

Cycloadditions of 1-Thia-3-azoniabutatriene Salts to Azomethines, Carbodiimides, and Ketene Imines

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Received August 2, 1989

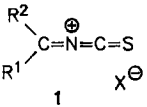
Key Words: Heterocumulenes, [2 + 2] cycloaddition reactions / 1-Thia-3-azoniabutatriene salts / 3-Azoniaallene salts / 2-Azoniaallene salts

A new method for the preparation of sulfur-substituted 2-azoniaallene salts (**3a–f**, **5a–d**, **7**) by [2 + 2] cycloadditions of 1-thia-3-azoniabutatriene salts (**1c, d**) to azomethines (**2a–f**), carbodiimides (**4a–d**), and the ketene imine **6** is described. The X-ray crystal analysis of the adduct **3b** of 4-(dimethylamino)-4-phenyl-1-thia-3-azoniabutatriene hexachloroantimon-

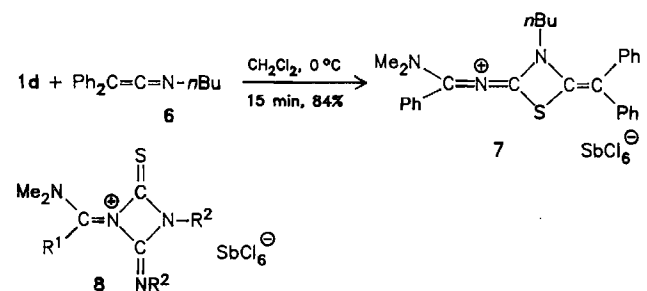
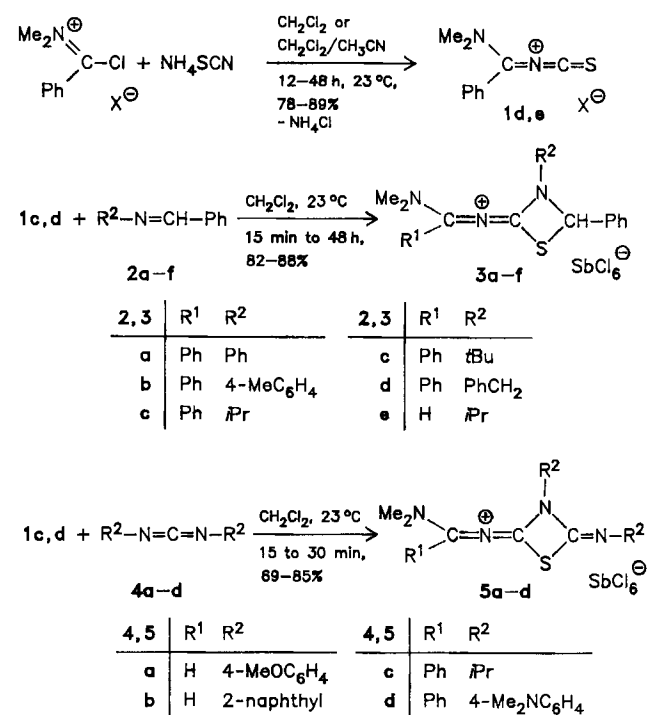
ate (**1d**) to *N*-benzylidene-*p*-toluidine (**2b**) shows an almost planar 2-azaallylium cation with a W-shaped arrangement of the N–C–N–C–N fragment, the plane of which also contains the 1,3-thiazetidine ring. Improved methods for the preparation of **1d** and the corresponding tetrachloroaluminate (**1e**) are given.

Stable 1-thia-3-azoniabutatriene salts **1** were isolated independently by three groups^{1–3}. According to an X-ray structural analysis the C=N=C unit of **1a** is bent (139°)². The C=S (157 pm) and the sp-C=N (120 pm) bond lengths are typical for aliphatic and aromatic isothiocyanates. It was therefore concluded that an important mesomeric form of the cation of **1a** is that of an α -isothiocyanatocarbenium ion. On the other hand, **1a** shows equivalent phenyl groups in the ¹³C-NMR spectra at –10°C suggesting that the sp²-C–N–sp²-C bending potential may be shallow.

Recently, further syntheses of the cumulenes **1** were published by us^{4,5}.

