61

OH⁺-N-Isopropyl-2-methylpropanamidium Hexachloroantimonate (**7a**): A mixture of **5a**[28] (1.12 g, 2.5 mmol) and acetamide (0.18 g, 3.0 mmol) in dichloromethane (10 ml) is stirred at 23°C for 17 h. On addition of ether an oil precipitates, which solidifies when stirred under ether (40 ml) to give a colourless powder (0.95 g, 82%); m.p. 149–157°C (dec.).

$[C_7H_{16}NO]SbCl_6$ (464.7) Calcd. C 18.09 H 3.47 N 3.02
Found C 18.06 H 3.56 N 3.03

OH⁺-N-Isopropylbenzamidium Hexachloroantimonate (**7b**): A mixture of **5b**[28] (1.20 g, 2.5 mmol) and benzamide (0.32 g, 2.6 mmol) in dichloromethane (15 ml) is stirred at 23°C for 3 h. After cooling to –50°C the product is precipitated by dropwise addition of ether (50 ml). Yield: 0.78 g (64%) of a colourless powder; m.p. 147–155°C (dec.).

$[C_{10}H_{14}NO]SbCl_6$ (498.7) Calcd. C 24.08 H 2.83 N 2.81
Found C 24.22 H 3.11 N 2.88

2-(N-Isopropylacetamido)-1-pyrrolinium Hexachloroantimonate (**10a**) *and NH⁺-N-Isopropyl-(N-(1-pyrrolin-2-yl)acetamidium Hexachloroantimonate* (**11a**): A mixture of **9a** (0.22 g, 2.5 mmol) and **5c**[2] (1.05 g, 2.5 mmol) in dichloromethane (10 ml) is stirred at 23°C for 2 h. Addition of ether (60 ml) at –60°C affords an oil, which solidifies when stirred under ether (30 ml) at –80°C. The product is reprecipitated from dichloromethane (2 ml)/ether (60 ml) at –50°C to give a colourless powder (0.92 g, 73%); m.p. 110 to 114°C. According to the ^{1}H-NMR spectra this product is an 1:1 mixture of **10a** and **11a**.

$[C_9H_{17}N_2O]SbCl_6$ (503.7) Calcd. C 21.46 H 3.40 N 5.56
Found C 21.45 H 3.44 N 5.57

The mixture of **10a** + **11a** is dissolved in acetonitrile (5 ml). Slow addition of ether (100 ml) furnishes pure **11a** (0.62 g, 49%); m.p. 156–159°C (dec.).

$[C_9H_{17}N_2O]SbCl_6$ (503.7) Calcd. C 21.46 H 3.40 N 5.56
Found C 21.31 H 3.49 N 5.50

2-(N-Isopropylacetamido)pyridinium Hexachloroantimonate (**10b**): A solution of **9b** (0.24 g, 2.5 mmol) in dichloromethane (10 ml) is added dropwise to a stirred suspension of **5c** (1.05 g, 2.5 mmol) in dichloromethane (10 ml) at –30°C. Stirring is continued at –30°C for 1 h. Slow addition of ether (60 ml) affords a precipitate, which is stirred under dichloromethane (10 ml) at 23°C for 2 h. After keeping at –20°C for 24 h a powder is filtered off. Reprecipitation from dichloromethane (10 ml)/ether (30 ml) gives a colourless powder (0.51 g, 40%); m.p. 130–132°C (dec.).

$[C_{10}H_{15}N_2O]SbCl_6$ (513.7) Calcd. C 23.38 H 2.94 N 5.45
Found C 23.34 H 3.00 N 5.45

2-(N-Isopropylbenzamido)pyridinium Hexachloroantimonate (**10c**): From **5b** (1.20 g, 2.5 mmol) as described for **10b**. The product (1.08 g, 75%) is precipitated from the reaction mixture by slow addition of ether (60 ml) at –50°C. Reprecipitation from dichloromethane (10 ml)/ether (30 ml) affords a colourless powder; m.p. 119–122°C (dec.).

