On the Reaction of Cyanamides with *N*-Alkylnitrilium and *N,N*-Dialkylcyanamidium Salts

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Z. Naturforsch. **2009**, *64b,* 297 – 306; received October 27, 2008

Dedicated to Professor Johannes C. Jochims on the occasion of his 75th birthday

N-Alkylnitrilium and *N,N*-dialkylcyanamidium salts **1** and **2** undergo ene reactions with cyanamides **4** to afford 2-azoniaallene salts **7** and **9** in which the *N*-alkylnitrilium salts **1** react as the ene, and the cyanamides **4** react as the enophile components. Competing with the ene reaction, *N*-alkylnitrilium salts **1** undergo [2$^+$+2+2] cycloaddition to furnish triazinium salts **8**. 2-Azoniaallene salts react with alcohols to afford alkoxy amino derivatives **10** and **12**, which yield iminium salts **11** and ketals/acetals upon further reaction with alcohols. The constitution of the 2-azoniaallene **7** and **9** and triazinium salts **8** was secured by elemental analyses and spectral properties (IR and NMR).

Key words: Ene Reaction, [2$^+$+2+2]-Cycloaddition, Nitrilium, Cyanamidium, 2-Azoniallene, Triazinium

Introduction

The existence of nitrilium salts **1** (Fig. 1) was predicted, and they were proposed as intermediates in organic synthesis and reaction mechanisms by Hantzsch [1] already in 1931.

Stable nitrilium salts **1** were first prepared by Klages [2] and Meerwein [3]. Also, they were proposed as reactive intermediates in numerous organic reaction mechanisms, such as the Beckmann rearrangement [4], and in the Ritter [5], von-Braun [6], Bischler-Napieralski [6], Houben-Hoesch [7], Gattermann [8], and Schmidt reactions [9].

Various types of reactions were reported for nitrilium and cyanamidium salts, such as their reaction with nucleophiles affording simple addition, cycloaddition and ene reactions, and reactions with alkynes [10], alkenes [11], carbonyl compounds [12], amides [13], 1,3-dipoles [14], substituted and unsubstituted imines [15] and carbodiimides [16]. Arenes react with *N*-aryl- or *N*-alkylnitrilium salts to give iminium ions [10a, 17]. In these reactions, the incoming nucleophilic groups become located in the position *cis* to the *N*-substituent [10a, 18]. An ene reaction was also proposed for the reaction of nitrilium ions with arenes, with inverse electron demand, where the nitrilium ion acts as the ene and the arene as the enophile [19].

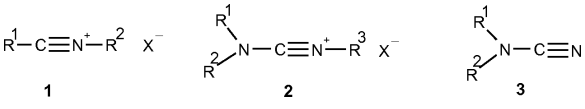


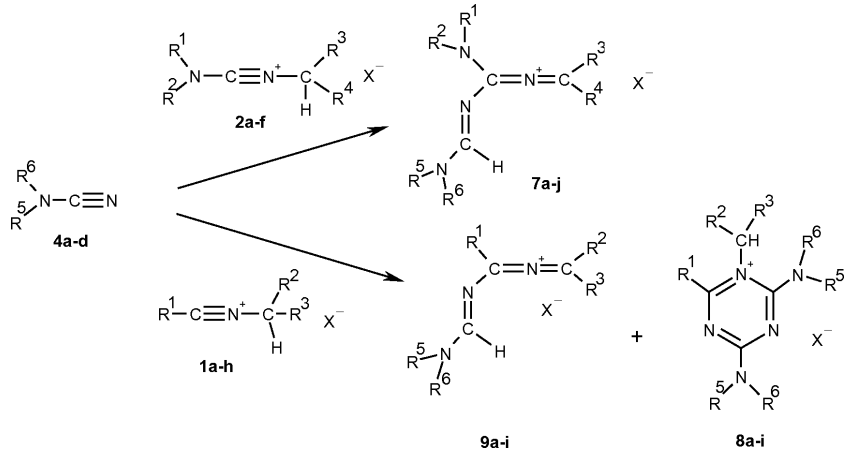
Fig. 1.

We have reported the reaction of nitrilium salts **1** and cyanamidium salts **2** with carbodiimiides [16] following our interest in the reaction of nitrilium salts **1** and cyanamidium salts **2** with nucleophiles [10a, 11b, 12b – c, 13a, 14a, 15, 16, 20]. The question arose whether and how cyanamides **4** would react with *N*-alkylnitrilium **1** and *N*-alkylcyanamidium salts **2**. In this work, the reactions between nitrilium and cyanamidium salts **1** and **2** with cyanamides **4** are reported, as shown in Scheme 1.

Results and Discussion

N-alkylnitrilium salts **1** were obtained by the alkylation of nitriles with alkyl halides [3, 21]. The cyanamidium salts **2** were prepared by the reaction of *N*-chlorodialkylamines with alkyl isonitriles in the presence of zinc chloride or mercurous chloride followed by the addition of antimony pentachloride as Lewis acid [20c].

Stirring a solution of 3-isopropyl-1,1-dimethylcyanamidium hexachloroantimonate (**2a**) and *N,N*-dimeth-



Compounds **1a – g**:

Entry	**a**	**b**	**c**	**d**	**e**	**f**	**g**
R^1	Me	Et	*i*-Pr	Bz	Ph	Ph	Ph
R^2	Me	Me	Me	Me	Me	Me	H
R^3	Me	Me	Me	Me	Me	Et	H

Compounds **2a – f**:

Entry	**a**	**b**	**c**	**d**	**e**	**f**
R^1	Me	Me	*i*-Pr	*i*-Pr	*i*-Pr	
R^2	Me	*i*-Pr	*i*-Pr	*i*-Pr	*i*-Pr	
R^3	Me	Me	H	H	Ph	Ph
R^4	Me	Me	H	Ph	Ph	Ph

Compounds **4a – d**:

Entry	**a**	**b**	**c**	**d**
R^5	Me	Me	*i*-Pr	
R^6	Me	*i*-Pr	*i*-Pr	

Compounds **7a – j**:

Entry	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**
R^1	*i*-Pr	*i*-Pr	*i*-Pr	*i*-Pr	*i*-Pr	*i*-Pr	*i*-Pr	*i*-Pr		Me
R^2	*i*-Pr	*i*-Pr	*i*-Pr	*i*-Pr	*i*-Pr	*i*-Pr	*i*-Pr	Me		Me
R^3	H	H	H	H	Me	Ph	Ph	Me	Ph	Me
R^4	H	Ph	Ph	Ph	Me	Ph	Ph	Me	Ph	Me
R^5	Me	Me	Me	*i*-Pr	Me	Me	*i*-Pr	Me		Me
R^6	Me	Me	*i*-Pr	*i*-Pr	Me	Me	*i*-Pr	Me		Me

Compounds **8a – i**:

Entry	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**
R^1	Me	Et	*i*-Pr	Bz	Ph	Ph	Ph	Ph	Ph
R^2	Me	Me	Me	Me	Me	Me	H	H	Me
R^3	Me	Me	Me	Me	Me	Et	H	H	Me
R^5	Me	Me	Me	Me	Me	Me	Me	*i*-Pr	
R^6	Me	Me	Me	Me	Me	Me	Me	*i*-Pr	

Compounds **9a – i**:

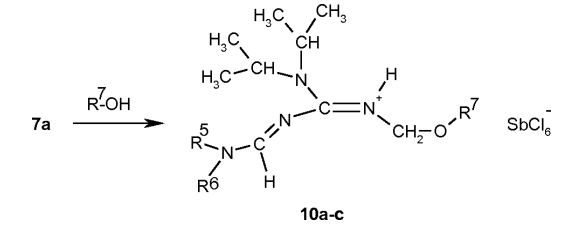
Entry	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j***
R^1	*i*-Pr	*i*-Pr	*t*-Bu	*t*-Bu	*t*-Bu	Ph	Ph	Ph	Ph	Bz
R^2	Me	Me	Me	Me	Me	Me	Me	Me	Me	Me
R^3	Me	Me	Me	Me	Me	Me	Me	Me	Et	Me
R^5	Me	*i*-Pr	Me	Me	*i*-Pr	*i*-Pr	Ph	Me	*i*-Pr	*i*-Pr
R^6	Me	*i*-Pr	Me	*i*-Pr	*i*-Pr	*i*-Pr	Ph	Ph	*i*-Pr	*i*-Pr

* Isolated as **12c**.