	1	R ¹	R ²	X	Ref.
	a	Ph	Ph	SbCl ₆	(2,4)
	b	C ₆ H ₄ -2-(NMe)-2'-C ₆ H ₄		CF ₃ SO ₃	(1)
	c	Me ₂ N	H	SbCl ₆	(4,5)
	d	Me ₂ N	Ph	SbCl ₆	(5)
	e	Me ₂ N	Ph	AlCl ₄	(5)
	f	Me ₂ N	4-MeC ₆ H ₄	SbCl ₆	(5)
	g	Me ₂ N	Me ₂ N	SbCl ₆	(5)
	h	Aryl	Me ₂ NCH=CH	ClO ₄	(3)

With exception of the vinylogous salts **1h**⁶ little is known about the chemical behaviour of these compounds. Will nucleophiles attack the position α to the isothiocyanate group or the carbon of the NCS group? *N,N*-Dimethylaniline and water react at the carbon atom in α position to the isothiocyanate group of **1a**². On the other hand, water attacks the sp carbon of the cumulene **1b** to give COS and amine¹. The formation of tetraphenyl-2-azoniaallene hexachloroantimonate was observed spectroscopically when **1a** was stirred in dichloromethane at 25°C with benzophenone⁷.



In this paper we describe cycloadditions of **1c,d** to the C=N double bonds of the azomethines **2a–f**, of the carbodiimides **4a–d**, and of the ketene imine **6**. For the preparation of the thiocyanates **1d,e** improved procedures are given.

Stirring a mixture of **1d** and *N*-benzylideneaniline in dichloromethane at room temperature for 15 minutes produces the adduct **3a** in almost quantitative yield. The other compounds **3** were obtained correspondingly. The ¹H-NMR, ¹³C-NMR, and IR spectra as well as the elemental analyses are in agreement with the proposed constitutions, which are further confirmed by an X-ray structural analysis of **3b**.

Carbodiimides **4** and *N*-(*n*-butyl)diphenylketene imine (**6**) behave as azomethines towards the butatrienium salts **1c,d** giving the coloured cycloadducts **5a–d** and **7**, respectively. For these compounds isomeric structures, e. g. **8**, resulting from an addition of the carbodiimide to the C=N double bond of the isothiocyanates **1**, can be ruled out spectroscopically. The ¹³C-NMR spectra of compounds **3**, **5**, and **7** closely resemble each other, all showing two C=N resonance lines between $\delta = 167$ and 174 but no signal around $\delta = 190$, which should be expected for 1,3-diazetidino-2-thiones like **8**⁹. For an uncharged 2,4-diimino-1,3-thiazetidino ¹³C=N signals at $\delta = 141$ and 145 were reported⁸. In the IR spectra compounds **3**, **5**, and **7** show strong and broad bands around 1560 cm^{-1} and smaller bands at about 1620 cm^{-1} . These IR absorptions are characteristic for 1,3-diamino-substituted 2-azoniaallene salts⁹. Thus, the isothiocyanatocarbenium salts **1** behave like other, more conventional isothiocyanates, which are known to undergo [2 + 2] cycloadditions across the C=S bond to many C=N and other double bonds^{8,10–14}. An exception to this rule has been noted recently⁹. Huisgen et al. described cycloadditions of two equivalents of sterically unhindered azomethines across the C=N bond of isothiocyanates leading to triazine-thiones¹⁵.

In contrast to cumulenes **1**, their 1-oxa analogs react with carbodiimides across the C=N bond of the isocyanate unit to give triazinium salts in a multistep reaction¹⁶.

The cycloadditions described in this communication constitute a new method for the preparation of stable thia-substituted 2-azoniaallene salts.

X-ray Diffraction Analysis of **3b**¹⁷

Selected bond lengths, bond angles, and dihedral angles for **3b** are represented in Table 1. Figure 1 shows a molecular plot for the cation of **3b**.

The crystal of **3b** consist of discrete cations [C₂₄H₂₄N₃S]⁺, anions SbCl₆⁻, and solvent molecules CHCl₃.

According to qualitative valence-bond arguments 2-azoniaallene cations are expected to show either local D_{2d} (A) or C_{2v} symmetry (B).