$[C_{15}H_{17}N_2O]SbCl_6$ (575.8) Calcd. C 31.29 H 2.98 N 4.87
Found C 31.08 H 3.04 N 4.87

2-[(Acetylisopropylcarbamoyl)isopropylamino]-1-pyrrolinium Hexachloroantimonate (**10d**): A mixture of **5d** (1.26 g, 2.5 mmol) and **9a** (0.26 g, 3.0 mmol) in dichloromethane (15 ml) is stirred at 23°C for 1 h. Precipitation by slow addition of ether (60 ml) at –20°C and reprecipitation from dichloromethane (25 ml)/ether (60 ml) at –20°C gives a colourless powder (0.99 g, 67%); m.p. 131–132°C (dec.).

$[C_{13}H_{24}N_3O_2]SbCl_6$ (588.8) Calcd. C 26.52 H 4.11 N 7.14
Found C 26.43 H 4.15 N 7.06

Benzoylisopropyl(2-pyridyl)ammonium Hexachloroantimonate (**11c**): A suspension of **10c** (1.00 g) in dichloromethane (5 ml)/formic acid (5 ml) is stirred at 23°C for 1 h. After addition of ether (50 ml) the product is filtered off. Reprecipitation from dichloromethane (5 ml)/ether (40 ml) affords a colourless powder (0.70 g, 70%); m.p. 128–131°C (dec.).

$[C_{15}H_{17}N_2O]SbCl_6$ (575.8) Calcd. C 31.29 H 2.98 N 4.87
Found C 31.13 H 3.00 N 4.87

3,4,5,6-Tetrahydro-3,5-diisopropyl-1-methyl-6-methylene-4-oxo-2-phenyl-1,3,5-triazinium Hexachloroantimonate (**12f**): A mixture of **5d** (2.52 g, 5 mmol) and **9f** (0.34 g, 2.5 mmol) in dichloromethane (10 ml) is stirred at 23°C for 3 h. Addition of pentane (50 ml) affords a yellow precipitate, which is dissolved in acetonitrile (5 ml). A yellow powder (0.65 g, 42%) is precipitated by slow addition of ether (60 ml); m.p. 152–155°C (dec.).

$[C_{17}H_{24}N_3O]SbCl_6$ (620.9) Calcd. C 32.89 H 3.90 N 6.77
Found C 32.71 H 3.93 N 6.83

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-6-methylene-4-oxo-1,3,5-triazinium Hexachloroantimonate (**12g**): A solution of *N*-isopropylformamide (0.87 g, 10 mmol) in dichloromethane (10 ml) is added dropwise to a solution of **5d** (10.07 g, 20 mmol) in dichloromethane (10 ml). The mixture is stirred at +25°C for 16 h. Addition of ether (50 ml) and filtration gives a yellow powder, which contains some **15g**. Reprecipitation from dichloromethane (10 ml)/chloroform (20 ml)/ether (50 ml) affords **12g** as a yellow powder (3.23 g, 56%), which slowly decomposes in solution in acetonitrile; m.p. 139–143°C.

$[C_{13}H_{24}N_3O]SbCl_6$ (572.8) Calcd. C 27.26 H 4.22 N 7.34
Found C 27.11 H 4.20 N 7.25

N¹-Acetyl-N¹,N²-dimethylacetamidinium Hexachloroantimonate (**14e**): A mixture of **5d** (2.52 g, 5.0 mmol) and **9e** (0.73 g, 10.0 mmol) in dichloromethane (10 ml) is stirred at 23°C for 14 h. Dropwise addition of ether (50 ml) affords a colourless powder (0.75 g, 32%). Reprecipitation from dichloromethane/ether yields the pure product; m.p. 178–180°C (dec.).

$[C_6H_{13}N_2O]SbCl_6$ (463.6) Calcd. C 15.55 H 2.83 N 6.04
Found C 15.56 H 2.86 N 6.01

N¹-Benzoyl-N¹,N²-dimethylbenzamidinium Hexachloroantimonate (**14f**): A mixture of **5d** (1.26, 2.5 mmol) and **9f** (1.69, 12.5 mmol) in dichloromethane (10 ml) is stirred at 23°C for 20 h. Precipitation by addition of pentane (50 ml) and reprecipitation from acetonitrile (2 ml)/ether (30 ml) affords a colourless foam, which solidifies when stirred under pentane (40 ml) to give a colourless powder (0.90 g) (61%); m.p. 158–161°C (dec.).

