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Ene Reactions and [2+2]Cycloadditions of Nitrilium Salts with Alkenes

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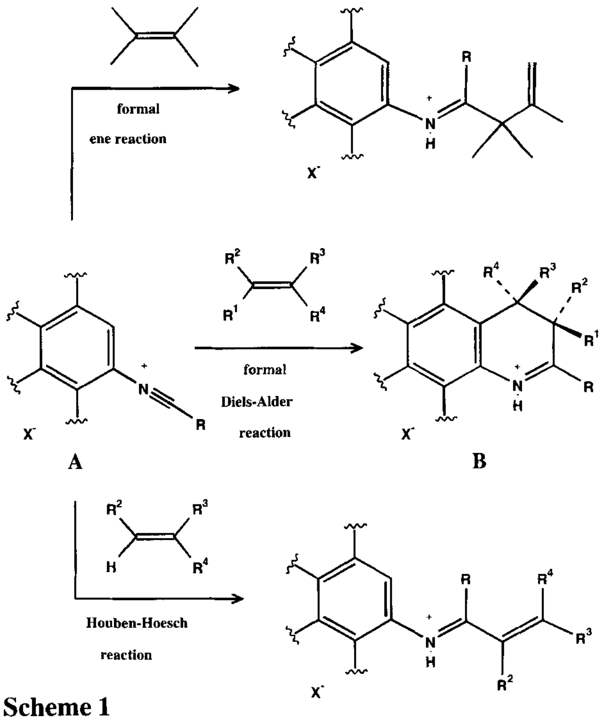
Abstract. *N*-Alkylnitrilium salts (**1**) undergo ene reactions with electron-rich di- and higher substituted alkenes **2** to afford either 2-azoniaallene salts (**3**, **6**, **9**, **11**) (the nitrilium salt reacting as ene and the alkene reacting as enophile) or 1-azonia-1,4-pentadiene salts (**10**, **12**) (the alkene reacting as ene and the nitrilium salt reacting as enophile). Competing with ene reactions tri- and tetrasubstituted alkenes and *N*-alkylnitrilium salts undergo [2+2]cycloaddition to furnish azetinium salts (**8**, **13**). In solution, alkyl substituted 2-azoniaallene salts tautomerize to 2-azonia-1,3-butadiene salts (**4**, **5**, **7**). The constitutions of the 2-azoniaallene salt **6c** and the azetinium salt **8** were secured by X-ray crystallographic analyses.

Reactions of easily accessible [1–8] nitrilium salts with alkenes have not yet been studied in detail. In the literature some intramolecular additions of nitrilium ions to olefinic double bonds are documented [9–14]. Recently, we reported three different intermolecular reaction modes of *N*-arylnitrilium salts **A** with alkenes (Scheme 1) [15]. Ethene and many mono- to tetrasubstituted alkenes undergo formal Diels–Alder reaction to afford 3,4-dihydroquinolinium salts **B**. With activated arenes (thiophene, anisole), respectively 1,1-diphenylethene, *N*-arylnitrilium salts **A** undergo electrophilic substitution (Houben–Hoesch reaction), while ene reactions were observed with 2,3-dimethyl-2-butene.

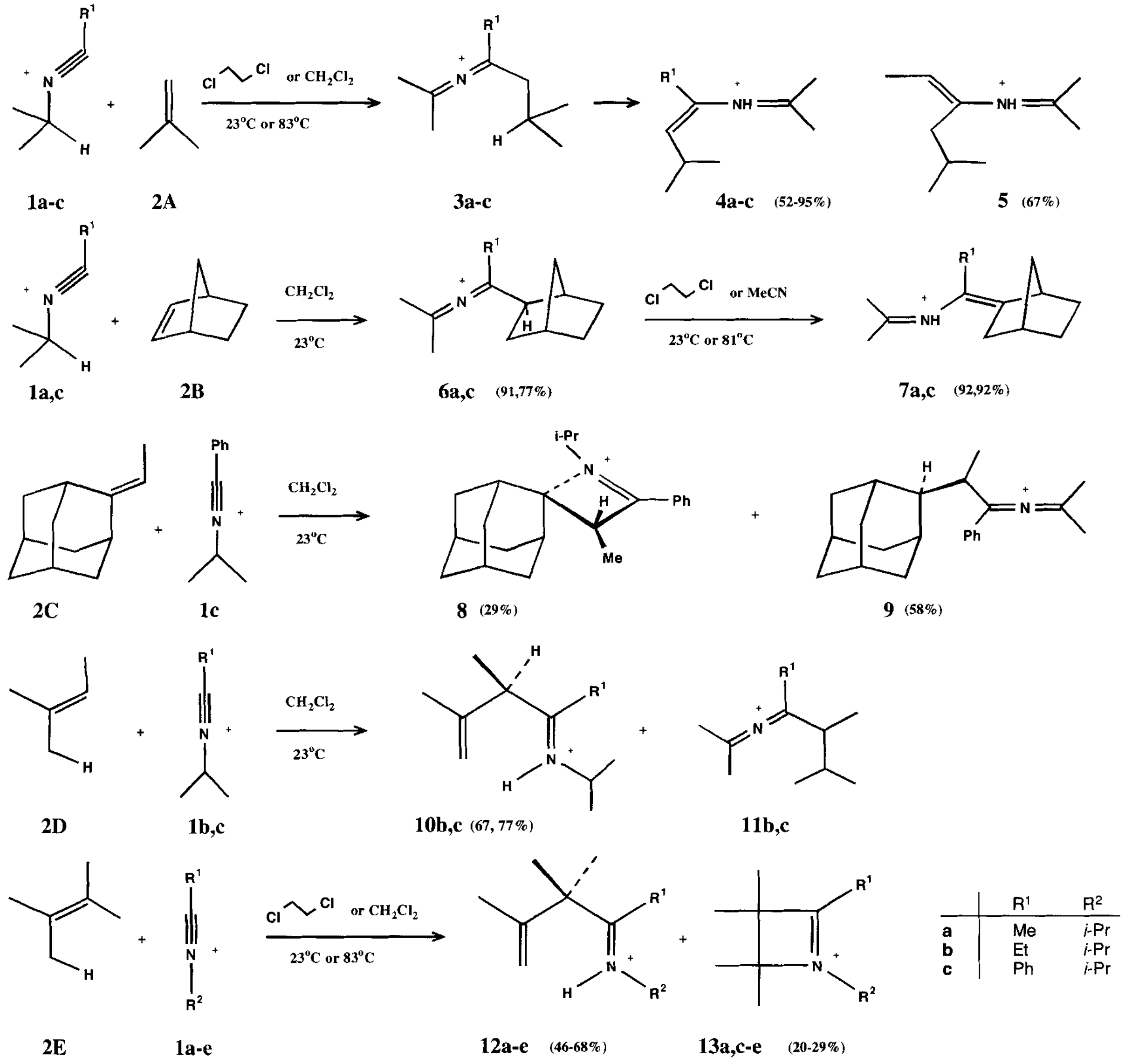


Scheme 1

The question remained open whether and how *N*-alkylnitrilium salts would react with alkenes. We now set out to study reactions of five *N*-alkylnitrilium salts **1a–e** with sixteen alkenes **2** (Scheme 2).