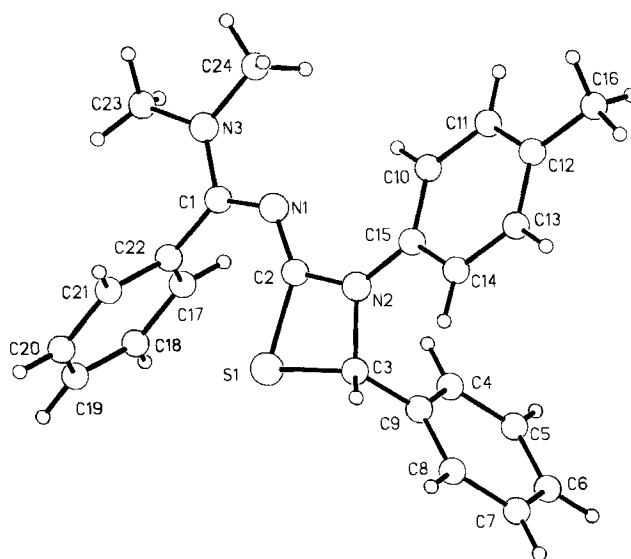
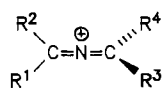


Figure 1. Molecular plot for the cation of **3b**

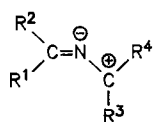
Table 1. Selected bond lengths [pm], bond angles [°], and torsional angles [°] for the cation **3b**

C1-N1	125 (3)	C1-N1-C2	122 (2)	N3-C1-N1	116 (2)	C23-N3-C1-N1	-178 (2)
N1-C2	123 (3)	N1-C2-S	138 (2)	N3-C1-C22	117 (2)	C23-N3-C1-C22	1 (4)
C1-N3	133 (3)	N1-C2-N2	126 (2)	C23-N3-C1	125 (2)	C24-N3-C1-N1	5 (3)
C1-C22	139 (3)	S-C2-N2	97 (2)	C24-N3-C1	118 (2)	C24-N3-C1-C22	-177 (2)
C2-N2	129 (3)	C2-N2-C15	134 (2)	C23-N3-C24	117 (2)	N3-C1-C22-C17	78 (2)
C2-S	173 (2)	C2-N2-C3	102 (2)	N3-C1-N1-C2	-176 (2)	C1-N1-C2-S	-3 (4)
S-C3	182 (3)	C3-N2-C15	125 (3)	C1-N1-C2-N2	172 (2)	C22-C1-N1-C2	6 (4)
N2-C3	145 (3)	S-C3-N2	88 (2)	N1-C2-S-C3	176 (3)	N1-C2-N2-C3	-177 (2)
C3-C9	142 (3)	C2-S-C3	74 (1)	N1-C2-N2-C15	0 (4)	C17-C22-C1-N1	-104 (3)
N2-C15	133 (2)	S-C3-C9	115 (2)	C2-S-C3-N2	-1 (1)	C2-S-C3-C9	-116 (2)
N3-C23	142 (3)	N2-C3-C9	114 (2)	C2-N2-C3-C9	117 (2)	C2-N2-C15-C10	-22 (3)
N3-C24	141 (3)	C22-C1-N1	127 (2)	C2-N2-C3-S	1 (2)	N2-C3-C9-C4	-42 (2)
N2-C2-S-C3	1 (1)	C3-N2-C15-C10	154 (2)			C3-N2-C2-S	-1 (2)
C9-C3-N2-C15	-61 (3)	S-C2-N2-C15	176 (2)			S-C3-N2C15	-177 (2)
S-C3-C9-C4	57 (2)						



A, local D_{2d} symmetry
 $\alpha = 180^\circ$, $\beta = 90^\circ$

α : bond angle C=N=C



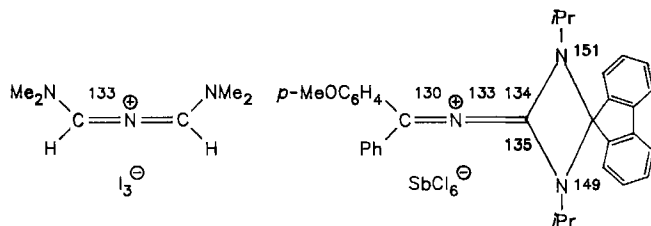
B, local C_{2v} symmetry
 $\alpha = 120^\circ$, $\beta = 0^\circ$

β : angle between the best planes
 through N, R¹, C, R² and N, R³, C, R⁴

X-ray diffraction analyses have been carried out for a number of 2-azoniaallene salts^{9,16,18–31}. In the crystal most of the cations show geometries in between the valence tautomeric extremes **A** and **B**. It should be recognized that the C=N=C unit of 2-azoniaallene cations is unusually flexible. The geometries of these cations are mainly determined by the substituents. Furthermore, the conformations of the cations can differ in solution from those in the solid state and are even influenced by the polarity of the solvent^{9,24,28,31,32}.