Scheme 1.

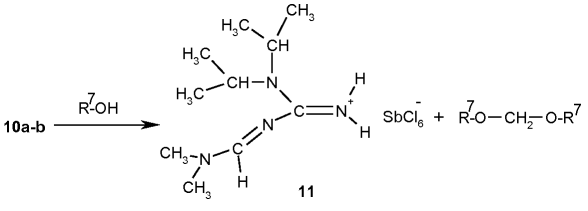
ylcyanamide (**4a**) in CH_2Cl_2 at low temperature afforded the 2-azoniaallene salt **7a** in 81 % yield. The product was formed through an ene reaction. Similarly, compounds **7b – j** were obtained in 48 – 90 % yield. Ene reactions of acetylenes [10a], alkenes [11] and 2-methylthiophene [19] with *N*-isopropylphenylnitrilium salts have been reported. Azoniaallenes **7a – j** are characterized by their strong and broad IR absorptions in the range $\nu = 1625 - 1700\ cm^{-1}$, which are assigned to the skeletal stretching vibration of a C=N$^+$=C unit [10a, 15a]. It was reported that the corresponding IR absorption of hetero-substituted 2-azoniaallene salts are shifted to longer wavelengths [15, 22]. Compounds **7** are formed completely stereoselectively with the *E*-configuration (*anti*) of the imine double bond, which may isomerize to the *Z*-configuration (*syn)* and lead to a *Z/E* mixture with time. This can be concluded from the similar results previously published for the addition of acetylenes [10a] and imines [15b] to the nitrilium salts.

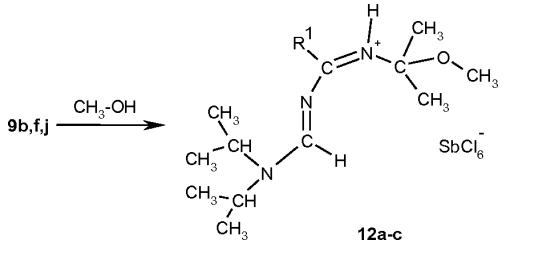
In the case of the addition of cyanamides **4** to nitrilium salts **1**, triazinium salts **8** and/or 2-azoniaallene salts **9** were formed. The triazinium salts **8** are formed through the [2$^+$+2+2] cycloaddition while the 2-azoniaallene salts are formed by the ene reaction.



Compounds **10a – c**

Entry	a	b	c
R^5	Me	Me	*i*-Pr
R^6	Me	Me	*i*-Pr
R^7	Me	Et	Me





Compounds **12a – c**

Entry	a	b	c
R^1	*i*-Pr	Ph	Bz

Scheme 2.

The competition between cycloaddition product **8** and the ene product **9** depends on the steric hindrance of the *C*-alkyl substituents of the nitrilium salts **1**, as shown in the case of the formation of **9c**, **d**, **e** (*C*-terminal is *t*-Bu) and the formation of **8a** in good yields (*C*-terminal is Me). In the case of an *N*-methyl substituent, the triazinium salts **8g**, **h** were formed in high yield (90 %). The addition of *N,N*-diisopropylcyanamide (**4c**) produced the 2-azoniaallene salts **9b**, **e**, **f**, **i** in good yields. Also, it was found that upon replacement of the *C*-alkyl substituent with an amino group as in the case of *N,N*-dialkylcyanamidium salts **2**, the only isolated products were the 2-azoniaallene salts **7**. The low yields of **8** can be explained by the formation of 2-azoniaallene salts **9**, which were not isolated due to their reaction with ethanol in the purification process leading to salts **12** which reacted further to iminium salts and other products. These results led

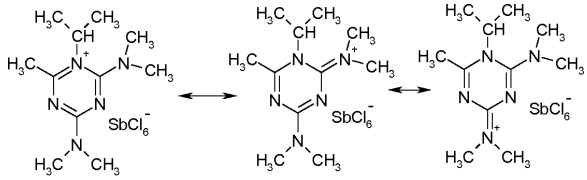


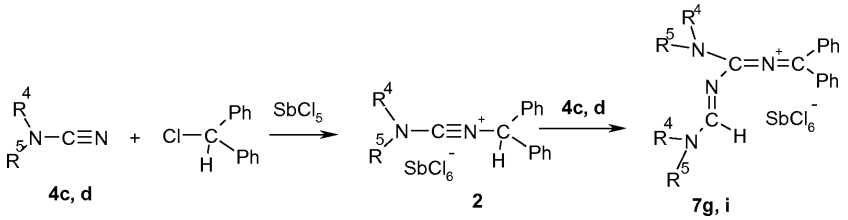
Fig. 2.

us to study the reaction of alcohols with the isolated 2-azoniaallene salts **7a** and **9b**, **f**, **j**. The first addition of alcohols leads to the formation of **10a – c** and **12a – c**. Further addition of alcohol to **10** leads to the formation of the iminium salt **11** and acetals or ketals, as shown in Scheme 2.

The structure of the triazinium salts **8** can be derived from the elemental analyses and NMR spectra *e. g.* the ^{1}H NMR spectrum of **8a** shows signals for one isopropyl group, one methyl group linked to a heteroaromatic ring (δ = 2.66), and two equivalent signals for the *N,N*-dimethyl group at δ = 3.21 and signals for non-equivalent *N,N*-dimethyl groups at δ = 3.26 and 3.33 ppm. The non-equivalence is probably due to slow rotation around the exocyclic partial double bond in $C{=}N^+Me_2$, as illustrated in the canonical forms **8A** and **8B** (Fig. 2). The ^{13}C NMR spectrum shows signals at δ = 158.8, 161.1 and 168.5 ppm, which can be assigned to two C=N groups and one $C{=}N^+$ unit. The IR (CH_2Cl_2) absorptions for the imine and iminium functional groups of the triazinium salt **8** were observed at 1550 and 1600 – 1610 cm^{-1}.

Spectroscopically, the 2-azoniaallene salts **7** and **9** are characterized by a very strong and broad IR band around 1610 – 1715 cm^{-1} assigned to the antisymmetric $C{=}N^+{=}C$ vibration. In the ^{13}C NMR spectra the resonance for the $C{=}N^+{=}C$ carbon atom appears as a broad weak signal in the range 163 – 186 ppm as reported for a similar salt [13, 15]. The ^{1}H and ^{13}C NMR spectra of the formamidine hydrogens and carbons are observed in the ranges 7.8 – 8.2 ppm and 155 – 160 ppm, respectively, which is in agreement with the data reported for amidines [23]. The IR absorptions of hetero-substituted 2-azoniaallene salts are shifted to longer wavelengths [10a]. The X-ray structure determination of similar amino-substituted 2-azoniaallene salts was reported [15a].

In another case, it was found that the alkylation of cyanamides **4a**,**f** with chlorodiphenylmethane in the presence of antimony pentachloride leads to the formation of 2-azoniaallene salts **7g** and **7i** through the for-



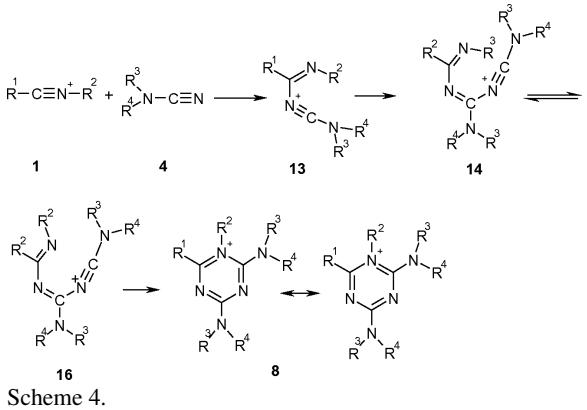
Scheme 3.

mation of a cyanamidium salt intermediate followed by the attack of another mole of the starting cyanamide, as shown in Scheme 3.