No reactions could be induced between *N*-alkylnitrilium salts **1a–e** and ethene or monosubstituted alkenes (1-hexene, styrene, vinyl chloride). No reactions were observed between *N*-alkylnitrilium salts **1** and 1,1-disubstituted alkenes with moderately electron-withdrawing substituents (2-phenylpropene, 3-chloro-2-chloromethyl-1-propene). 2,3-Dimethyl-1,3-butadiene polymerized in the presence of the nitrilium salt **1c**.

However, at room temperature a mixture of isobutene **2A** and *N*-isopropylacetonitrilium hexachloroantimonate **1a** in dichloromethane afforded an oil, which showed a very strong IR absorption at 1960 cm^{-1} (CH_2Cl_2) characteristic for a 2-azoniaallene cation **3**. Crystallization at –15 °C furnished colorless needles showing strong IR bands at 1662 (C=N) and 3216 (NH) cm^{-1} but not any more the absorption at 1960 cm^{-1}. On the basis of the ^1H and ^{13}C NMR spectra and the elemental analysis we assign constitution **4a** to the needles, which must have been formed from the 2-azonia-allene salt **3a** by [1, 3] rearrangement of hydrogen. An ene reaction with the nitrilium salt **1a** as ene and the alkene **2A** as enophile accounts for the formation of **3a**.



	R^1	R^2
a	Me	*i*-Pr
b	Et	*i*-Pr
c	Ph	*i*-Pr

Scheme 2

Ene reactions of acetylenes with *N*-isopropylnitrilium salts have been reported [16]. Also, 2-azoniaallene cations with a hydrogen atom in α-position to the cumulene unit are known to undergo spontaneous [1, 3] hydrogen shifts to *N*-protonated 2-azonia-1,3-butadienes **4** [16, 17]. The iminium salt **4a** was formed as a single geometrical stereoisomer of unknown configuration.

The crude product of the reaction of **1b** with isobutene **2A** showed a strong cumulene band at 1954 cm^{-1} (in CH$_2$Cl$_2$) indicative for **3b** formed by ene reaction. Crystallization afforded a mixture of one geometrical isomer each of **4b** and **5**, from which pure **5** was obtained by recrystallization. The formation of both 2-azonia-1,3-butadienes **4b** and **5** from **3b** is explained by [1, 3] shifts of hydrogen atoms.

Similarly, the benzonitrilium salt **1c** and isobutene **2A** reacted to produce cumulene **3c** (strong IR absorption at 1934 cm^{-1} in CH$_2$Cl$_2$), which rearranged in boiling 1,2-dichloroethane to a single geometrical isomer of the iminium salt **4c**.

No reactions took place between unstrained 1,2-disubstituted alkenes (3-hexene, cyclopentene) and *N*-alkylnitrilium salts **1a–c**. Activated arenes (thiophene, anisole) were recovered unchanged after treatment with nitrilium salt **1c**. In particular, no Houben–Hoesch substitution was observed (contrast to *N*-arylnitrilium salts) [15, 18]. Recently, Shudo *et al.* reported protonated *N*-alkylnitrilium dications undergoing Houben–Hoesch reactions even with benzene and toluene [19].

On the other hand, reaction of **1a** with the strained

1,2-disubstituted alkene norbornene **2B** in dichloromethane afforded the 2-azoniaallene salt **6a** (IR (CH_2Cl_2): 1951 cm^{-1}). In boiling 1,2-dichloroethane the cumulene band disappeared completely in the course of 90 minutes, after which a 2:3 mixture of the geometrical isomers of **7a** was isolated.

The rather stable cumulene **6c** [IR(CH_2Cl_2): 1926 cm^{-1}] was obtained by reaction of **1c** with norbornene **2B**. At room temperature after three days in dichloromethane or after one day in acetonitrile **6c** was completely transformed into a 1:1 mixture of the geometrical isomers of **7c** [16, 17].

The constitution of **6c** was secured by X-ray structural analysis (Fig.1, Table 1) [20]. The 2-azoniaallene unit of the exo substituted norbornyl derivative **6c** is almost linear (angle C1–N–C2 = 176(1)°). The C=N bonds are rather short (126(1) pm). Of the many X-ray structures of 2-azoniaallene salts reported [21–30], linear $C{=}N{=}C^+$ units were observed only exceptionally [31–36]. A linear relationship exists between the C=N=C bond angle and the valence vibration of this unit [37]. Similar to allenes, the planes through N, C2, C3, C4 and N, C1, C11, C5 of **6c** were found to be perpendicular with respect to each other (89(1)°).

With the trisubstituted alkene **2C** the benzonitrilium salt **1c** reacted to furnish a 1:2 mixture of compounds **8** and **9**, which were separated by crystallization.

The structure of the azetinium salt **8** was secured by X-ray crystallographic analysis (Fig. 2, Table 2) [20]. The crystal of **8** contains two independent cations with similar structural data. While X-ray data for azetinium cations without mesomeric stabilization seem to be unreported, a crystal structural analysis for a 1-substituted 2-dialkylamino-1-azetinium salt has been published [38]. The four-membered ring of **8** is almost planar (endocyclic torsional angles about 4°) but not rectangular. Atoms N1, C1, C3 and C13 are lying in one plane [39]. Azetinium cations have been prepared by *O*-alkylation of *β*-lactams, respectively by *S*-alkylation of *β*-thiolactams [40–43], by *N*-alkylation of 2-methylthioazetines [44], by treatment of azetidine-2-carboxylic acids with oxalyl chloride [45], or by cycloaddition of keteniminium salts to imines [46–48].

Under the reaction conditions, neither the azetinium salts **8** could be transformed into the heterocumulene **9** nor did **9** cyclize to **8**. It seems most likely that compounds **8** and **9** were formed *via* independent reaction paths. A concerted or stepwise [2+2]cycloaddition would account for the formation of **8**, while ene reaction with the nitrilium cation acting as ene afforded **9**. At room temperature in dichloromethane and even faster in acetonitrile the cumulene **9** decomposed to a mixture of compounds.

No reaction was observed between the nitrilium salt **1a** and 2-methyl-1-phenylpropene. On the other hand, the trisubstituted alkene **2D** reacted smoothly with nitrilium salts **1**. With **1b** the iminium salt **10b** was isolated in 67% yield. Again, **10b** is the product of an ene reaction, however, in contrast to the cases described above (**3a–c**, **6a**,**c**, **9**), now with the alkene in the part of the ene reacting with the nitrilium cation as enophile. The IR spectra (CH_2Cl_2) of crude **10b** showed an absorption at 1954 cm^{-1} indicating the presence of a small amount of the 2-azoniaallene salt **11b**. This leads to the conclusion that both ene reactions, either with the alkene acting as ene and the nitrilium cation reacting as enophile (formation of **10b**) or *vice versa* (formation of **11b**), must have similar activation energies. A single stereoisomer of compound **10b** was produced. A concerted ene reaction would suggest (*E*)-configuration.