Hetero substituents bearing free pairs of electrons stabilize geometry **B**. Thus, according to quantum-mechanical calculations, 1,1- or 1,3-diamino-substituted 2-azoniaallene cations should prefer the planar conformation **B**²⁴. This prediction has been confirmed by X-ray diffraction analyses^{19–22}.

Cation **3b**, too, crystallizes in an almost perfect 2-azaallium geometry **B**. Judging from the torsional angles N3–C1–N1–C2 [$-176(2)^\circ$] and C1–N1–C2–N2 [$172(2)^\circ$] the fragment N3–C1–N1–C2–N2 forms a W-shaped arrangement, the plane of which further containing the four-membered ring C2–N2–C3–S and the atoms C22, C23, C24, and C15. The hetero cumulene unit C=N=C is bent [$\alpha = 122(2)^\circ$]. The angle β between the best planes through N1, C1, N3, C22 and N1, C2, N2, S1 amounts to 6.3° . The bond lengths C1–N1 [$125(3)$ pm] and N1–C2 [$123(2)$ pm] are rather short suggesting that the positive charge is localized almost equally on C1 and C2. For Gold's triiodide **9** a C=N=C bond angle α of 113° has been reported²⁰. For the 2-azoniaallene salt **10**, which is structurally related to **3b**, a C=N=C bond angle of $\alpha = 127^\circ$ was found²⁹.



9: $\alpha = 113^\circ$, $\beta = 0^\circ$

10: $\alpha = 127^\circ$, $\beta = 119.5^\circ$

We thank the *Fonds der Chemischen Industrie* for financial support and Dipl.-Chem. H.-U. Hund, Dr. K. Evertz, and Dipl.-Chem. J. Hofmann for their help in the X-ray analysis as well as S. Herzberger for technical assistance.

Experimental

IR spectra: Mattson Polaris FT-IR spectrometer; solutions in dichloromethane. — ¹H-, ¹³C-NMR spectra: Bruker WM-250 and

CA-250; internal reference tetramethylsilane. — All experiments are carried out with exclusion of moisture. All solvents are dried by conventional methods. — The melting points are uncorrected.

*X-ray Diffraction Analysis of 3b*¹⁷: [C₂₄H₂₄N₃S]SbCl₆·CHCl₃, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 1225.5(8)$, $b = 1479(1)$, $c = 1725(1)$ pm, $V = 3127 \cdot 10^6 \cdot \text{pm}^3$, $d_{\text{calc.}} = 1.78 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 17.5 \text{ cm}^{-1}$, $T = 228 \text{ K}$, ω scan, $2.0 \geq \dot{\omega} \geq 29.3^\circ \text{ min}^{-1}$, $4.5 \geq 2\theta \geq 45.0^\circ$, 2329 reflections, 1549 independent significant reflections ($I > 2\sigma$), no absorption corrections. The cell constants and the reflections were measured with a Syntex P3 diffractometer with a graphite monochromator, $\lambda(\text{Mo-K}\alpha) = 71.069 \text{ pm}$. The structure was solved by the Patterson method using the program SHEL-XTL by G. M. Sheldrick (Göttingen, revision 1979). The phenyl rings were refined as ideal hexagons. The hydrogen atoms were fixed on calculated geometrically ideal positions and were not refined. The partial anisotropic refinement led to agreement factors $R^1 = 0.088$ and $R^2 = 0.073$.

A list of atomic coordinates and thermal parameters is given in Table 2.

Table 2. Fractional atomic coordinates and temperature factors [10^4 pm^2] for **3b**