$[C_{16}H_{17}N_2O]SbCl_6$ (587.8) Calcd. C 32.69 H 2.92 N 4.77
Found C 32.49 H 2.97 N 4.80

No reaction is observed, when a mixture of **12f** with a fourfold excess of **9f** is stirred for 20 h in dichloromethane/acetonitrile.

Isopropyl[3-isopropyl-5-(isopropylimino)-2-methylenoxazolidin-2-yliden]ammonium Hexachloroantimonate (**15g**)

a) If the reaction leading to **12g** is carried out at −20°C instead of +25°C a yellow suspension is obtained. Addition of ether (50 ml) and filtration affords a yellow powder (4.93 g, 86%); m.p. 141 to 143°C.

$[C_{13}H_{24}N_3O]SbCl_6$ (572.8) Calcd. C 27.26 H 4.22 N 7.34
Found C 27.20 H 4.20 N 7.27

The compound melts to a red liquid, which shows the ^{1}H-NMR spectrum of unchanged **15g**. A rearrangement of **15g** to **12g** is not observed. According to the ^{1}H-NMR spectrum a solution of **15g** in CD_3CN is stable at 23°C for at least 48 h.

b) A solution of isopropyl isocyanide (0.42 g, 6 mmol) in dichloromethane (20 ml) is added dropwise to a solution of **5d** (2.52 g, 5 mmol) in dichloromethane (20 ml). The mixture is stirred at 23°C for 3 h. Precipitation by slow addition of ether (100 ml) affords a beige polymeric material (2.18 g). Addition of pentane (100 ml) to the filtrate yields a yellow powder (0.41 g, 28%), which shows an ^{1}H-NMR spectrum identical to that of **15g** obtained according to a).

Isopropyl[3-isopropyl-5-(methylimino)-2-methylenoxazolidin-2-yliden]ammonium Hexachloroantimonate (**15h**): A solution of **5d** (2.52 g, 5.0 mmol) and **9h** (0.15 g, 2.5 mmol) in dichloromethane (10 ml) is stirred at 23°C for 15 h. Slow addition of ether (60 ml) affords a yellow product, which after reprecipitation first from dichloromethane (5 ml)/ether (10 ml) and then from dichloromethane (10 ml)/ether (30 ml) gives a yellow powder (0.71 g, 52%); m.p. 132–134°C (dec.).

$[C_{11}H_{20}N_3O]SbCl_6$ (544.8) Calcd. C 24.25 H 3.70 N 7.71
Found C 24.15 H 3.62 N 7.64

2-(Benzyloxy)-2,3,4,5-tetrahydro-3,5-diisopropyl-1,6-dimethyl-4-oxo-2-phenyl-1,3,5-triazinium Hexachloroantimonate (**16a**): A mixture of **12f** (1.24 g, 2.0 mmol) and benzyl alcohol (0.32 g, 3.0 mmol) in dichloromethane (40 ml) is stirred at 23°C for 3 h. Addition of pentane (100 ml) affords a colourless precipitate (0.77 g, 53%); m.p. 145–148°C (dec.).

$[C_{24}H_{32}N_3O_2]SbCl_6$ (729.0) Calcd. C 39.54 H 4.42 N 5.76
Found C 39.39 H 4.44 N 5.79

2-(Benzyloxy)-2,3,4,5-tetrahydro-1,3,5-triisopropyl-6-methyl-4-oxo-1,3,5-triazinium Hexachloroantimonate (**16b**): A mixture of **12g** (1.14 g, 2.0 mmol) and benzyl alcohol (0.32 g, 3.0 mmol) in dichloromethane (10 ml)/acetonitrile (1 ml) is stirred at 23°C for 16 h. Slow addition of ether (80 ml) affords a colourless precipitate (0.86 g, 63%); m.p. 139–141°C.

