On the Reaction of 1-Aza-2-azoniaallene Salts with Carbodiimides

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1-Aza-2-azoniaallene cations **3**, prepared in situ from geminal (chloroalkyl)azo compounds **2**, react with carbodiimides **4** to give 4,5-dihydro-5-imino-1*H*-1,2,4-triazolium salts **7**. An X-ray structural analysis was carried out for **7l**. According to AM1 calculations the cycloaddition of carbodiimides to 1-aza-2-azoniaallene cations occurs in a nonconcerted manner via cyanamidium cations **5** as intermediates. Hetero-Wagner-Meerwein rearrangements of the primary cycloadducts **6** provide the final products **7**.

While many 2-azoniaallene salts are quite stable and well crystallizing compounds[1-3], all attempts to isolate a representative of the related 1-aza-2-azoniaallene salts **3** have failed so far.

Short-lived salts **3** are formed in the reaction of arenediazonium salts with diazoalkanes[4,5] or on treatment of α-chloroazo compounds **2**[6-8] with Lewis acids like $SbCl_5$ or $AlCl_3$[9]. 1-Aza-2-azoniaallene cations **3** have been postulated as reactive intermediates in many oxidative reactions of hydrazones and azines[10-24]. Cycloadditions of cations **3** to azomethines have also been described[25].

Recently, we have reported the formation of 1,2,4-triazolium salts in high yields occurring by cycloaddition of nitriles to cations **3**[9]. We now found that cations **3** add to many types of multiple bonds.

In this paper we describe cycloadditions of heterocumulenes **3** to the C=N double bond of carbodiimides **4**.

When the (chloroalkyl)azo compound **2a** in dichlormethane was treated with antimony pentachloride at −60°C in the presence of diisopropylcarbodiimide a deep red solution was formed. After warming to 0°C the color faded to yellow. Workup afforded fine yellow needles (65%) of the triazolium salt **7a**. Correspondingly, the other compounds **7** were prepared. Dialkyl-, diaryl-, and alkylarylcarbodiimides reacted equally well. In most cases, a single product was obtained. However, the reaction mixture of **7l** contained a second product (ca. 20%) of unknown structure. The substituent R^3 should be inert to oxidation by *tert*-butyl hypochlorite[9]. Triazolium salts of type **7** seem to have not been reported so far in the literature.

From the *tert*-butylhydrazone **1j** and diisopropylcarbodiimide (**4a**) instead of the triazole **7j** the heterocycle **8** was isolated (90%), which must have been formed from **6j** or **7j** by loss of isobutene. The site of the protonation at nitrogen was inferred from a $^3J_{HH}$ coupling of NH to an isopropyl CH (Table 2). Similarly, in the reaction of **1a** with di-*tert*-butylcarbodiimide (**4k**) a *tert*-butyl group was lost. Instead of **7k** compound **9** was isolated (70%). Thus, with *tert*-butylhydrazones or *tert*-butylcarbodiimides special classes of triazolium salts can be prepared.

X-Ray Structural Analysis of 7l, Reaction Mechanism, and AM1 Calculations

It seems most likely that compounds **7** were formed from intermediates **6** by [1,2]-sigmatropic migrations of an alkyl group to the electron deficient N(2) (Figure 1). However, the alternative N(4)- or N(6)-alkylated products could not be excluded on the basis of the NMR spectra (Table 2). Furthermore, the configuration around the exocyclic C=N bond remained uncertain.

Therefore, for **7l** an X-ray structural analysis was performed, which confirmed that methyl migration had indeed occurred to N(2) (Table 1, Figure 1)[26]. The phenyl ring is *cis*-oriented with respect to the N(1)–aryl group. The heterocyclic ring is essentially planar with the planes of the two aryl rings almost perpendicular to it.