Atom	x/a	y/b	z/c	U ^{a, b}
Sb	0.7915(2)	0.5327(1)	0.3732(1)	0.057(1)
C11	0.7523(5)	0.6824(4)	0.3831(5)	0.090(3)
C12	0.7327(5)	0.5102(5)	0.4973(4)	0.077(3)
C13	0.6225(5)	0.4994(4)	0.3309(4)	0.075(3)
C14	0.8480(6)	0.5549(6)	0.2500(4)	0.095(4)
C15	0.9603(5)	0.5622(5)	0.4201(4)	0.083(3)
C16	0.8369(6)	0.3839(5)	0.3634(5)	0.087(3)
C17	0.6452(9)	0.3736(6)	0.1605(5)	0.120(4)
C18	0.4869(7)	0.2716(7)	0.0837(6)	0.127(5)
C19	0.7000(8)	0.2176(5)	0.0783(6)	0.121(4)
S	1.1820(5)	0.3069(5)	0.4305(4)	0.061(3)
N1	1.046(2)	0.258(1)	0.310(1)	0.051(8)
N2	1.044(2)	0.205(1)	0.432(1)	0.052(8)
N3	1.029(2)	0.317(1)	0.194(1)	0.063(9)
C1	1.080(2)	0.315(2)	0.262(2)	0.054(8)
C2	1.082(2)	0.254(2)	0.377(1)	0.049(7)
C3	1.113(2)	0.230(2)	0.496(2)	0.051(7)
C4	0.977(1)	0.338(1)	0.5475(8)	0.064(8)
C5	0.9248	0.3760	0.6116	0.083(9)
C6	0.9537	0.3490	0.6863	0.09(1)
C7	1.0345	0.2837	0.6969	0.08(1)
C8	1.0865	0.2456	0.6329	0.062(8)
C9	1.0576	0.2726	0.5582	0.050(8)
C10	0.873(1)	0.1517(9)	0.3855(8)	0.063(8)
C11	0.7845	0.0928	0.3937	0.045(6)
C12	0.7840	0.0293	0.4536	0.056(6)
C13	0.8715	0.0248	0.5051	0.061(7)
C14	0.9596	0.0837	0.4969	0.062(8)
C15	0.9601	0.1472	0.4371	0.057(8)
C16	0.694(2)	-0.029(2)	0.462(1)	0.080(8)
C17	1.142(1)	0.4647(1)	0.2866(9)	0.067(8)
C18	1.2251	0.5275	0.2974	0.079(8)
C19	1.3338	0.5001	0.2933	0.054(8)
C20	1.3590	0.4098	0.2784	0.068(8)
C21	1.2756	0.3469	0.2675	0.074(8)
C22	1.1668	0.3744	0.2716	0.045(7)
C23	1.058(2)	0.374(2)	0.131(2)	0.074(8)
C24	0.937(2)	0.261(2)	0.184(2)	0.079(9)
C25	0.617(2)	0.310(2)	0.080(2)	0.080(9)

^a) Anisotropic refinements for antimony, the chlorine, sulfur, and nitrogen atoms. — ^b) The anisotropic temperature factors are defined by the equation $T = \exp(-2\pi^2[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*])$ and $U = (U_{11}U_{22}U_{33})^{1/3}$.

*4-(Dimethylamino)-4-phenyl-1-thia-3-azoniabutatriene Hexachloroantimonate*⁵⁾ (**1d**): A suspension of (chlorophenylmethylene)-dimethylammonium hexachloroantimonate³³⁾ (25.16 g, 50 mmol) and ammonium thiocyanate (3.81 g, 50 mmol) in dichloromethane (100 ml) is stirred at 23°C for 48 h. Filtration and evaporation of the solvent affords a yellow moisture-sensitive powder (23.40 g, 89%); m. p. 138–140°C (ref.⁵⁾ 137–140°C).

*4-(Dimethylamino)-4-phenyl-1-thia-3-azoniabutatriene Tetrachloroaluminate*⁵⁾ (**1e**): Aluminum chloride (13.33 g, 100 mmol) is added to a cold (–20°C) solution of (chlorophenylmethylene)dimethylammonium chloride (20.41 g, 100 mmol) in dichloromethane (100 ml). After stirring for 1 h at –20°C ammonium thiocyanate (7.61 g, 100 mmol) in acetonitrile (50 ml) is added. The mixture is stirred for 12 h at 23°C, filtered, and evaporated under reduced pressure. The residue solidifies when stirred under ether (50 ml). Yield 28.09 g (78%) of a yellow powder; m. p. 77–81°C (ref.⁴⁾ 80–81°C).

N²-(3,4-Diphenyl-1,3-thiazetidin-2-ylidene)-N¹,N¹-dimethylbenzamidinium Hexachloroantimonate (**3a**): A solution of **2a** (1.81 g, 10 mmol) in dichloromethane (20 ml) is added dropwise to a stirred solution of **1d** (5.26 g, 10 mmol) in dichloromethane (20 ml). After 15 min the solvent is evaporated under reduced pressure, and the residue is dissolved in dichloromethane (10 ml). Slow addition of ether (40 ml) affords a precipitate, which is crystallized from chloroform (50 ml) at 5°C giving yellow needles (6.22 g, 88%); m. p. 122–124°C. – IR (CH₂Cl₂): $\tilde{\nu}$ = 1550 (vs), 1580 (shoulder), 1620 (m) cm⁻¹. – ¹H NMR (CD₃CN): δ = 3.17, 3.58 (CH₃), 6.54 (CH). – ¹³C NMR (CD₃CN, 263 K): δ = 41.1, 42.8 (CH₃), 66.9 (CH), 169.7, 171.1 (C=N).