$[C_{20}H_{32}N_3O_2]SbCl_6$ (681.0) Calcd. C 35.27 H 4.74 N 6.17
Found C 35.07 H 4.73 N 6.16

2,3,4,5-Tetrahydro-1,3,5-triisopropyl-2-methoxy-6-methyl-4-oxo-1,3,5-triazinium Hexachloroantimonate (**16c**): A mixture of **12g** (1.14 g, 2 mmol) and methanol (1 ml) are stirred in dichloromethane (10 ml) at 23°C for 16 h. Addition of ether (100 ml) affords a colourless precipitate (0.90 g, 74%); m.p. 149–151°C.

$[C_{14}H_{28}N_3O_2]SbCl_6$ (604.9) Calcd. C 27.80 H 4.67 N 6.95
Found C 27.73 H 4.55 N 6.86

N^1-Acetyl-N^1-isopropyl-N^2-methyl-N^2-phenylformamidinium Hexachloroantimonate (**18a**): A mixture of **5c** (1.05 g, 2.5 mmol) and **17a** (0.41 g, 3.0 mmol) in dichlormethane (10 ml) is stirred at 23°C for 2 h. Precipitation by slow addition of ether (60 ml) at −60°C affords a colourless powder (1.38 g, 100%), which is reprecipitated from dichloromethane (5 ml)/ether (40 ml). Yield: 1.31 g (95%) of a colourless powder; m.p. 97–100°C (dec.).

$[C_{13}H_{19}N_2O]SbCl_6$ (553.8) Calcd. C 28.19 H 3.45 N 5.06
Found C 28.07 H 3.57 N 5.22

N^1-Benzoyl-N^1-isopropyl-N^2-methyl-N^2-phenylformamidinium Hexachloroantimonate (**18b**): From **5b** (1.20 g, 2.5 mmol) as described for **18a**. Reprecipitation of the product from dichloromethane (10 ml)/ether (50 ml) at −40°C gives a colourless powder (1.18 g, 77%); m.p. 124–126°C (dec.).

$[C_{18}H_{21}N_2O]SbCl_6$ (615.8) Calcd. C 35.10 H 3.44 N 4.55
Found C 35.20 H 3.42 N 4.60

1-(N-Isopropylacetamido)-1,3,3-triphenyl-2-azoniaallene Hexachloroantimonate (**18c**): A mixture of **5c** (1.05 g, 2.5 mmol) and **17c**[30] (0.86 g, 3.0 mmol) in dichloromethane (20 ml) is stirred at 23°C for 4 h. Evaporation of the solvent and stirring the residue under ether (40 ml) gives a powder, which is crystallized from dichloromethane (2 ml)/ether (10 ml) affording a colourless powder (1.06 g, 60%); m.p. 115–117°C (dec.).

$[C_{25}H_{25}N_2O]SbCl_6$ (703.9) Calcd. C 42.65 H 3.58 N 3.98
Found C 42.61 H 3.50 N 3.96

1-(N-Isopropylbenzoylamido)-1,3,3-triphenyl-2-azoniaallene Hexachloroantimonate (**18d**): A solution of **17c** (0.86 g, 3.0 mmol) in dichloromethane (10 ml) is added dropwise to a stirred suspension of **5b** (1.20 g, 2.5 mmol) in dichloromethane (10 ml). After 3.5 h the clear solution is cooled to −60°C and ether (60 ml) is added dropwise. The precipitate crystallizes from dichloromethane (12 ml) at −20°C to yield colourless prisms (1.18 g, 62%); m.p. 116–118°C (dec.).

$[C_{30}H_{27}N_2O]SbCl_6$ (766.0) Calcd. C 47.04 H 3.55 N 3.66
Found C 46.83 H 3.54 N 3.63

N^1-Acetyl-N^1-isopropyl-N^2,N^2-dimethyl-3-phenylpropynamidinium Hexachloroantimonate (**18e**): A mixture of **5c** (1.05 g, 2.5 mmol) and **17e**[30] (0.44 g, 2.5 mmol) in dichloromethane (20 ml) is stirred at 23°C for 6 h. Flash chromatography of the yellow solution with dichloromethane as eluent yields a foam, which solidifies when stirred under ether (40 ml). Precipitation of the product from dichloromethane (10 ml)/ether (60 ml) at −60°C gives a yellow powder (0.76 g, 52%); m.p. 130–133°C (dec.).