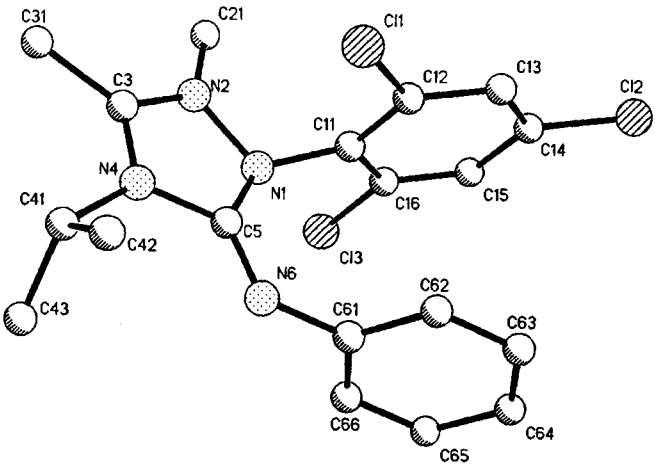
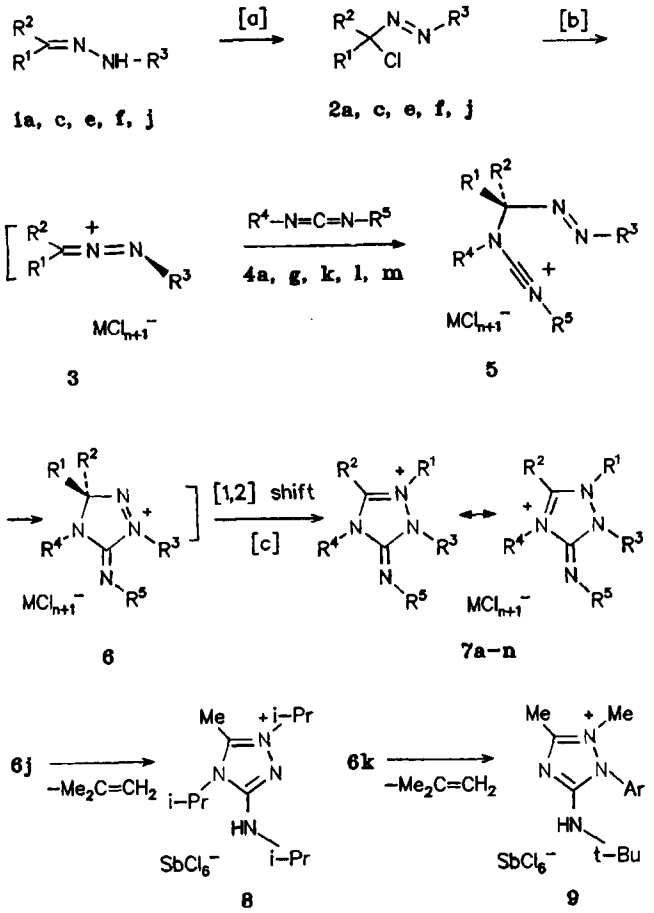


Figure 1. Structure of the cation **7l** in the crystal

Scheme 1. [a] tBuOCl, $CHCl_3$, −50 to 0°C, 3 h, 88–99%. — [b] $SbCl_5$ or $AlCl_3$, CH_2Cl_2, −60°C. — [c] −60 to 0°C, 2 h, 65–100%.



	R¹	R²	R³	R⁴	R⁵	MCl$_{n+1}$
a	Me	Me	2,4,6–$Cl_3C_6H_2$	i–Pr	i–Pr	$SbCl_6$
b	Me	Me	2,4,6–$Cl_3C_6H_2$	i–Pr	i–Pr	$AlCl_4$
c	Et	Me	2,4,6–$Cl_3C_6H_2$	i–Pr	i–Pr	$SbCl_6$
d	Et	Me	2,4,6–$Cl_3C_6H_2$	i–Pr	i–Pr	$AlCl_4$
e	i–Pr	Me	2,4,6–$Cl_3C_6H_2$	i–Pr	i–Pr	$SbCl_6$
f	$(CH_2)_4$		2,4,6–$Cl_3C_6H_2$	i–Pr	i–Pr	$SbCl_6$
g	Me	Me	2,4,6–$Cl_3C_6H_2$	C_6H_{11}	C_6H_{11}	$SbCl_6$
h	Et	Me	2,4,6–$Cl_3C_6H_2$	C_6H_{11}	C_6H_{11}	$SbCl_6$
i	$(CH_2)_4$		2,4,6–$Cl_3C_6H_2$	C_6H_{11}	C_6H_{11}	$SbCl_6$
j	i–Pr	Me	t–Bu	i–Pr	i–Pr	$SbCl_6$
k	Me	Me	2,4,6–$Cl_3C_6H_2$	t–Bu	t–Bu	$SbCl_6$
l	Me	Me	2,4,6–$Cl_3C_6H_2$	i–Pr	Ph	$SbCl_6$
m	Me	Me	2,4,6–$Cl_3C_6H_2$	Ph	Ph	$SbCl_6$
n	Me	Me	2,4,6–$Cl_3C_6H_2$	Ph	Ph	$AlCl_4$