Similarly, the reaction of **2D** with the benzonitrilium salt **1c** afforded a mixture of **10c** and **11c**, from which pure **10c** was obtained in 77% yield by crystallization. The tetrasubstituted alkene **2E** and the nitrilium salts **1a–e** underwent ene reaction and competitive [2+2] cycloaddition to furnish ca 2:1 mixtures of the iminium compounds **12a–e** and the azetinium salts **13a**, **c–e**. An azetinium salt **13b** was not isolated. The other mixtures were separated by fractional crystallization. Recently, we reported formation of ene products **12** by reaction of *N*-arylnitrilium salts with **2E** [15].

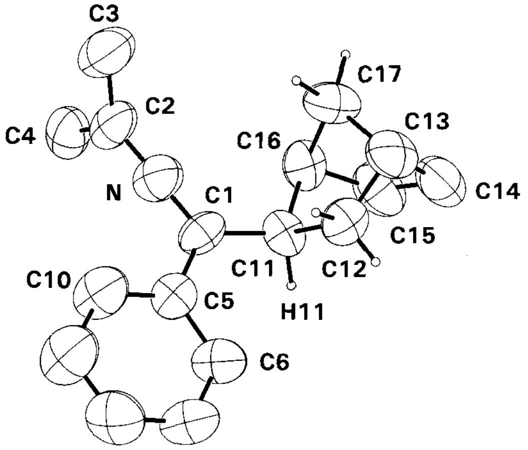


Fig. 1 ORTEP plot for the cation of 3,3-dimethyl-1-phenyl-1-[(1*R*,*S*,2*R*,*S*,4*S*,*R*)-8,9,10-trinorbornyl-2-]-2-azoniaallene hexachloroantimonate (**6c**)

Spectroscopically, the 2-azoniaallene salts (**3**, **6**, **9**, **11**) are characterized by a very strong IR band around 1950 cm^{-1} assigned to the antisymmetric C=N=C vibration. In the ^{13}C NMR spectra the resonances for the C=N=C carbon atoms appear as broad weak signals at 154–162 ppm. The resonances for the iminium carbon atoms of the azetinium salts **8**, **13** (IR(CH_2Cl_2): $C{=}N^+$: 1620–1700 cm^{-1}) were observed at much lower field (190–202 ppm). Similarly, the $^{13}C{=}N^+$ resonances of

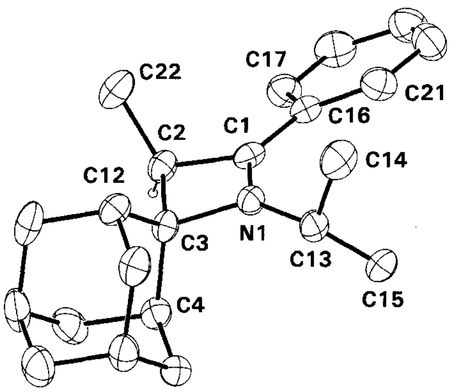


Fig. 2 ORTEP plot for the cation of (3,4-dihydro-1-isopropyl-3-methyl-2-phenylazetium-4)-spiro-2'-tricyclo[3.3.1.1^{3,7}] decane hexachloroantimonate (**8**)

the iminium salts **4**, **5**, **7**, **10**, **12** were found at 195–201 ppm. The ^{1}H NMR spectra of most compounds **4**, **5**, **10**, **12** showed well resolved triplets for NH with ^{1}H-^{14}N coupling constants of 56–64 Hz.

In summary, for *N*-alkylnitrilium salts and electron-rich 1,1-di- and higher substituted alkenes three different reaction paths were observed: (a) ene reaction with the nitrilium salt acting as ene and the alkene reacting as enophile, (b) ene reaction with the alkene acting as ene and the nitrilium salt reacting as enophile, and (c) [2+2] cycloaddition. The first reaction constitutes a new synthesis for 2-azoniaallene salts, the second reaction furnishes β,γ-unsaturated iminium salts, while the third reaction affords elusive azetinium salts (Scheme 2).

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Experimental

All experiments were carried out with exclusion of moisture in solvents dried by standard methods. IR: Perkin-Elmer FTIR 1600; absorptions in cm^{-1}; solvent: CH_2Cl_2. ^{1}H and ^{13}C NMR spectra: Bruker AC-250 spectrometer; internal reference TMS; δ-scale, ppm; coupling constants *J* in Hz; solvent: CD_3CN; 295 K.

X-Ray Structural Analyses of 6c and 8 [20]

Reflections were measured with an Enraf-Nonius CAD4 diffractometer (graphite monochromator, $\lambda_{Mo-K}\alpha$ = 71.069 pm).

Solutions by direct methods with subsequent difference-Fourier syntheses and full-matrix least squares refinements using programs SHELXS-86 and SHELXL-93, respectively. **6c**, $[C_{17}H_{22}N]^+SbCl_6^-$; MW = 574.8; crystal size (mm): 0.5 × 0.3 × 0.2; space group R-3; Z = 6; rhombohedral; a = 1952.3 (1) pm, α = 116.56(1)°; V = 3504·10^6 pm^3; d_{calcd} = 1.635 Mg

Tab. 1 Selected bond lengths (pm), bond angles, and torsional angles (°) for the cation **6c** [20]

C1-N	126(1)	C5-C6	139(1)	C6-C5-C1	120(1)	C5-C1-C11-C12	-67(1)
N-C2	126(1)	C11-H11	107(1)	C10-C5-C1	121(1)	C5-C1-C11-C16	178(1)
C2-C3	149(2)	C1-N-C2	176(1)	C11-C1-N	120(1)	C6-C5-C1-N	175(1)
C2-C4	147(2)	N-C2-C3	120(1)	C12-C11-C1	112(1)	C6-C5-C1-C11	-8(1)
C1-C11	151(1)	N-C2-C4	121(1)	C16-C11-C1	115(1)	C10-C5-C1-N	-2(1)
C11-C12	159(1)	C3-C2-C4	120(1)	C1-N-C2-C3	-172(14)	C10-C5-C1-C11	176(1)
C11-C16	155(1)	C5-C1-N	119(1)	C1-N-C2-C4	7(15)	C12-C11-C1-N	111(1)
C1-C5	148(1)	C5-C1-C11	121(1)	C5-C1-N-C2	-100(14)	C16-C11-C1-N	-4(1)

Tab. 2 Selected bond lengths (pm), bond angles, and torsional angles (°) for the independent cations **8** [20]