Mechanism

Under the reaction conditions, neither the triazinium salts **8** could be transformed into the azoniaallene salts **9**, nor did **9** cyclize to **8**. It seems most likely that compounds **8** and **9** are formed *via* independent reaction paths. *N*-Alkylnitrilium and *N*-alkylcyanamidium salts **1** and **2** undergo ene reactions with electron-rich cyanamides to afford 2-azoniaallene salts **9** and **7**, respectively, in which the nitrilium cation reacts as the ene, and the cyanamide reacts as the enophile. However, the reaction of *N*-alkylnitrilium salts **1** with cyanamides **4** furnished triazinium salts **8** *via* concerted or stepwise [2$^+$+2+2] cycloaddition which is competing with the normal ene reaction (Scheme 4). Stepwise [2$^+$+2+2] cycloaddition and nucleophilic addition to nitrilium ions have been shown by Hegarty *et al*. [18] to be stereoelectronically controlled. The nitrogen lone pair develops always *trans* to the intruding nucleophile (*Z*-isomer). In the resulting imines, the nucleophile and the *N*-substituent are *cis* with respect to each other.

It is likely, therefore, that the successive addition of the cyanamide **4** to a nitrilium ion gives new cyanimidium salt adducts **13** and **14** (*Z*-isomers). Thermal isomerization around the R-C=N-R bond furnishes the *E*-isomer **15**. The formation of a resonance-stabilized guanidinium moiety in triazinium salts **8** must be the driving force for the addition of another molecule of cyanamide to **6** and formation of the cycloproduct, as shown in Scheme 4.



Scheme 4.

Experimental Section

General information

All reactions involving moisture sensitive compounds were carried out in dried glassware under Ar atmosphere. The organic solvents were dried and stored over molecular sieves. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer in CH_2Cl_2 solution; the frequencies are expressed in cm^{-1}. Melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. NMR spectra were recorded on Bruker AC-250 and Bruker DPX-300 instruments, using TMS as internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Elemental analyses were preformed with an Electrothermal 9100 apparatus. Chemical substances were purchased from Acros Organics, Merck and Aldrich. Nitrilium salts **1a** [15a], **b** [10a], **c** [15a], **d** [13a], **e** [10a], **f** [2], **g** [3b] and **2a – e** [20c] were synthesized by literature procedures.

Synthesis

*General procedure for the preparation of substituted azoniaallene salts (**7a – j**)*

A solution of 5 mmol of a cyanamide **4a – d** dissolved in 20 mL of dichloromethane was added dropwise to a cooled (−20 °C) and stirred solution of 5 mmol of the appropriate cyanamidium hexachloroantimonate **2a – f**. The solution was stirred at this temperature for 1 h, then the temperature was allowed to rise to 10 °C and stirring continued for an additional 1 h, after which time the IR spectrum of the solution showed the disappearance of the absorption of the nitrilium peak of the nitrilium salts (2230 cm^{-1}). The solution was reduced to half volume *in vacuo* and then cooled to −20 °C. 100 mL of absolute diethyl ether was added dropwise to give a powder precipitate, which was collected and vacuum

dried. The precipitate was purified by recrystallization from 10 mL/100 mL diethyl ether.

*{[(E)-(Dimethylamino)methylidene]amino}(dipropan-2-ylamino)-N-methylidenemethan-iminium hexachloroantimonate (**7a**)*

Yellow powder (81 %). – M. p. 136 – 138 °C. – IR (CH_2Cl_2): ν = 1640, 1550 (C=N) cm^{-1}. – ^1H NMR (CD_2Cl_2): δ = 1.29 (d, 6 H, J = 6.7 Hz, CHMe_2), 1.52 (d, 6 H, J = 6.7 Hz, CHMe_2), 3.22 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 3.28 (s, 3H, NCH_3), 3.35 (s, 3H, NCH_3), 4.01 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 7.81 (s, 1 H, CH=N), 7.89 (s, 2H, N^+=CH_2). – ^{13}C NMR (CD_2Cl_2): δ = 20.4, 20.8, 37.2, 43.2, 50.2, 51.9, 159.4 (CH=N), 164.1, 166.9 (CH=N^+). – $C_{11}H_{23}N_4$ $SbCl_6$ (545.8): calcd. C 24.21, H 4.25, N 10.27; found C 24.48, H 4.35, N 10.29.

*N-[(Dipropan-2-ylamino){[(E)-(dimethylamino)methylidene]amino}methylidene]-1-phenylethaniminium hexachloroantimonate (**7b**)*

Yellow powder (67 %). – M. p. 135 – 137 °C. – IR (CH_2Cl_2): ν = 1635, 1625, 1540 (C=N) cm^{-1}. – ^1H NMR (CD_2Cl_2): δ = 1.32 (d, 6 H, J = 6.7 Hz, CHMe_2), 1.53 (d, 6 H, J = 6.7 Hz, CHMe_2), 3.25 (s, 3H, NCH_3), 3.29 (s, 3H, NCH_3), 4.13 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 4.32 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 7.74 (m, 5H, Ph), 7.97, 8.04 (2s, 1 H, CH=N), 8.59 (s, 1 H, PhHC=N). – ^{13}C NMR (CD_2Cl_2): δ = 20.2, 20.5, 37.2, 43.0, 50.4, 51.5, 129.8, 131.0, 133.2, 135.3, 159.1 (CH=N), 167.3, 168.9 (CH=N^+). – $C_{17}H_{27}N_4$ $SbCl_6$ (621.9): calcd. C 32.83, H 4.38, N 9.01; found C 32.75, H 4.27, N 8.89.

*N-[(Dipropan-2-ylamino){[(E)-[methyl(propan-2-yl)amino]methylidene]amino}methylidene]-1-phenylethaniminium hexachloroantimonate (**7c**)*

Yellow powder (86 %). – M. p. 139 – 140 °C. – IR (CH_2Cl_2): ν = 1625, 1545 (C=N) cm^{-1}. – ^1H NMR (CD_2Cl_2): δ = 1.29 (d, 6 H, J = 7 Hz, CHMe_2), 1.32 (d, 6 H, J = 7 Hz, CHMe_2), 1.53 (d, 6 H, J = 6.7 Hz, CHMe_2), 3.09 (s, 3H, NCH_3), 4.12 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 4.27 (sept., 1 H, J = 7 Hz, CHMe$_2$), 4.89 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 7.63 (m, 5H, Ph), 7.96, 8.04 (2s, 1 H, CH=N), 8.53 (s, 1 H, PhHC=N). – ^{13}C NMR (CD_2Cl_2): δ = 19.2, 20.6, 20.9, 31.2, 35.3, 49.5, 50.35, 51.5, 129.3, 130.5, 133.2, 138.9, 156.8 (CH=N), 167.3, 168.9 (CH=N^+). – $C_{19}H_{31}N_4$ $SbCl_6$ (650.0): calcd. C 35.11, H 4.81, N 8.62; found C 35.02, H 4.88, N 8.54.

*N-Benzylidene(dipropan-2-ylamino){[(E)-(dipropan-2-ylamino)methylidene]amino}methaniminium hexachloroantimonate (**7d**)*

Yellow powder (66 %). – M. p. 155 – 157 °C. – IR (CH_2Cl_2): ν = 1642, 1553 (C=N) cm^{-1}. – ^1H NMR (CD_2Cl_2): δ = 1.25 (d, 6 H, J = 6.7 Hz, CHMe_2), 1.33 (d, 6 H, J = 6.7 Hz, CHMe_2), 1.39 (d, 6 H, J = 7 Hz), 1.51 (d, 6 H, J = 6.7 Hz), 3.82 (sept., 1 H, J = 7 Hz, CHMe$_2$), 4.13 (sept., 1 H, J = 7 Hz, CHMe$_2$), 4.40 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 4.75 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 7.74 (m, 5 H, Ph), 8.04 (2s, 1 H, CH=N), 8.59 (s, 1 H, PhHC=N). – ^{13}C NMR (CD_2Cl_2): δ = 20.0, 20.7, 20.9, 23.8, 50.3, 50.4, 50.7, 51.3, 129.9, 130.8, 133.2, 135.4, 157.8, 159.9 (CH=N), 167.1, 168.9 (CH=N^+). – $C_{21}H_{35}N_4$ $SbCl_6$ (678.0): calcd. C 37.20, H 5.20, N 8.26; found C 37.31, H 5.35, N 8.17.