C₂₃H₂₂Cl₆N₃SSb (707.0) Calcd. C 39.08 H 3.14 N 5.94
Found C 39.03 H 3.12 N 5.97

N¹,N¹-Dimethyl-N²-[3-(4-methylphenyl)-4-phenyl-1,3-thiazetidin-2-ylidene]benzamidinium Hexachloroantimonate (**3b**): As described for **3a** from **2b** (1.95 g, 10 mmol). Recrystallization from chloroform (60 ml) affords orange needles (5.98 g, 83%); m. p. 179–181°C. – IR (CH₂Cl₂): $\tilde{\nu}$ = 1550 (vs), 1580 (sh), 1620 (m) cm⁻¹. – ¹H NMR (CD₃CN): δ = 2.28, 3.15, 3.56 (CH₃), 6.50 (CH). – ¹³C NMR (CD₃CN, 263 K): δ = 21.1, 40.9, 41.0 (CH₃), 66.9 (CH), 169.4, 171.1 (C=N).

C₂₄H₂₄Cl₆N₃SSb (721.0) Calcd. C 39.98 H 3.36 N 5.83
Found C 39.94 H 3.40 N 5.87

N²-(3-Isopropyl-4-phenyl-1,3-thiazetidin-2-ylidene)-N¹,N¹-dimethylbenzamidinium Hexachloroantimonate (**3c**): As described for **3a** from **2c** (1.47 g, 10 mmol). Recrystallization from methanol (50 ml) affords yellow needles; m. p. 100–102°C (dec.). – IR (CH₂Cl₂): $\tilde{\nu}$ = 1560 (vs), 1620 (m) cm⁻¹. – ¹H NMR (CD₃CN): δ = 1.14 (d, *J* = 6.7 Hz), 1.31 (d, *J* = 6.7 Hz), 3.08, 3.50 (CH₃), 4.10 (sept, *J* = 6.7 Hz), 6.01 (CH). – ¹³C NMR (CD₃CN, 263 K): δ = 20.1, 20.9, 40.2, 42.2 (CH₃), 52.3, 66.5 (CH), 170.5, 171.7 (C=N).

C₂₀H₂₄Cl₆N₃SSb (673.0) Calcd. C 35.70 H 3.59 N 6.24
Found C 35.77 H 3.61 N 6.22

N²-(3-tert-Butyl-4-phenyl-1,3-thiazetidin-2-ylidene)-N¹,N¹-dimethylbenzamidinium Hexachloroantimonate (**3d**): As described for **3a** from **2d** (1.61 g, 10 mmol). The reaction mixture is stirred for 48 h at 23°C. Recrystallization of the product from methanol (40 ml) or dichloromethane (10 ml) affords yellow prisms (5.63 g, 82%); m. p. 182–183°C (dec.). – IR (CH₂Cl₂): $\tilde{\nu}$ = 1560 (vs), 1620 (w) cm⁻¹. – ¹H NMR (CD₃CN): δ = 1.40, 3.09, 3.50 (CH₃), 6.07 (CH). – ¹³C NMR (CD₃CN): δ = 27.9, 40.7, 42.4 (CH₃), 63.0 (C), 66.1 (CH), 170.5, 172.1 (C=N).

C₂₁H₂₆Cl₆N₃SSb (687.0) Calcd. C 36.72 H 3.81 N 6.12
Found C 36.71 H 3.78 N 6.06

N²-(3-Benzyl-4-phenyl-1,3-thiazetidin-2-ylidene)-N¹,N¹-dimethylbenzamidinium Hexachloroantimonate (**3e**): As described for **3a** from **2e** (1.95 g, 10 mmol). Yield 5.98 g (83%) of yellow prisms; m. p. 175–176°C. – IR (CH₂Cl₂): $\tilde{\nu}$ = 1560 (vs), 1630 (m) cm⁻¹. – ¹H NMR (CD₃CN): δ = 3.10, 3.52 (CH₃), 4.29 (d, *J* = 15.3 Hz), 4.98 (d, *J* = 15.3 Hz, CH₂), 5.87 (CH). – ¹³C NMR (CD₃CN): δ = 40.2, 42.1 (CH₃), 50.3 (CH₂), 67.8 (CH), 170.8, 172.4 (C=N).