C1-N1	130.6(4)	130.6(4)	N1-C3-C4	112.7(2)	112.9(2)	C3-N1-C1-C2	4.5(2)	4.7(2)
N1-C3	153.7(4)	153.7(3)	N1-C3-C12	116.3(2)	115.9(2)	N1-C1-C2-C22	117.6(3)	117.2(3)
C3-C2	157.6(4)	157.1(4)	N1-C13-C14	112.0(3)	111.4(3)	N1-C1-C16-C17	160.2(3)	155.7(3)
C2-C1	150.5(4)	149.6(4)	N1-C13-C15	111.1(3)	111.4(3)	C1-C2-C3-C4	–108.3(2)	–108.5(2)
C2-C22	151.8(4)	153.0(4)	C1-C2-C22	113.7(3)	113.1(3)	C1-C2-C3-C12	120.5(3)	120.4(3)
C3-C4	153.1(4)	153.0(4)	C1-C16-C17	116.0(3)	115.7(3)	C1-N1-C13-C14	75.9(4)	80.2(4)
C3-C12	152.5(4)	153.0(4)	C1-C16-C21	125.1(3)	125.5(3)	C1-N1-C3-C4	108.4(3)	108.3(2)
N1-C13	149.1(4)	148.8(4)	C1-N1-C13	134.8(3)	134.4(2)	C2-C3-N1-C13	–179.1(3)	–178.2(3)
C1-C16	145.5(4)	145.8(4)	C2-C1-C16	129.4(3)	129.1(2)	C2-C1-C16-C17	–19.5(4)	–24.0(4)
C16-C17	139.8(4)	139.5(4)	C2-C3-C4	113.3(2)	113.2(2)	C3-N1-C1-C16	–175.3(3)	–175.1(3)
C16-C21	139.1(4)	139.4(4)	C2-C3-C12	119.1(2)	119.6(2)	C3-N1-C13-C14	–111.4(3)	–108.5(3)
C13-C14	151.8(5)	151.6(5)	C3-C2-C22	120.8(3)	120.8(3)	C3-N1-C13-C15	117.7(3)	120.4(3)
C13-C15	151.7(5)	150.7(5)	C3-N1-C13	130.1(2)	131.1(2)	C12-C3-C2-C22	5.3(4)	6.0(4)
N1-C1-C2	95.1(2)	95.7(2)	C4-C3-C12	109.6(2)	109.2(2)	C4-C3-C2-C22	136.5(3)	137.0(3)
C1-C2-C3	85.9(2)	85.8(2)	C14-C13-C15	115.6(3)	116.0(3)	C22-C2-C1-C16	–62.6(4)	–63.1(4)
C2-C3-N1	83.8(2)	84.1(2)	N1-C1-C2-C3	–4.4(2)	–4.5(2)	C16-C1-N1-C13	–0.9(6)	–1.6(5)
C3-N1-C1	94.9(2)	94.2(2)	C1-C2-C3-N1	3.7(2)	3.9(2)	C4-C3-N1-C13	–66.4(4)	–65.5(3)
N1-C1-C16	135.5(3)	135.3(3)	C2-C3-N1-C1	–4.3(2)	–4.4(2)	C12-C3-N1-C13	61.4(4)	61.6(4)

m^{-3}; $F(000) = 1704$; $\mu(Mo\text{-}K_\alpha) = 1.870$ mm^{-1}; $T = 253$ K; ω-scan; $4 \leq 2\Theta \leq 54°$; 5812 reflections collected; 5071 independent reflections; 2750 observed reflections ($I > 2\sigma(I)$). Three hydrogen atoms were calculated in fixed positions. All other H atoms were located by difference Fourier synthesis. The anisotropic refinement of all non hydrogen atoms converged to R_F ($I > 2\sigma(I)$) = 6.60% and R_F (all data) = 14.75%. **8**, $[C_{22}H_{30}N]^+SbCl_6^- \cdot CH_3CN$; MW = 684.0; crystal size (mm): 0.5 × 0.3 × 0.2; space group P-1; $Z = 4$; triclinic; a = 1238.5(1) pm; b = 1533.4(2) pm; c = 1717.4(2) pm; α = 101.91(1)°; β = 97.02(1)°; γ = 112.23(1)°; $V = 2881 \cdot 10^6$ pm^3; d_{calcd} = 1.577 Mg m^{-3}; $F(000) = 1376$; $\mu(Mo\text{-}K_\alpha) = 1.531$ mm^{-1}; $T = 183$ K; $\omega/2\Theta$-scan; $3 \leq 2\Theta \leq 46°$; 8411 reflections collected; 7974 independent reflections; 6901 observed reflections ($I > 2\sigma(I)$). All hydrogen atoms were located by difference Fourier synthesis. The anisotropic refinement of all non H atoms together with isotropic refinement of all H atoms converged to R_F ($I > 2\sigma(I)$) = 2.29% and R_F (all data) = 3.21%.

(1,3-Dimethyl-1-butenyl)isopropylideneammonium Hexachloroantimonate (**4a**)

Excess of **2A** was bubbled into a cold (–40 °C) solution of **1a** [22] (4.19 g, 10 mmol) in CH_2Cl_2 (80 ml). After stirring at –40 °C for 1 h, then at 23 °C for 12 h the solvent of the clear colorless solution was evaporated and the oily residue [IR: strong band at 1960(C=N=C), **3a**] was crystallized at –15 °C from CH_2Cl_2 (10 ml)/CCl_4 (4 ml) to furnish colorless needles (2.47 g, 52%), *m.p.* 117–119 °C (dec). – IR: 1662 (C=N), 3216 (NH). – ^{1}H NMR: 0.97 (d, J = 6.6, 6H), 1.92(d, J = 1.1), 2.40, 2.55 (CH_3), 2.29 (m, coupled to 0.96 and 5.55, 1H), 5.55 (d, J = 10.7, 1H) (CH), 11.13 (br, t, J = 58, NH). – ^{13}C NMR: 20.6, 22.2(2C), 23.0, 26.8, 27.8 (CH_3, CH), 128.2, 138.2 (C=), 195.8 (br, C=N).

$C_9H_{18}Cl_6NSb$ calcd.: C 22.77 H 3.82 N 2.95
(474.7) found: C 22.74 H 3.81 N 2.94.

Isopropylidene(3-methyl-1-phenyl-1-butenyl)ammonium Hexachloroantimonate (**4c**)

From **1c**^{2}(4.81 g, 10 mmol) as described for **4a**. A solution of the yellow crude product [**3c**. – IR: strong band at 1934 (C=N=C). – ^{1}H NMR: 1.06 (6H, d, J = 6.6), 2.58 (6H) (CH_3), 2.05 (m, CH), 3.09 (d, J = 7.1, coupled to 2.05, CH_2)] in $ClCH_2CH_2Cl$ (40 ml) was boiled under reflux for 2 h. Evaporation of the solvent afforded **4c** as a dark grey foam (5.12 g, 95%), which could not be crystallized. – IR: 1594, 1632 (br), 3210 (NH). – ^{1}H NMR: 1.12 (6H, d, J = 6.5), 2.34, 2.77 (CH_3), 2.56 (m, CH), 6.29 (dd, J = 10.7 and 1.1, coupled to 2.56 and 11.66, CH=), 11.66 (br, NH). – ^{13}C NMR: 22.2 (2C), 23.7, 27.3, 28.6 (CH_3, CH), 126.0, 130.1, 130.3, 131.2, 133.6, 138.8 (phenyl, C=), 199.0 (C=N).