*N-[{[(E)-(Dimethylamino)methylidene]amino}(dipropan-2-ylamino)methylidene]propan-2-iminium hexachloroantimonate (**7e**)*

Yellow powder (90 %). – M. p. 156 – 158 °C. – IR (CH_2Cl_2): ν = 1640, 1670 (C=N) cm^{-1}. – ^1H NMR (CD_2Cl_2, 303 K): δ = 1.26 (d, 6 H, J = 7 Hz, CHMe_2), 1.52 (d, 6 H, J = 6.7 Hz, CHMe_2), 2.21 (s, 6 H, =CMe_2), 3.24 (s, 3 H, NMe), 3.32 (s, 3 H, NMe), 3.95 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 4.10 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 8.65 (s, 1 H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ = 20.1, 20.9, 26.7, 37.0, 43.1, 49.9, 51.7, 158.7 (CH=N), 165.5, 180.3 (CH=N^+). – $C_{13}H_{27}N_4$ $SbCl_6$ (573.9): calcd. C 27.21, H 4.74, N 9.76; found C 27.23, H 4.68, N 9.65. – ^1H NMR (CD_2Cl_2, 213 K): δ = 1.26 (d, 6 H, J = 7 Hz, CHMe_2), 1.63, 183 (2d, 6 H, J = 6.7 Hz), 2.06, 2.37 (2s, 6 H, =CMe_2), 3.25, 3.33 (2s, 6 H, NMe), 3.84, 3.98 (m, 2 H, CHMe$_2$), 7.78 (s, 1 H, CH=N).

*{[(E)-(Dimethylamino)methylidene]amino}(dipropan-2-ylamino)-N-(diphenylmethylidene)methaniminium hexachloroantimonate (**7f**)*

Yellow powder (65 %). – M. p. 164 – 168 °C. – IR (CH_2Cl_2): ν = 1560, 1610 (C=N) cm^{-1}. – ^1H NMR (CD_2Cl_2, 263 K): δ = 1.10 (d, 6 H, J = 6.7 Hz, CHMe_2), 1.21 (d, 6 H, J = 6.7 Hz, CHMe_2), 3.25 (s, 3 H, NMe), 3.31 (s, 3 H, NMe), 3.72 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 4.13 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 7.33 (m, 10 H, Ph), 8.65 (s, 1 H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ = 19.4, 22.7, 38.9, 39.3, 49.5, 129.5, 129.6, 133.4, 134.9, 156.2, 166.0 (CH=N), 175.9 (CH=N^+). – $C_{23}H_{31}N_4$ $SbCl_6$ (698.0): calcd. C 39.58, H 4.48, N 8.03; found C 39.40, H 4.20, N 7.94.

*{[(E)-(Dipropan-2-amino)methylidene]amino}(dipropan-2-ylamino)-N-(diphenylmethylidene)methaniminium hexachloroantimonate (**7g**)*

Yellow powder (48 %). – M. p. 165 – 167 °C. – IR (CH_2Cl_2): ν = 1525, 1610 (C=N) cm^{-1}. – ^1H NMR (CD_2Cl_2, 263 K): δ = 1.11 (d, 6 H, J = 6.7 Hz, CHMe_2), 1.22 (d, 6 H, J = 6.7 Hz, CHMe_2), 1.29 (d, 6 H, J = 6.7 Hz, CHMe_2), 1.46 (d, 6 H, J = 6.7 Hz, CHMe_2), 3.73 (sept., 1 H, J = 7 Hz, CHMe$_2$), 4.21 (sept., 1 H, J = 6.7 Hz, CHMe$_2$),

4.28 (sept., 2 H, J = 6.7 Hz, C*H*Me$_2$), 7.65 (m, 10 H, Ph), 7.81 (s, 1 H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ = 19.8, 20.0, 20.8, 23.7, 49.5, 49.9, 51.2, 129.4, 129.8, 133.4, 135.1, 155.6 (CH=N), 164.8, 175.0 (CH=N$^+$). – $C_{27}H_{39}N_4$ $SbCl_6$ (754.1): calcd. C 43.00, H 5.21, N 7.43; found C 42.94, H 5.43, N 7.43.

*N-({[(E)-(Dimethylamino)methylidene]amino}[methyl (propan-2-yl)amino]methylidene)-propan-2-iminium hexachloroantimonate (**7h**)*

Yellow powder (73 %). – M. p. 154 – 157 °C. – IR (CH_2Cl_2): ν = 1570, 1645, 1670, 1700 (C=N) cm^{-1}. – ^{1}H NMR (CD_2Cl_2, 263 K): δ = 1.25, 127 (d, 6 H, J = 7 Hz, CH*Me*$_2$), 2.20, 2.23 (s, 3 H, N=C(CH$_3$)$_3$), 2.83 (s, 3 H, NCH$_3$), 3.16 (s, 3 H, NCH$_3$), 3.23 (s, 3H, NCH$_3$), 3.32 (s, 3 H, NCH$_3$), 3.97 (sept., 1 H, J = 6.7 Hz, C*H*Me$_2$), 5.12 (sept., 1 H, J = 6.7 Hz, C*H*Me$_2$), 7.79, 7.87 (2s, 1 H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ = 19.4, 19.9, 26.6, 26.8, 29.9, 30.1, 36.7, 43.1, 50.2, 51.2, 159.2, 159.4, 165.6, 166.1, 180.3, 180.9 (CH=N$^+$). – $C_{11}H_{23}N_4$ $SbCl_6$ (549.8): calcd. C 24.21, H 4.25, N 10.27; found C 24.07, H 4.07, N 10.37.

*N-(Morpholin)-4-yl{[(E)-morpholin-4-ylmethylidene] amino}-N-(diphenylmethylidene)-methaniminium hexachloroantimonate (**7i**)*

Yellow powder (79 %). – M. p. 184 – 187 °C. – IR (CH_2Cl_2): ν = 1525, 1610 (C=N) cm^{-1}. – ^{1}H NMR (CD_2Cl_2, 263 K): δ = 3.41 – 4.92 (m, 16 H, CH_2), 7.65 (m, 10 H, Ph), 8.11 (s, 1 H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ = 45.8, 46.8, 47.8, 52.2, 66.0, 66.2, 66.5, 67.1, 129.6, 129.8, 133.7, 135.0, 158.3 (CH=N), 165.6, 176.2 (CH=N$^+$). – $C_{23}H_{27}N_4O_2$ $SbCl_6$ (726.0): calcd. C 38.05, H 3.75, N 7.72; found C 38.10, H 3.59, N 7.67.

*N-[(Dimethylamino){[(E)-(dimethylamino)methylidene]-amino}methylidene]propan-2-iminium hexachloroantimonate (**7j**)*

Yellow powder (69 %). – M. p. 129 – 133 °C. – IR (CH_2Cl_2): ν = 1545, 1640, 1670 (C=N) cm^{-1}. – ^{1}H NMR (CD_2Cl_2, 263 K): δ = 2.21 (s, 6 H, N=C(CH$_3$)$_3$), 3.03 (s, 3 H, NCH$_3$), 3.23 (s, 3 H, NCH$_3$), 3.32 (s, 3 H, NCH$_3$), 3.36 (s, 3 H, NCH$_3$), 8.25 (s, 1 H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ = 26.8, 36.7, 38.8, 43.2, 159.4 (CH=N), 166.7, 181.1 (CH=N$^+$). – $C_9H_{19}N_4$ $SbCl_6$ (517.8): calcd. C 20.88, H 3.70, N 10.82; found C 21.00, H 3.65, N 10.69.