C₂₄H₂₄Cl₆N₃SSb (721.0) Calcd. C 39.98 H 3.36 N 5.83
Found C 39.94 H 3.29 N 5.85

N²-(3-Isopropyl-4-phenyl-1,3-thiazetidin-2-ylidene)-N¹,N¹-dimethylformamidinium Hexachloroantimonate (**3f**): As described for **3a** from **1c**⁵⁾ (4.50 g, 10 mmol) and **2c** (1.47 g, 10 mmol). The reaction mixture is stirred for 1 h at 23°C. Recrystallization of the product from methanol (60 ml) at –20°C affords a yellow powder (5.01 g, 84%); m. p. 113–115°C (dec.). – IR (CH₂Cl₂): $\tilde{\nu}$ = 1600 (vs), 1670 (sh) cm⁻¹. – ¹H NMR (CD₃CN): δ = 1.13 (d, *J* = 6.7 Hz), 1.30 (d, *J* = 6.7 Hz), 3.26 (d, *J* = 0.9 Hz), 3.32 (CH₃), 4.03 (sept, *J* = 6.7 Hz), 6.29, 8.02 (d, *J* = 0.9, CH). – ¹³C NMR (CD₃CN, 263 K): δ = 20.2, 21.0, 37.6, 43.2 (CH₃), 52.8, 64.7 (CH), 162.4, 174.2 (C=N).

C₁₄H₂₀Cl₆N₃SSb (596.9) Calcd. C 28.17 H 3.38 N 7.04
Found C 28.19 H 3.43 N 7.00

N²-[3-(4-Methoxyphenyl)-4-(4-methoxyphenylimino)-N¹,N¹-dimethyl-1,3-thiazetidin-2-ylidene]formamidinium Hexachloroantimonate (**5a**): A solution of **4a**³⁴⁾ (2.54 g, 10 mmol) in dichloromethane (20 ml) is added dropwise to a suspension of **1c** (4.50 g, 10 mmol) in dichloromethane (20 ml) at 23°C. After 15 min the solvent is evaporated under reduced pressure, and the residue is stirred under ether (50 ml) giving a powder, which is recrystallized from acetonitrile (50 ml)/ether (50 ml) affording red crystals (5.26 g, 75%); m. p. 145°C (dec.). – IR (CH₂Cl₂): $\tilde{\nu}$ = 1508 (s), 1578 (vs) cm⁻¹. – ¹H NMR (CD₃CN): δ = 3.37, 3.48, 3.81, 3.85 (CH₃), 8.29 (CH). – ¹³C NMR (CD₃CN, 263 K): δ = 39.4, 44.7, 56.2, 56.3 (CH₃), 159.8, 160.3, 170.8 (C=N).

C₁₉H₂₁Cl₆N₄O₂SSb (703.9) Calcd. C 32.42 H 3.01 N 9.96
Found C 32.27 H 3.21 N 8.12

N¹,N¹-Dimethyl-N²-[3-(2-naphthyl)-4-(2-naphthylimino)-1,3-thiazetidin-2-ylidene]formamidinium Hexachloroantimonate (**5b**): A mixture of **4b**³⁵⁾ (2.94 g, 10 mmol) and **1c** (4.50 g, 10 mmol) in dichloromethane (50 ml) is stirred for 30 min at 23°C. Addition of pentane (60 ml), filtration, and fast recrystallization of the residue from hot acetonitrile (25 ml) affords red-brown needles (5.13 g, 69%); m. p. 170–171°C (dec.). The product decomposes in solution. – IR (KBr): $\tilde{\nu}$ = 1580 (vs, broad) cm⁻¹. – ¹H NMR (CD₃CN): δ = 3.43 (d, *J* = 0.9 Hz), 3.50 (CH₃).