$[C_{16}H_{21}N_2O]SbCl_6$ (591.8) Calcd. C 32.47 H 3.58 N 4.73
Found C 32.66 H 3.54 N 4.77

N^1-Benzoyl-N^1-isopropyl-N^2,N^2-dimethyl-3-phenylpropynamidinium Hexachloroantimonate (**18f**): From **5b** (1.20 g, 2.5 mmol) as described for **18e**. Yield after flash chromatography: 1.06 g (65%). Precipitation from dichloromethane (10 ml)/ether (35 ml) gives a colourless powder; m.p. 119–122°C (dec.).

$[C_{21}H_{23}N_2O]SbCl_6$ (653.9) Calcd. C 38.57 H 3.55 N 4.29
Found C 38.92 H 3.68 N 4.04

N^1-(Acetylisopropylcarbamoyl)-N^1-isopropyl-N^2,N^2-dimethylformamidinium Hexachloroantimonate (**18g**): A solution of diisopropylcarbodiimide (0.63 g, 5.0 mmol) and acetyl chloride (0.40 g, 5.0 mmol) in dichloromethane (10 ml) is stirred at 23°C for 4 h. The reaction mixture is added dropwise to a cold (−78°C) solution of antimony pentachloride (1.50 g, 5.0 mmol) in dichloromethane (10 ml). After 15 min of stirring a solution of dimethylformamide (0.37 g, 5.0 mmol) in dichloromethane (5 ml) is added. Stirring is

continued at −30°C for 2 h, and then ether (60 ml) is added dropwise to afford a precipitate, which is reprecipitated from dichloromethane (20 ml)/ether (60 ml) at −30°C. Yield: 2.42 g (84%) of a colourless powder; m.p. 155−157°C (dec.).

$[C_{12}H_{24}N_3O_2]SbCl_6$ (576.8) Calcd. C 24.99 H 4.19 N 7.29
Found C 24.94 H 4.27 N 7.27

2-[(Acetylisopropylcarbamoyl)isopropylamino]-1-methyl-1-pyrrolinium Hexachloroantimonate (**18h**): From **5d** (1.26 g, 2.5 mmol) and **17h** (0.30 g, 3.0 mmol) as described for **10d**. Yield: 1.37 g (91%); m.p. 135−136°C (dec.).

$[C_{14}H_{26}N_3O_2]SbCl_6$ (602.9) Calcd. C 27.89 H 4.35 N 6.97
Found C 27.80 H 4.30 N 6.94

N^1-(Acetylisopropylcarbamoyl)-N^1-isopropyl-N^2-methyl-N^2-phenylformamidinium Hexachloroantimonate (**18i**): A mixture of **5d** (10.07 g, 20 mmol) and **17i** (3.38 g, 25 mmol) in dichloromethane (30 ml) is stirred at 23°C for 2 h. After cooling to −30°C pentane (70 ml) is added dropwise. A yellow oil is obtained, which is stirred under ether (50 ml) at −30°C to afford a colourless powder (9.27 g, 73%); m.p. 115−117°C (dec.).

$[C_{17}H_{26}N_3O_2]SbCl_6$ (638.9) Calcd. C 31.96 H 4.10 N 6.58
Found C 31.97 H 4.20 N 6.54

N^1-(Acetylisopropylcarbamoyl)-N^1-isopropyl-N^2,N^2-dimethylbenzamidinium Hexachloroantimonate (**18j**): A mixture of **5d** (1.26 g, 2.5 mmol) and **17j** (0.45 g, 3.0 mmol) in dichloromethane (15 ml) is stirred at 23°C for 2 h. After cooling to −50°C ether (60 ml) is added. The precipitating oil solidifies when stirred under ether (40 ml) to give a colourless powder (0.90 g, 55%); m.p. 133−134°C (dec.).