$C_{14}H_{20}Cl_6NSb$ calcd.: C 31.33 H 3.76 N 2.61
(536.8) found: C 31.39 H 3.96 N 2.91.

(1-Isobutyl-1-propenyl)isopropylideneammonium Hexachloroantimonate (**5**)

From **1b** [16] (4.33 g, 10 mmol) as described for **4a**. The crude brown oil [IR: strong band at 1954 (C=N=C), **3b**] was crystallized at –15 °C from CH_2Cl_2 (10 ml)/CCl_4 (10 ml) to furnish a colorless powder (3.27 g, 67%), *m.p.* 112–115 °C (dec). – IR: 1658 (C=N), 3216 (br, NH). – ^{1}H NMR: 0.93 (d, J = 6.5, 6H), 1.58 (dd, J = 7.0 and 1.1), 2.39, 2.59 (CH_3), 1.73 (m, coupled to 0.93 and 2.12, 1H), 2.12 (d, J = 7.2, CH_2), 5.79 (q, J = 7.0, HC=), 11.10 (br, t, J = 56, NH). – ^{13}C NMR: 13.2, 22.2 (2C), 23.1, 26.1, 26.8, 43.9 (CH_3, CH_2, CH), 127.2, 134.5 (C=), 195.8 (C=N).

$C_{10}H_{20}Cl_6NSb$ calcd.: C 24.58 H 4.12 N 2.87
(488.7) found: C 24.90 H 4.27 N 3.02.

In another experiment, a colorless powder (3.62 g, 74%) was isolated, the ^{1}H NMR spectrum of which showed a (3:1) mixture **5**/**4b**, which could not be separated by crystallization. – ^{1}H NMR of **4b**: 0.98 (d, J = 6.6, 6 H), 1.06 (t, J = 7.4), 2.40, 2.60 (CH_3), 2.23 (qd, J = 7.4 and 1.3, CH_2), ca 2.3 (m, coupled to 0.98 and 5.51, CH), 5.51 (d, J = 10.6, HC=), 11.51(br, NH). – ^{13}C NMR of **4b**: 11.6, 22.4 (?) (2C), 23.1 (?), 27.6, 28.0, 43.9 (?) (CH_3, CH_2, CH), 127.0 (?), 136.1 (C=), 195.8 (C=N).

$C_{10}H_{20}Cl_6NSb$ calcd.: C 24.58 H 4.12 N 2.87
(488.7) found: C 24.81 H 4.26 N 3.09.

1,3,3-Trimethyl-1-[(1R,S,2R,S,4S,R)-8,9,10-trinorbornyl-2-]-2-azoniaallene Hexachloroantimonate (**6a**)

At 23 °C a solution of **2B** (0.94 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a solution of **1a** (4.19 g, 10 mmol) in CH_2Cl_2 (20 ml). – After stirring at 23 °C for 48 h the solvent was evaporated. – On drying the yellow oily residue solidified to a colorless powder (4.66 g, 91%), which could not be crystallized, *m.p.* 60–65 °C (dec). – IR: 1951 (vs, C=N=C). – ^{1}H NMR (263 K): 2.38, 2.40, 2.43 (CH_3), 1.04–1.79 (m, 9H), 2.70 (m, 1H). – ^{13}C NMR (263 K): 22.6, 24.1, 24.5, 28.5, 29.7, 35.3, 37.1, 37.2, 41.0, 49.2, 55.4 (CH_3, CH_2, CH), 155.7 (br), 158.3 (br) (C=N).

$C_{12}H_{20}Cl_6NSb$ calcd.: C 28.11 H 3.93 N 2.73
(512.8) found: C 28.13 H 3.87 N 2.86.

3,3-Dimethyl-1-phenyl-1-[(1R,S,2R,S,4S,R)-8,9,10-trinorbornyl-2-]-2-azoniaallene Hexachloroantimonate (**6c**)

At 23 °C a solution of **2B** (0.94 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a solution of **1c** (4.81 g, 10 mmol) in CH_2Cl_2 (20 ml). After stirring at 23 °C for 12 h the solvent was evaporated, and the yellow residue was crystallized at –15 °C from CH_2Cl_2 (10 ml)/CCl_4 (4 ml) to give a yellow powder (4.42 g, 77%), *m.p.* 185–189 °C (dec). Crystals suitable for X-ray structural analysis were obtained by slow crystallization at –15 °C from CH_2Cl_2/CCl_4 (2:1). – IR: 1926 (vs, C=N=C), 1600. At 23 °C in CH_2Cl_2 the band at 1926 cm^{-1} faded away within 3 d, while new intensive bands grew at 1662 (br, C=N) and 3220 (br, NH) cm^{-1}. – ^{1}H NMR(263 K): 2.57, 2.58(CH_3), 1.19–1.72(m, 7H), 1.97(m, 2H), 3.46 (dd, J = 5.8 and 9.5, coupled to 1.97, H-2), 7.63–7.85 (phenyl). – ^{13}C NMR (263 K): 24.4, 25.0, 28.7, 29.6, 37.6, 37.7, 37.8, 41.7, 45.2 (CH_3, CH_2, CH), 126.9, 130.8, 131.2, 136.4 (phenyl), 154.6 (br), 160.7 (br) (C=N).

$C_{17}H_{22}Cl_6NSb$ calcd.: C 35.52 H 3.86 N 2.44
(574.8) found: C 35.27 H 3.81 N 2.60.

Isopropylidene[1-(8,9,10-trinorborn-2-ylidene)ethyl]ammonium Hexachloroantimonate (**7a**)

A solution of oily **6a** (5.13 g, 10 mmol) in $ClCH_2CH_2Cl$ (20 ml) was boiled under reflux for 90 min. Evaporation of the solvent afforded a brown oil (4.72 g, 92%), which could not be crystallized. – IR: 3218 (br, NH), 1666 (C=N). – ^{1}H NMR (ca 2:3 mixture of the geometrical isomers): 1.82,

1.96 (d, J = 1.7), 2.36, 2.38, 2.54, 2.57 (CH_3), 11.56 (br, t, *J*≈50), 11.66 (br, t, *J*≈50) (NH). – ^{13}C NMR: 17.2, 17.6, 22.6, 23.0, 26.5, 26.6, 28.3, 28.4, 28.5, 28.7, 37.1, 37.2, 37.3, 37.5, 39.8, 39.9, 42.2, 42.5 (CH_3, CH_2, CH), 119.2, 120.3, 147.6, 147.7 (C=), 193.8, 193.9 (C=N).
$C_{12}H_{20}Cl_6NSb$ calcd.: C 28.11 H 3.93 N 2.73
(512.8) found: C 27.93 H 3.98 N 2.86.