C₂₅H₂₁Cl₆N₄SSb (744.0) Calcd. C 40.36 H 2.85 N 7.53
Found C 40.37 H 2.85 N 7.52

N²-[3-Isopropyl-4-(isopropylimino)-1,3-thiazetidin-2-ylidene]-N¹,N¹-dimethylbenzamidinium Hexachloroantimonate (**5c**): A solution of **4c** (1.26 g, 10 mmol) in dichloromethane (10 ml) is added dropwise to a stirred solution of **1d** (5.26 g, 10 mmol) in dichloromethane (20 ml). After 15 min the solvent is evaporated, and the residue is dissolved in dichloromethane (10 ml). Slow addition of pentane (50 ml) affords a precipitate, which is crystallized from dichloromethane (20 ml)/ether (30 ml) yielding a pale yellow powder (5.26 g, 81%); m. p. 130°C (dec.). – IR (CH₂Cl₂): $\tilde{\nu}$ = 1570 (vs), 1590 (sh), 1630 (sh), 1680 (m) cm⁻¹. – ¹H NMR (CD₃CN): δ = 1.10 (d, *J* = 6.4 Hz), 1.49 (d, *J* = 6.7 Hz), 3.22, 3.58 (CH₃), 3.09 (sept, *J* = 6.4 Hz), 4.40 (sept, *J* = 6.7 Hz, CH). – ¹³C NMR (CD₃CN, 263 K): δ = 20.5, 24.0, 41.6, 43.8, 50.6, 57.2 (CH₃, CH), 136.7, 166.9, 171.3 (C=N).

C₁₇H₂₅Cl₆N₄SSb (651.9) Calcd. C 31.32 H 3.87 N 8.59
Found C 31.19 H 3.74 N 8.65

N^2 -[3-[4-(Dimethylamino)phenyl]-4-[4-(dimethylamino)phenylimino]-1,3-thiazetidin-2-ylidene]- N^1,N^1 -dimethylbenzamidinium Hexachloroantimonate (**5d**): From **4d**³⁶⁾ (2.80 g, 10 mmol) as described for **5c**. After evaporation of the solvent the residue is stirred under ether (40 ml) for 30 min and then recrystallized from dichloromethane (40 ml)/ether (40 ml) giving a red-brown powder (6.84 g, 85%); m. p. 145–146 °C (dec.). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1510 (sh), 1560 (vs), 1600 (sh). – ^1H NMR (CD_3CN): δ = 2.96 (6H, broad), 3.02 (6H), 3.26, 3.54 (CH_3).

$\text{C}_{27}\text{H}_{31}\text{Cl}_6\text{N}_6\text{SSb}$ (806.1) Calcd. C 40.23 H 3.88 N 10.43
Found C 40.05 H 4.00 N 10.59

N^2 -[3-Butyl-4-(diphenylmethylene)]-1,3-thiazetidin-2-ylidene]- N^1,N^1 -dimethylbenzamidinium Hexachloroantimonate (**7**): A solution of **6**³⁷⁾ (4.98 g, 20 mmol) in dichloromethane (20 ml) is added dropwise to a cold (0 °C) solution of **1d** (5.26 g, 10 mmol). After 15 min the mixture is cooled to –78 °C, and tetrachloromethane (100 ml) is added in portions. The precipitate is collected and reprecipitated from dichloromethane (10 ml)/tetrachloromethane (50 ml) affording a yellow powder (6.52 g, 84%); m. p. 164 °C (dec.). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1560 (w), 1660 (vs) cm^{-1} . – ^1H NMR (CD_3CN): δ = 0.72 (t, J = 7.0 Hz), 3.13, 3.52 (CH_3). – ^{13}C NMR (CD_3CN): δ = 13.6, 20.3, 30.6, 40.9, 43.0, 47.6 (CH_3 , CH_2), 169.4, 170.4 (C=N).

$\text{C}_{28}\text{H}_{30}\text{Cl}_6\text{N}_6\text{SSb}$ (775.1) Calcd. C 43.39 H 3.90 N 5.42
Found C 43.61 H 4.15 N 5.65

CAS Registry Numbers

1c: 106292-41-5 / **1d**: 113290-08-7 / **1e**: 113054-32-3 / **2a**: 538-51-2 / **2b**: 2272-45-9 / **2c**: 6852-56-8 / **2d**: 6852-58-0 / **2e**: 780-25-6 / **3a**: 123438-85-7 / **3b**: 123438-87-9 / **3b** · CHCl_3 : 123439-04-3 / **3c**: 123438-89-1 / **3d**: 123438-91-5 / **3e**: 123438-93-7 / **3f**: 123438-95-9 / **4a**: 10076-13-8 / **4b**: 742-50-7 / **4c**: 693-13-0 / **4d**: 738-65-8 / **5a**: 123438-97-1 / **5b**: 123463-16-1 / **5c**: 123438-99-3 / **5d**: 123439-01-0 / **6**: 21843-89-0 / **7**: 123439-03-2 / (chlorophenylmethylene)dimethylammonium hexachloroantimonate: 110090-12-5 / (chlorophenylmethylene)dimethylammonium chloride: 113054-33-4

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