*General procedure for the reaction of cyanamides **4** and nitrilium salts **1** to afford azoniaaallene and triazinium salts **8** and **9***

A solution of **4** (10 mmol) in CH_2C1_2 (20 mL) was added dropwise to a cold (−30 °C) suspension of **1** (10 mmol) in CH_2C1_2 (20 mL). The mixture was stirred at 23 °C for 24 h. The reaction mixture showed disappearance of the broad IR band at 2220 cm^{-1} and appearance of a strong IR band at 1690 – 1715 cm^{-1}. Cooling to −30 °C and addition of Et_2O (60 mL) precipitated **8** as a yellow powder. The mother liquor of **8** was evaporated, and the residue was crystallized at −20 °C from CH_2C1_2 (10 mL)/Et_2O (40 mL) to furnish **9** as yellow powder.

*2,4-Bis(dimethylamino)-6-methyl-1-(propan-2-yl)-1,3,5-triazin-1-ium hexachloroantimonate (**8a**)*

Yellow powder (25 %). – M. p. 167 – 168 °C. – IR (CH_2Cl_2): ν = 1510, 1610 (C=N) cm^{-1}. – ^{1}H NMR (CD_2Cl_2): δ = 1.64 (d, 6 H, J = 7 Hz, CH*Me*$_2$), 2.66 (s, 3 H, CH$_3$), 3.22 (s, 6 H, NCH$_3$), 3.26 (s, 3H, NCH$_3$), 3.33 (s, 3H, NCH$_3$), 4.40 (sept., 1 H, J = 7 Hz, C*H*Me$_2$). – ^{13}C NMR (CD_2Cl_2): δ = 22.8, 24.5, 37.9, 41.6, 58.1, 158.4 (C=N), 161.1, 168.5 (C=N$^+$). – $C_{11}H_{22}N_5$ $SbCl_6$ (558.8): calcd. C 23.64, H 3.97, N 12.53; found C 23.48, H 3.86, N 12.38.

*2,4-Bis(dimethylamino)-6-ethyl-1-(propan-2-yl)-1,3,5-triazin-1-ium hexachloroantimonate (**8b**)*

Yellow powder (18 %). – M. p. 145 – 147 °C. – IR (CH_2Cl_2): ν = 1550, 1570, 1600 (C=N) cm^{-1}. – ^{1}H NMR (CD_3CN): δ = 1.28 (t, 3H, J = 7 Hz, CH_2CH_3), 1.65 (d, 6 H, J = 7 Hz, CH*Me*$_2$), 2.87 (q, 2H, J = 7 Hz, CH_2CH$_3$), 3.13 (s, 6 H, NCH$_3$), 3.21 (s, 3H, NCH$_3$), 3.92 (s, 3H, NCH$_3$), 4.38 (sept., 1 H, J = 7 Hz, C*H*Me$_2$). – ^{13}C NMR (CD_3CN): δ = 10.8, 22.7, 30.1, 37.7, 41.5, 58.3, 159.7 (C=N), 161.9, 173.5 (C=N$^+$). – $C_{12}H_{24}N_5$ $SbCl_6$ (572.8): calcd. C 25.16, H 4.22, N 12.23; found C 25.13, H 3.97, N 12.03.

*2,4-Bis(dimethylamino)-1,6-di(propan-2-yl)-1,3,5-triazin-1-ium hexachloroantimonate (**8c**)*

Yellow powder (32 %). – M. p. 142 – 144 °C. – IR (CH_2Cl_2): ν = 1550, 1615 (C=N) cm^{-1}. – ^{1}H NMR (CD_2Cl_2): δ = 1.35 (d, 6 H, J = 6.7 Hz, CH*Me*$_2$), 1.66 (d, 6 H, J = 7 Hz, CH*Me*$_2$), 3.23 (s, 6 H, NCH$_3$), 3.25 (sept., 1 H, J = 6.7 Hz, C*H*Me$_2$), 3.28 (s, 3H, NCH$_3$), 3.35 (s, 3H, NCH$_3$), 4.35 (sept., 1 H, J = 7 Hz, C*H*Me$_2$). – ^{13}C NMR (CD_2Cl_2): δ = 21.5, 23.6, 34.5, 37.9, 41.7, 58.5, 158.9 (C=N), 161.4, 177.7 (C=N$^+$). – $C_{13}H_{26}N_5$ $SbCl_6$ (586.9): calcd. C 26.61, H 4.47, N 11.93; found C 26.53, H 4.44, N 11.97.

*2-Benzyl-4,6-bis(dimethylamino)-1-(propan-2-yl)-1,3,5-triazin-1-ium hexachloroantimonate (**8d**)*

Yellow powder (42 %). – M. p. 154 – 156 °C. – IR (CH_2Cl_2): ν = 1550, 1570, 1600 (C=N) cm^{-1}. – ^{1}H NMR (CD_2Cl_2, 263 K): δ = 1.71 (d, 6 H, J = 7 Hz, CH*Me*$_2$), 3.18 (s, 3 H, NCH$_3$), 3.21 (s, 6H, NCH$_3$), 3.24 (s, 3H, NCH$_3$), 4.21 (s, 2H, CH_2), 4.41 (sept., 1 H, J = 6.8 Hz, C*H*Me$_2$), 7.27 – 7.42 (m, 5 H, Ph). – ^{13}C NMR (CD_2Cl_2): δ = 23.3,

37.7, 41.5, 42.1, 58.5, 127.8, 129.0, 129.6, 133.7, 158.2 (C=N), 160.8, 170.0 (C=N^+). – $C_{17}H_{26}N_5$ $SbCl_6$ (634.9): calcd. C 32.16, H 4.13, N 11.03; found C 31.92, H 4.26, N 10.71.

*2,4-Bis(dimethylamino)-6-phenyl-1-(propan-2-yl)-1,3,5-triazin-1-ium hexachloroantimonate (**8e**)*

Yellow powder (40 %). – M. p. 179 – 180 °C. – IR (CH_2Cl_2): ν = 1550, 1575, 1600 (C=N) cm^{-1}. – ^{1}H NMR (CD_2Cl_2): δ = 1.22 (d, 6 H, J = 6.7 Hz, CHMe_2), 3.35 (s, 3 H, NCH_3), 3.36 (s, 6H, NCH_3), 3.42 (s, 3H, NCH_3), 4.18 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 7.56 – 7.75 (m, 5H, Ph). – ^{1}H NMR (CD_3CN, 295 K): δ = 1.23 (d, 6 H, J = 7 Hz, CHMe_2), 3.26 (s, 6 H, NCH_3), 3.29 (s, 3H, NCH_3), 3.35 (s, 3H, NCH_3), 4.22 (sept., 1 H, J = 7 Hz, CHMe$_2$), 7.56 – 7.78 (m, 5H, Ph). – ^{13}C NMR (CD_2Cl_2): δ = 23.6, 38.8, 38.3, 41.1, 62.4, 129.0, 130.7, 130.9, 133.6, 158.3 (CH=N), 161.9, 170.1 (CH=N^+). – ^{13}C NMR (CD_3CN, 295 K): δ = 23.5, 38.1, 41.0, 62.0, 129.4, 131.8, 134.2, 134.8, 160.3 (CH=N), 162.5, 170.5 (CH=N^+). – $C_{16}H_{24}N_5$ $SbCl_6$ (620.8): calcd. C 30.95, H 3.90, N 11.28; found C 30.84, H 4.04, N 11.09.

*1-(Butan-2-yl)-2,4-bis(dimethylamino)-6-phenyl-1,3,5-triazin-1-ium hexachloroantimonate (**8f**)*

Yellow powder (24 %). – M. p. 146 °C (dec). – IR (CH_2Cl_2): ν = 1545, 1570, 1600 (C=N) cm^{-1}. – ^{1}H NMR (CD_3CN): δ = 0.69 (t, 3H, J = 7.3 Hz, CH_3CH_2), 1.17 (d, 3 H, J = 6.8 Hz, CHEtMe), 1.27, 1.62 (2m, 2H, CH_3CH_2), 3.27 (s, 6 H, NCH_3), 3.29 (s, 3H, NCH_3), 3.35 (s, 3H, NCH_3), 3.87 (m, 1 H, CHEtMe), 7.65 (m, 5 H, Ph). – ^{13}C NMR (CD_3CN): δ = 11.5, 21.7, 31.8, 38.1, 41.1, 67.7, 129.2, 131.6, 133.9, 134.7, 159.9 (C=N), 162.9, 170.3 (C=N^+). – $C_{17}H_{26}N_5$ $SbCl_6$ (634.9): calcd. C 32.16, H 4.13, N 11.03; found C 31.97, H 4.11, N 10.89.