Isopropylidene[phenyl(8,9,10-trinorborn-2-ylidene)methyl] ammonium Hexachloroantimonate (**7c**)

At 23 °C a solution of **6c** (5.75 g, 10 mmol) in MeCN (30 ml) was stirred for 24 h. Evaporation of the solvent and precipitation of the residue from CH_2Cl_2 (15 ml)/CCl_4 (30 ml) afforded an orange powder (5.29 g, 92%), *m.p.* 145–149 °C (dec). – IR: 3220 (br, NH), 1662 (C=N). – ^{1}H NMR: ca 1:1-mixture of the geometrical isomers: 2.26, 2.29, 2.61, 2.65 (d, *J*=0.8) (CH_3), 3.00 (m, 1H), 3.10 (m, 1H), 11.46 (br), 11.63 (br) (NH). – ^{13}C NMR: 23.5, 23.7, 27.0, 27.1, 28.2, 28.3, 28.6, 29.0, 36.9, 37.4, 38.5, 38.7, 39.6, 40.4, 43.5, 43.9 (CH_3, CH_2, CH), 122.9, 124.2, 128.4, 128.7, 129.5, 129.7, 129.8, 129.9, 134.5, 134.6, 151.9, 152.1 (=C, phenyl), 196.5, 196.7 (C=N).
$C_{17}H_{22}Cl_6NSb$ calcd.: C 35.52 H 3.86 N 2.44
(574.8) found: C 35.14 H 3.87 N 2.60.

(3,4-Dihydro-1-isopropyl-3-methyl-2-phenylazetium-4)-spiro-2'-tricyclo[3.3.1.1^{3,7}]decane Hexachloroantimonate (**8**) and *3,3-Dimethyl-1-phenyl-1-[1-(tricyclo[3.3.1.1^{3,7}]-2-decyl)ethyl]-2-azoniaallene Hexachloroantimonate* (**9**)

At 23 °C a solution of **2C** [49] (1.63 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a suspension of **1c** (4.81 g, 10 mmol) in CH_2Cl_2 (40 ml). After stirring for 28 h, the reaction mixture showed a strong IR band at 1920 cm^{-1}. Evaporation of the solvent afforded a yellow foam, which was dissolved in CH_2Cl_2 (20 ml). Addition of Et_2O (40 ml) and crystallization at –15 °C afforded **8** as colorless powder (1.87 g, 29%), *m.p.* 214–218 °C (dec). Prisms suitable for X-ray structural analysis were obtained by slow crystallization at –15 °C from CH_2Cl_2/CCl_4 (2:1). – IR: 1598, 1625 (br). – ^{1}H NMR: 1.34 (d, *J*=7.0), 1.41 (d, *J*=7.6), 1.67 (d, *J*=6.9) (CH_3), 1.85–2.55 (m, 14H, adamantylidene), 3.77 (q, *J*=7.6), 4.88 (sept, *J*=7.0) (CH), 7.68–7.86 (m, phenyl). – ^{13}C NMR (gated decoupling): 11.7, 19.9, 23.6 (CH_3), 27.3, 27.4, 33.1, 33.6, 33.7, 36.3, 37.2, 38.1, 38.9 (CH_2, CH), 52.0, 56.6 (CH), 90.4 (C), 126.2 (*i*-C), 130.6 (*m*-C), 130.9 (*o*-C), 136.2 (*p*-C), 195.3 (C=N).
$C_{22}H_{30}Cl_6NSb$ calcd.: C 41.10 H 4.70 N 2.18
(642.9) found: C 41.19 H 4.85 N 2.26.
The mother liquor of the crystallization of **8** was evaporated, and the residue was crystallized at –20 °C from CH_2Cl_2 (20 ml)/Et_2O (40 ml) to furnish **9** as colorless powder (3.73 g, 58%), *m.p.* 142–148 °C (dec). – IR: 1921 (vs, C=N=C), 1594. At 23 °C in CH_2Cl_2 the band at 1921 cm^{-1} faded away within 3 d, while new intensive bands grew at 1666 (br) and 1712 cm^{-1}. – ^{1}H NMR: 1.35 (d, *J*=6.7), 2.58, 2.59 (CH_3), 3.88 (qd, *J*=6.7 and 11.3, CH), 7.70 (m, *m*-H), 7.83 (m, *p*-H), 7.93 (m, *o*-H). – ^{13}C NMR: 17.2, 24.3, 25.1, 28.3, 28.7, 29.2, 31.5, 31.8, 32.5, 38.3, 39.1, 39.3, 49.4 (CH_3, CH_2, CH, C), 127.4, 130.9, 131.0, 136.9 (phenyl), 158.3 (br), 161.5 (br) (C=N).
$C_{22}H_{30}Cl_6NSb$ calcd.: C 41.10 H 4.70 N 2.18
(642.9) found: C 41.18 H 4.85 N 2.65.

(1-Ethyl-2,3-dimethyl-3-buten-1-ylidene)isopropylammonium Hexachloroantimonate (**10b**)

A mixture of **1b** (4.33 g, 10 mmol) and **2D** (1.40 g, 20 mmol) in CH_2Cl_2 (40 ml) was stirred first at –30 °C for 30 min, then at 23 °C for 48 h. Evaporation of the solvent afforded a brown oil, which crystallized at –15 °C from CH_2Cl_2 (10 ml)/CCl_4 (6 ml) to afford a colorless powder (3.37 g, 67%), *m.p.* 134–136 °C (dec). – IR: 1657 (C=N), 3226 (br, NH). – ^{1}H NMR: 1.25 (t, *J*=7.6), 1.40 (d, *J*=7.0), 1.42 (d, *J*=6.4), 1.74 (t, *J*=1.0) (CH_3), 2.73 (q, *J*=7.6, CH_2), 3.56 (br, q, *J*=7.0), 4.36 (m, *J*=6.4 and 9.5) (CH), 5.07 (br), 5.22 (q, *J*=1.5) (=CH), 10.03 (br, td, *J*≈63 and 8, NH). – ^{13}C NMR: 11.8, 15.7, 21.3, 21.4, 21.7, 25.8, 50.1, 53.0 (CH_3, CH_2, CH), 117.5, 141.9 (C=), 197.9 (C=N).
$C_{11}H_{22}Cl_6NSb$ calcd.: C 26.28 H 4.41 N 2.79
(502.7) found: C 26.53 H 4.39 N 2.88.
The solvent of the mother liquor of the crystallization of **10b** was evaporated. – IR (CH_2Cl_2) of the oily residue: 1954 (vs, **11b**), 2372 (unreacted **1b**).