$[C_{18}H_{28}N_3O_2]SbCl_6$ (652.9) Calcd. C 33.11 H 4.32 N 6.44
Found C 32.90 H 4.34 N 6.25

N^1-(Acetylisopropylcarbamoyl)-N^1-isopropyl-N^2,N^2-dimethyl-3-phenylpropynamidinium Hexachloroantimonate (**18k**): From **17k** (0.69 g, 4 mmol) as described for **18g**. After stirring the reaction mixture at 23°C for 20 h the solvent is evaporated under reduced pressure, and the residue is stirred under ether (40 ml) for 3 h to afford a yellow powder (1.88 g, 69%). Flash chromatography on silica gel with dichloromethane as eluent gives a yellow oil as the first fraction, which is dissolved in dichloromethane (10 ml). On addition of ether (40 ml) at −30°C a yellow oil precipitates, which solidifies to a yellow powder on drying; m.p. 74−77°C (dec.).

$[C_{20}H_{28}N_3O_2]SbCl_6$ (676.9) Calcd. C 35.48 H 4.17 N 6.21
Found C 35.14 H 4.25 N 5.82

Acetyl[3-(dimethylamino)-1-phenyl-2-propenyliden]isopropylammonium Hexachloroantimonate (**20a**): A solution of **19**[31] (0.44 g, 2.5 mmol) in dichloromethane (10 ml) is added dropwise at −78°C to a stirred suspension of **5b** (1.04 g, 2.5 mmol) in dichloromethane (10 ml). Stirring is continued at −30°C for 2 h. On slow addition of ether (60 ml) at −60°C a yellow precipitate is formed, which after reprecipitation from dichloromethane (10 ml)/ether (50 ml) at −50°C yields a pale yellow powder (0.97 g, 65%); m.p. 186−188°C (dec.).

$[C_{16}H_{23}N_2O]SbCl_6$ (593.8) Calcd. C 32.36 H 3.90 N 4.72
Found C 32.23 H 3.94 N 4.68

Benzoyl[3-(dimethylamino)-1-phenyl-2-propenyliden]isopropylammonium Hexachloroantimonate (**20b**): From **5b** (1.20 g, 2.5 mmol) as described for **20a**. Yield: 1.49 g (91%) of a pale yellow powder; m.p. 171−173°C (dec.).

$[C_{21}H_{25}N_2O]SbCl_6$ (655.9) Calcd. C 38.45 H 3.84 N 4.27
Found C 38.27 H 3.90 N 4.00

CAS Registry Numbers

5a: 90616-05-0 / **5b**: 20126-95-8 / **5c**: 20126-93-6 / **5d**: 126578-39-0 / **7a**: 126578-40-3 / **7b**: 126578-41-4 / **9a**: 616-45-5 / **9b**: 142-08-5 / **9e**: 79-16-3 / **9f**: 613-93-4 / **9h**: 123-39-7 / **10a**: 126578-43-6 / **10b**: 126578-45-8 / **10c**: 126578-47-0 / **10d**: 126578-49-2 / **12f**: 126578-51-6 / **12g**: 126578-53-8 / **14e**: 126578-55-0 / **14f**: 126578-56-1 / **15g**: 126578-58-3 / **15h**: 126578-60-7 / **16a**: 126578-62-9 / **16b**: 126578-64-1 / **16c**: 126578-66-3 / **17a**: 93-61-8 / **17c**: 1585-45-1 / **17e**: 26218-50-8 / **17h**: 872-50-4 / **17j**: 611-74-5 / **18a**: 126578-68-5 / **18b**: 126578-70-9 / **18c**: 126578-72-1 / **18d**: 126578-74-3 / **18e**: 126578-76-5 / **18f**: 126578-78-7 / **18g**: 126578-80-1 / **18h**: 126578-82-3 / **18i**: 126578-84-5 / **18j**: 126578-86-7 / **18k**: 126578-88-9 / **19**: 1201-93-0 / **20a**: 126578-90-3 / **20b**: 126578-92-5 / diisopropylcarbodiimide: 693-13-0 / acetamide: 60-35-5 / benzamide: 55-21-0 / *N*-isopropylformamide: 16741-46-1 / isopropyl isocyanide: 598-45-8

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