*2,4-Bis(dimethylamino)-1-methyl-6-phenyl-1,3,5-triazin-1-ium hexachloroantimonate (**8g**)*

Yellow powder (92 %). – M. p. 201 °C. – IR (CH_2Cl_2): ν = 1550, 1570, 1605 (C=N) cm^{-1}. – ^{1}H NMR (CD_2Cl_2/CD_3CN, 263 K): δ = 3.24 (s, 6 H, NCH_3), 3.29 (s, 3H, NCH_3), 3.37 (s, 3H, NCH_3), 3.44 (s, 3H, NCH_3), 7.76 (m, 3H, Ph), 7.87 (d, 2 H, J = 7 Hz, Ph). – ^{13}C NMR (CD_2Cl_2/CD_3CN, 263 K): δ = 37.8, 40.9, 43.9, 53.9, 129.7, 130.7, 131.9, 134.1, 159.9 (C=N), 160.6, 168.5 (C=N^+). – $C_{14}H_{20}N_5$ $SbCl_6$ (592.8): calcd. C 28.37, H 3.40, N 11.81; found C 28.54, H 3.21, N 11.68.

*2,4-Bis(dipropan-2-ylamino)-1-methyl-6-phenyl-1,3,5-triazin-1-ium hexachloroantimonate (**8h**)*

Yellow powder (90 %). – M. p. 237 °C (dec). – IR (CH_2Cl_2): ν = 1551, 1570, 1606 (C=N) cm^{-1}. – ^{1}H NMR (CD_2Cl_2/CD_3CN, 263 K): δ = 1.31 (d, 6 H, J = 6.4 Hz, 3 H, CHMe_2), 1.47 (d, 12 H, J = 6.4 Hz, 6 H, CHMe_2), 1.54 (d, 6 H, J = 6.4 Hz, 3 H, CHMe_2), 3.39 (s, 3 H, NCH_3), 3.98 (m, 3 H, N^+CH_3), 3.98 (m, 2 H, CHMe$_2$), 5.06 (m, 1 H, CHMe$_2$), 7.66 (m, 3H, Ph), 7.87 (d, 2 H, J = 7 Hz, Ph). – ^{13}C NMR (CD_2Cl_2/CD_3CN, 263 K): δ = 19.70, 21.47, 45.0, 47.8, 50.1, 51.6, 129.8, 130.7, 132.6, 134.1, 159.1 (C=N), 159.7, 168.0 (C=N^+). – $C_{22}H_{36}N_5$ $SbCl_6$ (705.9): calcd. C 37.48, H 5.15, N 9.93; found C 37.42, H 4.94, N 9.71.

*4,6-Di(morpholin-4-yl)-1-(propan-2-yl)-6-phenyl-1,3,5-triazin-1-ium hexachloroantimonate (**8i**)*

Yellow powder (29 %). – M. p. 185 °C (dec). – IR (CH_2Cl_2): ν = 1520, 1570, 1600 (C=N) cm^{-1}. – ^{1}H NMR (CD_2Cl_2/CD_3CN): δ = 1.18 (d, 6 H, J = 7 Hz, CHMe_2), 3.77 – 4.05 (m, 16 H, 8CH_2), 4.05 (sept., 1 H, J = 6.7 Hz, CHMe$_2$), 7.55 – 7.78 (m, 5 H, Ph). – ^{13}C NMR (CD_2Cl_2/CD_3CN): δ = 23.5, 23.7, 27.4, 46.3, 49.5, 63.3, 66.6, 66.7, 66.9, 129.1, 131.3, 133.8, 134.1, 159.1 (C=N), 161.9, 171.2 (C=N^+). – $C_{20}H_{28}N_5$ $SbCl_6$ (705.0): calcd. C 34.08, H 4.00, N 9.93; found C 34.28, H 4.19, N 9.81.

*(1E)-1-(Dimethylamino)-4-methyl-N-(propan-2-ylidene)-pent-1-en-3-iminium hexachloroantimonate (**9a**)*

Yellow powder (22 %). – M. p. 167 – 168 °C. – IR (CH_2Cl_2): ν = 1532, 1623 (C=N) cm^{-1}. – ^{1}H NMR (CD_3CN): δ = 1.30 (d, 6 H, J = 7 Hz, CHMe_2), 2.28 (s, 6 H, C=(CH_3)$_2$), 2.86 (sept., 1 H, CH(CH_3)$_2$), 3.42 (s, 3 H, NCH_3), 3.56 (s, 3 H, N–CH_3), 8.07 (s, 1 H, CH=N). – ^{13}C NMR ($CDCl_3$): δ = 19.9, 22.4, 22.9, 40.9, 44.8, 160.1, 169.8, 185.7 (C=N^+). – $C_{10}H_{20}N_3$ $SbCl_6$ (516.8): calcd. C 23.24, H 3.90, N 8.13; found C 23.48, H 3.77, N 8.28.

*(1E)-1-(Dipropan-2-ylamino)-4-methyl-N-(propan-2-ylidene)pent-1-en-3-iminium hexachloroantimonate (**9b**)*

Yellow powder (80%). – M. p. 111 – 113 °C. – IR (CH_2Cl_2): ν = 1530, 1620 (C=N) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.31 (d, 6 H, J = 7 Hz, CHMe_2), 1.50, 1.52 (2d, 12 H, J = 7 Hz, CHMe_2), 2.28 (s, 6 H, N=C(CH_3)$_2$), 2.86 (sept., 1 H, CH(CH_3)$_2$), 4.27 (sept., 1 H, CH(CH_3)$_2$), 4.47 (sept., 1 H, CH(CH_3)$_2$), 8.22 (s, 1 H, CH=N). – ^{13}C NMR ($CDCl_3$): δ = 20.0, 20.22, 22.4, 36.8, 51.9, 158.2, 170.3, 184.4. – $C_{14}H_{28}N_3$ $SbCl_6$ (572.9): calcd. C 29.35, H 4.93, N 7.34; found C 29.54, H 4.79, N 7.53.

*(1E)-1-(Dimethylamino)-4,4-dimethyl-N-(propan-2-ylidene)pent-1-en-3-iminium hexachloroantimonate (**9c**)*

Yellow powder (80 %). – M. p. 111 – 113 °C. – IR (CH_2Cl_2): ν = 1585, 1610 (C=N) cm^{-1}. – ^{1}H NMR (CD_3CN): δ = 1.28 (s, 9 H, C(CH_3)$_3$), 2.27 (s, 6 H, C=(CH_3)$_2$), 3.41 (s, 3 H, NCH_3), 3.56 (s, 3 H, N–CH_3), 8.05 (s, 1 H, CH=N). – ^{13}C NMR (CD_3CN): δ = 27.2, 28.1, 38.3, 40.9, 44.8, 160.1, 169.8, 185.7 (C=N^+). – $C_{11}H_{22}N_3$ $SbCl_6$

(530.8): calcd. C 24.89, H 4.18, N 7.92; found C 24.63, H 4.44, N 7.69.

*(1E)-4,4-Dimethyl-1-[methyl(propan-2-yl)amino]-N-(propan-2-ylidene)pent-1-en-3-iminium hexachloroantimonate (**9d**)*

Yellow powder (89 %). – M. p. 78 – 80 °C. – IR (CH_2Cl_2): ν = 1640, 1715 (C=N) cm^{-1}. – ^1H NMR (CD_2Cl_2): δ = 1.28 (s, 9 H, C(CH_3)$_3$), 1.35 (d, 6 H, J = 7 Hz, CHMe_2), 2.26 (s, 6 H, N=C(CH_3)$_2$), 3.41 (s, 3 H, NCH_3), 4.89 (sept., 1 H, CH(CH_3)$_2$), 8.01 (s, 1 H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ = 19.3, 27.2, 28.2, 37.4, 40.9, 52.0, 159.6, 169.8, 185.8 (C=N^+). – $C_{13}H_{26}N_3$ $SbCl_6$ (558.8): calcd. C 27.94, H 4.69, N 7.52; found C 27.69, H 4.49, N 7.33.