Isopropyl(1-phenyl-2,3-dimethyl-3-buten-1-ylidene)ammonium Hexachloroantimonate (**10c**)

A solution of **2D** (1.40 g, 20 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (–30 °C) suspension of **1c** (4.81 g, 10 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred first at –30 °C for 30 min, then at 23 °C for 48 h. Evaporation of the solvent afforded a brown oil. Crystallization at –15 °C from CH_2Cl_2 (10 ml)/CCl_4 (6 ml) furnished a colorless powder (4.24 g, 77%, including workup of the mother liquor), *m.p.* 116–120 °C (dec). – IR: 1634 (C=N), 3204 (br, NH). – ^{1}H NMR: 1.37 (d, *J*=6.4), 1.38 (d, *J*=7.0), 1.45 (d, *J*=6.4), 1.77 (CH_3), 3.88 (q, *J*=7.0), 4.09 (m, *J*=6.4 and 9.5) (CH), 4.98 (q, *J*=0.6), 5.21 (q, *J*=1.2) (vinyl), 7.44–7.75 (phenyl), 10.51 (br, t, *J*≈59, NH). – ^{13}C NMR: 16.1, 21.4, 21.5, 21.6 (CH_3), 51.5, 55.1 (CH, C), 118.7, 127.5, 129.5, 130.1, 133.6, 141.0 (phenyl, vinyl), 191.5 (C=N).
$C_{15}H_{22}Cl_6NSb$ calcd.: C 32.66 H 3.96 N 2.41
(550.8) found: C 32.89 H 4.00 N 2.30.
Evaporation of the solvent of the crystallization of **10c** furnished a brown oil, which could not be crystallized. – IR: 1604, 1632 (vs, C=N), 1934 (vs, C=N=C, **11c**), 3204, 3310 (NH).

Isopropyl(1,2,2,3-tetramethyl-3-buten-1-ylidene)ammonium Hexachloroantimonate (**12a**) and *3,4-Dihydro-1-isopropyl-2,3,3,4,4-pentamethylazetium Hexachloroantimonate* (**13a**)

A solution of **2E** (1.68 g, 20 mmol) in $ClCH_2CH_2Cl$ (20 ml) was added dropwise to a suspension of **1a** (4.19 g, 10 mmol) in $ClCH_2CH_2Cl$ (20 ml). The mixture was stirred at 23 °C for 24 h. Addition of Et_2O (160 ml) to the clear reaction mixture afforded a colorless precipitate, which was reprecipitated from CH_2Cl_2 (4 ml)/CCl_4 (16 ml) to furnish **13a** as colorless powder (0.98 g, 20%), *m.p.* 212–214 °C (dec). – IR: 1667. – ^{1}H NMR: 1.32 (6H), 1.46 (d, *J*=6.9, 6H), 1.57 (6H), 2.38 (CH_3), 4.25 (sept, *J*=6.9, CH). – ^{13}C NMR: 14.6, 18.4 (2C), 21.1 (2C), 22.4 (2C) (CH_3), 53.3, 53.5, 84.1 (CH, C), 201.7 (C=N).
$C_{11}H_{22}Cl_6NSb$ calcd.: C 26.28 H 4.41 N 2.79
(502.8) found: C 26.05 H 4.57 N 2.76.
Evaporation of the combined mother liquors of the preparation of **13a** afforded a colorless residue, which was precipitated

first from CH_2Cl_2 (10 ml)/Et_2O (160 ml), and then from CH_2Cl_2 (6 ml)/Et_2O (30 ml) to furnish **12a** as colorless powder (3.36 g, 67%), *m.p.* 193–198 °C (dec). – IR: 1651 (C=N), 3232 (br), 3322 (br) (NH). – ${}^1H$ NMR: 1.43 (d, J=6.5, 6H), 1.43 (6H), 1.68 (t, J=0.7), 2.41 (d, J=0.7) (CH_3), 4.34 (m, coupled to 1.43 and 9.65, CH), 5.08 (br, 1H), 5.21 (m, 1H) (HC=), 9.65 (br, td, J=63 and 8, NH). – ${}^{13}C$ NMR: 18.5, 20.1, 20.7 (2C), 24.2 (2C) (CH_3), 51.9, 53.8 (CH, C), 116.6, 145.6 (C=), 197.8 (C=N).

$C_{11}H_{22}Cl_6NSb$ calcd.: C 26.28 H 4.41 N 2.79
(502.8) found: C 26.03 H 4.28 N 2.94.

(1-Ethyl-2,2,3-trimethyl-3-buten-1-ylidene)isopropylammonium Hexachloroantimonate (**12b**)

A solution of **2E** (1.68 g, 20 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (–30 °C) suspension of **1b** (4.33 g, 10 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred first at –30 °C for 30 min, then at 23 °C for 48 h. At –40 °C a colorless powder was precipitated by slow addition of Et_2O (100 ml). No cumulene band around 1950 cm^{-1} was observed in the IR spectrum. Reprecipitation at –15 °C from CH_2Cl_2 (10 ml)/Et_2O (40 ml) afforded a colorless powder (2.62 g, 51%), which according to the NMR spectra was a 7:1 mixture of **12b** and a second compound, probably **13b** (${}^{13}C$ NMR: 83.5 (C–N), 204.4 (br, C=N)). Crystallization at –15 °C from CH_2Cl_2 (6 ml)/CCl_4 (4 ml) afforded **12b** as colorless powder (2.40 g, 46%), *m.p.* 198–200 °C (dec). – IR: 1645 (C=N), 3220 (br), 3316 (br) (NH). – ${}^1H$ NMR: 1.24 (t, J=7.7), 1.45 (d, J=6.4, 6H), 1.45 (6H), 1.68 (dd, J=0.6 and 1.5) (CH_3), 2.74 (q, J=7.7, CH_2), 4.39 (m, J=6.4 and 9.8, coupled to 1.45 and 9.70), 5.10 (br, 1H), 5.34 (m, 1H) (HC=), 9.70 (br, td, $J\approx$62 and 9, NH). – ${}^{13}C$ NMR: 12.4, 20.2, 21.2 (2C), 24.2 (2C), 24.7 (CH_3, CH_2), 52.1, 53.8 (CH, C), 117.3, 145.2 (C=), 200.6 (C=N).

$C_{12}H_{24}Cl_6NSb$ calcd.: C 27.89 H 4.68 N 2.71
(516.8) found: C 27.90 H 4.65 N 2.66.

Isopropyl(2,2,3-trimethyl-1-phenyl-3-buten-1-ylidene)ammonium Hexachloroantimonate (**12c**) and *3,4-Dihydro-1-isopropyl-3,3,4,4-tetramethyl-2-phenylazetium Hexachloroantimonate* (**13c**)

A solution of **2E** (1.68 g, 20 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (–40 °C) suspension of **1c** (4.81 g, 10 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at 23 °C for 24 h. Cooling to –30 °C and addition of Et_2O (60 ml) precipitated **13c** as colorless powder (1.62 g, 29%), *m.p.* 183–188 °C (dec). – IR: 1602, 1626 (br). – ${}^1H$ NMR: 1.56 (6H), 1.58 (d, $J\approx$6.8, 6H), 1.74 (6H) (CH_3), 4.71 (sept, J=6.8, CH), 7.70–7.90 (phenyl). – ${}^{13}C$ NMR: 20.4, 21.4, 23.4 (CH_3), 53.8, 55.1, 83.7 (CH, C), 125.2, 130.9, 131.5, 137.0 (phenyl), 192.4 (C=N).

$C_{16}H_{24}Cl_6NSb$ calcd.: C 34.02 H 4.28 N 2.48
(564.8) found: C 34.09 H 4.28 N 2.46.

Evaporation of the mother liquor of the preparation of **13c** afforded **12c** as a pale yellow oil. Precipitation from CH_2Cl_2 (10 ml)/Et_2O (40 ml) afforded a colorless powder (3.84 g, 68%), *m.p.* 128–130 °C (dec) – IR: 1604, 1642 (C=N), 3210 (br), 3268 (br) (NH). – ${}^1H$ NMR: 1.36 (d, J=6.6, 6H), 1.41 (6H), 1.85 (t, J=0.8) (CH_3), 3.85 (m, coupled to 1.36 and 10.36, CH), 5.14 (br), 5.36 (q, J=0.8) (HC=), 7.30–7.72 (m, phenyl), 10.36 (br, td, J=64 and 8, NH). – ${}^{13}C$ NMR: 20.5, 21.1 (2C), 25.3 (2C) (CH_3), 51.6, 56.3 (CH, C), 119.3, 126.6, 129.3, 130.1, 132.7, 143.8 (phenyl, C=), 195.6 (br, C=N).

$C_{16}H_{24}Cl_6NSb$ calcd.: C 34.02 H 4.28 N 2.48
(564.8) found: C 34.06 H 4.31 N 2.52.

Methyl(1,2,2,3-tetramethyl-3-buten-1-ylidene)ammonium Hexachloroantimonate (**12d**) and *3,4-Dihydro-1,2,3,3,4,4-hexamethylazetium Hexachloroantimonate* (**13d**)

A solution of **2E** (1.68 g, 20 mmol) in $ClCH_2CH_2Cl$ (20 ml) was added dropwise to a suspension of **1d** [50] (3.91 g, 10 mmol) in $ClCH_2CH_2Cl$ (20 ml). The mixture was first stirred at 23 °C for 6 h, and was then boiled under reflux for 30 min. After cooling Et_2O (100 ml) was added. After 1 h at 23 °C a colorless powder was isolated by filtration. Reprecipitation from CH_2Cl_2 (4 ml)/MeCN (1 ml)/Et_2O (20 ml) afforded **13d** as colorless powder (1.28 g, 27%), *m.p.* 216–218 °C (dec). – IR (nujol): 1699 (C=N). – ${}^1H$ NMR: 1.32 (6H), 1.46 (6H), 2.29, 3.24 (CH_3). – ${}^{13}C$ NMR: 13.8, 18.3 (2C), 20.1 (2C), 31.3 (CH_3), 54.1, 81.2 (C), 201.5 (C=N).

$C_9H_{18}Cl_6NSb$ calcd.: C 22.77 H 3.82 N 2.95
(474.7) found: C 22.68 H 3.78 N 3.16.

Evaporation of the combined mother liquors of the preparation of **13d** afforded a colorless residue, which was precipitated first from CH_2Cl_2 (10 ml)/Et_2O (40 ml), and then from CH_2Cl_2 (6 ml)/MeCN (1 ml)/ Et_2O (100 ml) to furnish **12d** as colorless powder (2.94 g, 62%), *m.p.* 190–196 °C (dec). – IR: 1670, 1674, 3262 (br). – ${}^1H$ NMR: 1.40 (6H), 1.68 (q, J=0.7, coupled to 5.20), 2.32, 3.31 (dq, J=5.2 and 0.9, coupled to 9.97) (CH_3), 5.07 (br), 5.20 (q, $J\approx$1)(HC=), 9.97 (br, t, J=62, NH). – ${}^{13}C$ NMR: 18.6, 20.2, 24.1 (2C), 35.4, 51.8 (CH_3, C), 116.6, 145.7 (C=), 199.6 (br, C=N).

$C_9H_{18}Cl_6NSb$ calcd.: C 22.77 H 3.82 N 2.95
(474.7) found: C 22.72 H 3.80 N 3.20.

Methyl(2,2,3-trimethyl-1-phenyl-3-buten-1-ylidene) ammonium Hexachloroantimonate (**12e**) and *3,4-Dihydro-1,3,3,4,4-tetramethyl-2-phenylazetium Hexachloroantimonate* (**13e**)

A solution of **2E** (1.68 g, 20 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (– 40 °C) suspension of **1e** [50] (4.53 g, 10 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at 23 °C for 24 h. Cooling to – 30 °C and addition of Et_2O (100 ml) afforded **13e** as colorless powder (1.26 g, 23%), *m.p.* 181–183 °C (dec). – IR: 1598, 1651. – ${}^1H$ NMR: 1.57 (6H), 1.60 (6H), 3.59 (CH_3), 7.70–7.98 (phenyl). – ${}^{13}C$ NMR: 20.3 (2C), 20.6 (2C), 33.6 (CH_3), 54.0, 80.5 (C), 125.3, 131.0, 132.2, 137.8 (phenyl), 190.4 (C=N).

$C_{14}H_{20}Cl_6NSb$ calcd.: C 31.33 H 3.76 N 2.61
(536.8) found: C 31.33 H 3.63 N 2.55.

Evaporation of the mother liquor of the preparation of **13e** afforded a pale yellow oil, which was first precipitated from CH_2Cl_2 (10 ml)/Et_2O (100 ml), and then from CH_2Cl_2 (10 ml)/CCl_4 (20 ml) to furnish **12e** as colorless powder (3.40 g, 63%), *m.p.* 138–140 °C (dec). – IR: 1604, 1655 (C=N), 3204 (br), 3306 (br) (NH). – ${}^1H$ NMR: 1.41 (6H), 1.86 (q, J=0.8), 3.17 (d, J=5.3) (CH_3), 5.16 (br), 5.35 (m) (HC=), 7.31–7.69 (m, phenyl), 10.47 (br, *t*, J=64, coupled to 3.17, NH). – ${}^{13}C$ NMR: 20.7, 25.2, 37.7, 51.6 (CH_3, C), 119.1, 127.0, 129.3, 130.1, 132.9, 144.1 (phenyl, C=), 196.6 (C=N).

$C_{14}H_{20}Cl_6NSb$	calcd.:	C 31.33	H 3.76	N 2.61
(536.8)	found:	C 31.62	H 3.77	N 2.63.

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