*(1E)-1-(Dipropan-2-ylamino)-4,4-dimethyl-N-(propan-2-ylidene)pent-1-en-3-iminium hexachloroantimonate (**9e**)*

Yellow powder (66 %). – M. p. 119 – 121 °C. – IR (CH_2Cl_2): ν = 1615, 1715 (C=N) cm^{-1}. – ^1H NMR (CD_2Cl_2): δ = 1.30 (s, 9 H, C(CH_3)$_3$), 1.45 (d, 6 H, J = 6.7 Hz, CH(CH_3)$_2$), 1.47 (d, 6 H, J = 6.7 Hz, CH(CH_3)$_2$), 2.22 (s, 6 H, N=C(CH_3)$_2$), 4.17 (sept., 1 H, J = 6.7 Hz, CH(CH_3)$_2$), 4.49 (sept., 1 H, J = 6.7 Hz, CH(CH_3)$_2$), 8.10 (s, 1 H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ = 20.3, 23.8, 27.0, 28.1, 40.9, 158.0, 170.2, 185.9 (C=N^+). – $C_{15}H_{30}N_3$ $SbCl_6$ (558.8): calcd. C 30.70, H 5.15, N 7.16; found C 30.91, H 5.11, N 7.09.

*N-[{[(E)-(Dipropan-2-ylamino)methylidene]amino}(phenyl)methylidene]propan-2-iminium hexachloroantimonate (**9f**)*

Yellow powder (85 %). – M. p. 115 °C (dec). – IR (CH_2Cl_2): ν = 1610, 1715 (C=N) cm^{-1}. – ^1H NMR (CD_2Cl_2): δ = 1.51 (d, 6 H, J = 6.7 Hz, CH(CH_3)$_2$), 1.55 (d, 6 H, J = 6.7 Hz, CH(CH_3)$_2$), 2.31 (s, 6 H, N=C(CH_3)$_2$), 4.22 (sept., 1 H, J = 6.7 Hz, CH(CH_3)$_2$), 4.75 (sept., 1 H, J = 6.7 Hz, CH(CH_3)$_2$), 7.60 – 8.04 (m, 5 H, Ph), 8.45 (s, 1 H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ = 20.3, 23.0, 27.0, 52.7, 53.2, 129.5, 129.8, 130.61, 136.3, 158.6, 174.2, 175.8 (C=N^+). – $C_{17}H_{26}N_3$ $SbCl_6$ (606.9): calcd. C 33.65, H 4.32, N 6.92; found C 33.65, H 4.32, N 6.92.

*N-[({(E)-[Diphenylamino]methylidene}amino)(phenyl)methylidene]propan-2-iminium hexachloroantimonate (**9g**)*

Yellow powder (85 %). – M. p. 115 °C (dec). – IR (CH_2Cl_2): ν = 1610, 1690 (C=N) cm^{-1}. – ^1H NMR (CD_2Cl_2): δ = 2.11 (s, 6 H, N=C(CH_3)$_2$), 7.13 – 7.52 (m, 15 H, Ph), 8.62 (s, 1 H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ = 27.5, 124.6, 126.5, 126.6, 127.1, 128.8, 129.2, 129.5, 129.6, 130.2, 130.4, 139.1, 140.2, 140.7, 142.0, 159.0, 167.2, 181.5 (C=N^+). – $C_{23}H_{22}N_3$ $SbCl_6$ (674.9): calcd. C 40.93, H 3.29, N 6.23; found C 40.73, H 3.48, N 6.41.

*N-[({(E)-[Methyl(phenyl)amino]methylidene}amino)(phenyl)methylidene]propan-2-iminium hexachloroantimonate (**9h**)*

Green powder (81 %). – M. p. 75 °C. – IR (CH_2Cl_2): ν = 1570, 1620 (C=N) cm^{-1}. – ^1H NMR (CD_3CN): δ = 2.75 (s, 6 H, N=C(CH_3)$_2$), 3.99 (s, 3 H, NCH_3), 7.53 – 8.12 (m, 10 H, Ph), 8.65 (s, 1 H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ = 27.4, 39.6, 123.1, 128.8, 130.0, 130.5, 130.7, 131.2, 137.1, 141.7, 159.6, 175.5, 175.8 (C=N^+). – $C_{18}H_{20}N_3$ $SbCl_6$ (612.9): calcd. C 35.28, H 3.29, N 6.89; found C 35.05, H 3.38, N 6.79.

*N-[{[(E)-(Dipropan-2-ylamino)methylidene]amino}(phenyl)methylidene]butan-2-iminium hexachloroantimonate (**9i**)*

Yellow powder (81 %). – M. p. 90 – 93 °C (dec). – IR (CH_2Cl_2): ν = 1600, 1670 (C=N) cm^{-1}. – ^1H NMR (CD_3CN, 263 K): δ = 1.20 (t, 3 H, J =7.1, CH_3CH$_2$), 1.42 (d, 6 H, J = 7 Hz, CH(CH_3)$_2$), δ = 1.49 (d, 6 H, J = 7 Hz, CH(CH_3)$_2$), 2.08 (s, 3 H, CH_3), 2.65 (q, 2 H, J =7.1, CH_3CH_2), 4.22 (sept., 2 H, J = 7 Hz, CH(CH_3)$_2$), 4.71 (sept., 2 H, J = 7 Hz, CH(CH_3)$_2$), 7.65 (m, 3 H, Ph), 8.05 (d, 2 H, Ph), 8.45 (s, 1 H, CH=N). – ^{13}C NMR (CD_3CN, 263 K): δ = 10.3, 20.7, 22.5, 25.0, 33.8, 53.7, 55.8, 130.4, 130.8, 130.9, 136.3, 160.4, 174.5, 180.3 (C=N^+). – $C_{18}H_{28}N_3$ $SbCl_6$ (620.9): calcd. C 34.82, H 4.55, N 6.77; found C 34.62, H 4.71, N 6.65.

*N-[{[(E)-(Dimethylamino)methylidene]amino}(dipropan-2-ylamino)methylidene]-(methoxy)methanaminium hexachloroantimonate (**10a**)*

Yellow powder (85 %). – M. p. 147 – 151 °C. – IR (CH_2Cl_2): ν = 1520, 1580, 1650 (C=N), 3250 (NH, d) cm^{-1}. – ^1H NMR (CD_2Cl_2): δ = 1.36 (d, 12 H, J = 7 Hz, CH(CH_3)$_2$), 3.13 (s, 3H, NCH_3), 3.22 (s, 3H, NCH_3), 3.40 (s, 3 H, OCH_3), 4.13 (sept., 2 H, J = 7 Hz, CH(CH_3)$_2$), 4.53 (d, 2 H, J = 6.1 Hz, CH_2), 6.30 (br., 1H, exchangeable with D_2O), 7.88 (s, 1 H, CH=N). – ^{13}C NMR (CD_2Cl_2): δ = 21.0, 35.5, 41.7, 49.9, 56.3, 76.3, 158.4, 163.1. – $C_{12}H_{27}N_4O$ $SbCl_6$ (577.8): calcd. C 24.94, H 4.71, N 9.70; found C 25.13, H 4.76, N 9.77.

*N-[{[(E)-(Dimethylamino)methylidene]amino}(dipropan-2-ylamino)methylidene](ethoxy) methanaminium hexachloroantimonate (**10b**)*

Yellow powder (86 %). – M. p. 134 – 136 °C. – IR (CH_2Cl_2): ν = 1520, 1575, 1640 (C=N), 3250 (NH, d) cm^{-1}. – ^1H NMR (CD_2Cl_2): δ = 1.15 (t, 3 H, J = 6.7 Hz, CH_3CH$_2$), 1.36 (d, 12 H, J = 7 Hz, CH(CH_3)$_2$), 3.12 (s, 3 H, NCH_3), 3.22 (s, 3 H, NCH_3), 3.61 (q, 2 H, J = 6.7 Hz, CH_3CH_2), 4.12 (sept., 2 H, J = 6.7 Hz, CH(CH_3)$_2$), 4.58 (d, 2 H, J = 6.1 Hz, CH_2), 6.25 (br., 1H, exchangeable with D_2O

and coupled with CH_2), 7.92 (s, 1 H, C*H*=N). – ^{13}C NMR (CD_2Cl_2): δ = 15.3, 21.0, 35.5, 41.7, 49.9, 64.7, 74.8, 158.5, 163.1. – $C_{13}H_{29}N_4O$ $SbCl_6$ (591.9): calcd. C 26.38, H 4.94, N 9.47; found C 26.21, H 4.90, N 9.58.

*N-[{[(E)-(dipropan-2-ylamino)methylidene]amino}(dipropan-2-ylamino)methylidene](ethoxy)methanaminium hexachloroantimonate (**10c**)*

Yellow powder (60 %). – M. p. 122 – 125 °C. – IR (CH_2Cl_2): ν = 1520, 1570, 1625 (C=N), 3250 (NH, d) cm^{-1}. – ^{1}H NMR (CD_2Cl_2): δ = 1.25 (3 d, 24 H, J = 6.7 Hz, CH(CH_3)$_2$), 3.42 (s, 3H, CH_3O), 3.80 (sept., 1 H, J = 6.7 Hz, C*H*(CH$_3$)$_2$), 4.09 (sept., 1 H, J = 6.7 Hz, C*H*(CH$_3$)$_2$), 4.52 (m, 3 H, C*H*(CH$_3$)$_2$ + C*H*2), 6.31 (br., 1H, exchangeable with D_2O), 7.94 (s, 1 H, C*H*=N). – ^{13}C NMR (CD_2Cl_2): δ = 20.0, 21.1, 23.5, 48.6, 49.9, 50.0, 56.4, 67.3, 156.0, 163.4. – $C_{16}H_{35}N_4O$ $SbCl_6$ (634.0): calcd. C 30.31, H 5.56, N 8.84; found C 30.42, H 5.65, N 8.73.

*(Dipropan-2-ylamino){[(E)-(dipropan-2-ylamino)methylidene]amino}methaniminium hexachloroantimonate (**11**)*

Yellow powder (83 %). – M. p. 120 – 122 °C. – IR (CH_2Cl_2): ν = 1565, 1623, 1645 (C=N), 3400 (NH, br), 3500 (br) cm^{-1}. – ^{1}H NMR (CD_2Cl_2): δ = 1.36 (d, 12 H, J = 7 Hz, CH(CH_3)$_2$), 3.13 (s, 3H, NCH_3), 3.22 (s, 3H, NCH_3), 4.13 (sept., 2 H, J = 7 Hz, C*H*(CH$_3$)$_2$), 4.53 (d, 2 H, J = 6.1 Hz, CH_2), 5.55 (br., 2 H, exchangeable with D_2O), 7.88 (s, 1 H, C*H*=N). – ^{13}C NMR (CD_2Cl_2): δ = 21.0, 35.5, 41.7, 49.9, 76.3, 158.4, 163.1. – $C_{10}H_{23}N_4$ $SbCl_6$ (533.8): calcd. C 22.50, H 4.34, N 10.50; found C 22.58, H 4.50, N 10.37.

*N-(1-{[(E)-(Dipropan-2-ylamino)methylidene]amino}-2-methylpropylidene)-2-methoxypropan-2-aminium hexachloroantimonate (**12a**)*

White powder (78 %). – M. p. 78 °C (dec). – IR (CH_2Cl_2): ν = 1550, 1570, 1600 (C=N) cm^{-1}. – ^{1}H NMR (CD_2Cl_2, 263 K): δ = 1.31 (d, 6 H, J = 6.7 Hz, CH(CH_3)$_2$), 1.40 (d, 6H, J = 6.7 Hz, CH(CH_3)$_2$), 1.46 (d, 6 H, J = 6.7 Hz, CH(CH_3)$_2$), 1.67 (s, 6 H, C(CH$_3$)$_2$), 3.20 (sept., 1 H, J = 6.7 Hz, C*H*(CH$_3$)$_2$), 3.31 (s, 3 H, OCH_3), 4.03 (sept., 1 H, J = 6.7 Hz, C*H*(CH$_3$)$_2$), 4.60 (sept., 1 H, J = 6.7 Hz, C*H*(CH$_3$)$_2$), 6.62 (br., NH, exchangeable with D_2O), 8.3 (s, 1 H, C*H*=N). – ^{13}C NMR (CD_2Cl_2): δ = 19.8, 20.5, 23.4, 25.3, 33.3, 50.4, 50.7, 89.7, 156.7, 177.1. – $C_{15}H_{32}N_3O$ $SbCl_6$ (604.9): calcd. C 29.78, H 5.33, N 6.95; found C 29.63, H 5.46, N 7.06.

*N-(1-{[(E)-(Dipropan-2-ylamino)methylidene]amino}-2-phenylethylidene)-2-methoxypropan-2-aminium hexachloroantimonate (**12b**)*

White powder (88 %). – M. p. 84 °C (dec). – IR (CH_2Cl_2): ν = 1550, 1570, 1600 (C=N) cm^{-1}. – ^{1}H NMR (CD_3C1): δ = 1.31 (d, 6 H, J = 6.7 Hz, CH(CH_3)$_2$), 1.40 (d, 6H, J = 6.7 Hz, CH(CH_3)$_2$), 1.46 (d, 6 H, J = 6.7 Hz, CH(CH_3)$_2$), 1.80 (s, 6 H, C(CH$_3$)$_2$), 3.40 (s, 3 H, OCH_3), 3.93 (sept., 1 H, J = 6.7 Hz, C*H*(CH$_3$)$_2$), 4.78 (sept., 1 H, J = 6.7 Hz, C*H*(CH$_3$)$_2$), 7.00 (br., NH), 7.45 – 7.80 (m, 5H, Ph), 7.82 (s, 1 H, C*H*=N). – ^{13}C NMR ($CDCl_3$): δ = 19.91, 23.3, 25.4, 51.0, 51.1, 90.4, 129.4, 130.3, 131.2, 134.2, 160.9, 171.9. – $C_{19}H_{32}N_3O$ $SbCl_6$ (653.0): calcd. C 34.95, H 4.94, N 6.44; found C 34.74, H 4.73, N 6.48.

*N-(1-{[(E)-(Dipropan-2-ylamino)methylidene]amino}(phenyl)methylidene)-2-methoxypropan-2-aminium hexachloroantimonate (**12c**)*

White powder (86 %). – M. p. 110 °C (dec). – IR (CH_2Cl_2): ν = 1550, 1570, 1600 (C=N) cm^{-1}. – ^{1}H NMR (CD_2Cl_2): δ = 1.31 (d, 6 H, J = 6.7 Hz, CH(CH_3)$_2$), 1.47 (d, 6H, J = 6.7 Hz, CH(CH_3)$_2$), 1.80 (s, 6 H, C(CH$_3$)$_2$), 3.40 (s, 3 H, OCH_3), 3.93 (sept., 1 H, J = 6.7 Hz, C*H*(CH$_3$)$_2$), 4.75 (sept., 1 H, J = 6.7 Hz, C*H*(CH$_3$)$_2$), 6.90 (br., 1 H, NH, exchangeable with D_2O), 7.45 – 7.80 (m, 5 H, Ph), 8.82 (s, 1 H, C*H*=N). – ^{13}C NMR (CD_2Cl_2): δ = 19.9, 23.3, 35.4, 90.4 (N–C–O), 129.1, 130.3, 131.2, 134.2, 160.9 (*C*H=N), 171.9 (*C*=N$^+$). – $C_{18}H_{30}N_3O$ $SbCl_6$ (604.9): calcd. C 33.84, H 4.73, N 6.58; found C 33.88, H 4.61, N 6.47.

Acknowledgements

This work was supported by Al al-Bayt University. Financial support from DFG (Germany) is gratefully acknowledged. The author is indebted to Prof. G. Maas (University of Ulm), V. Jäger (University of Stuttgart), Prof J. C. Jochims (University of Konstanz) and Prof. M. El-Abadelah and Dr. J. Zahra (University of Jordan) for their kind encouragement, advice and criticism.

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