The X-ray data may be compared with the results of an AM1 calculation[27,28] for this compound (Table 1). Other isopropyl rotamers of **7l** were calculated to be more stable

Table 1. Selected bond lengths [pm], bond angles, and torsional angles [°] for the cation **7l** as found by the X-ray diffraction analysis and as calculated by the AM1 method[27,28]

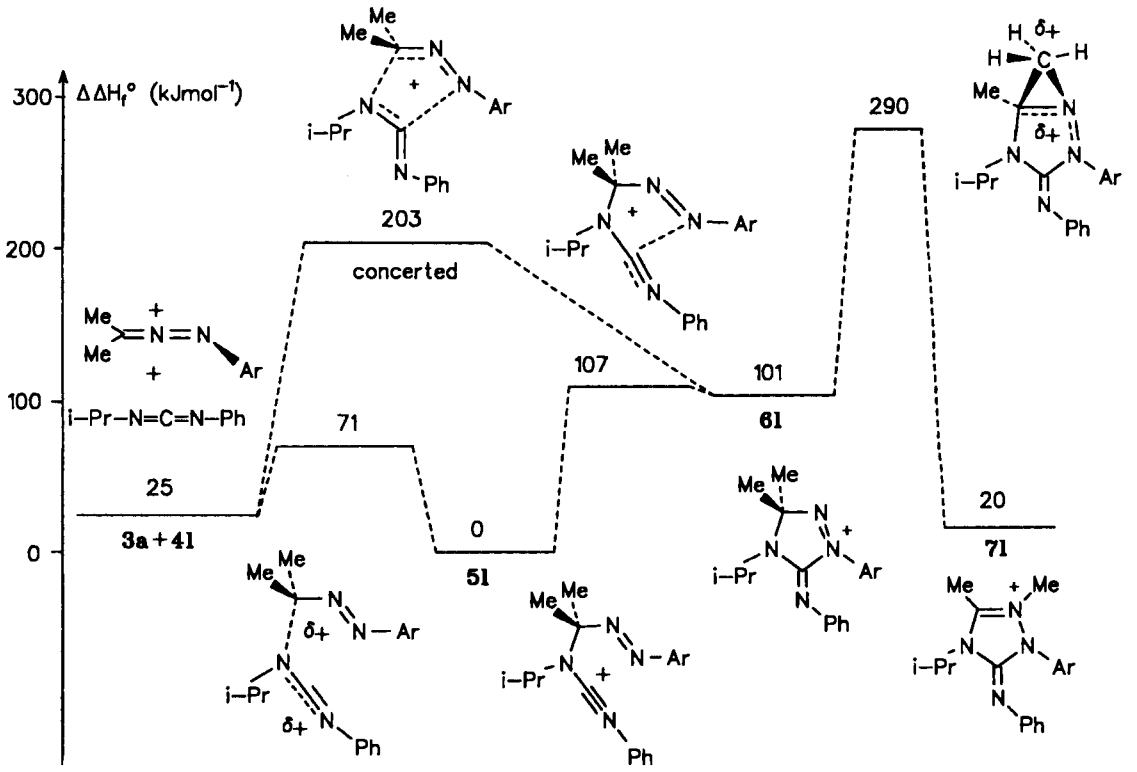
	X-ray	AM1
N(1)–N(2)	142.1(7)	139
N(2)–C(3)	130.3(9)	137
C(3)–N(4)	132(1)	138
N(4)–C(5)	139.4(7)	146
C(5)–N(6)	125.9(8)	129
C(5)–N(1)	139.9(9)	146
N(1)–N(2)–C(3)	109.1(6)	109
N(2)–C(3)–N(4)	109.8(5)	110
C(3)–N(4)–C(5)	110.3(6)	108
N(4)–C(5)–N(1)	105.1(6)	104
C(5)–N(6)–C(61)	122.2(3)	127
C(5)–N(1)–C(11)	124.6(5)	128
N(1)–N(2)–C(3)–N(4)	2.9(8)	−4
N(2)–C(3)–N(4)–C(5)	0.3(9)	1
C(5)–N(1)–N(2)–C(3)	−5.0(7)	4
C(3)–N(4)–C(41)–C(42)	−121.2(8)	−127
C(3)–N(4)–C(41)–C(43)	110.1(8)	108
N(1)–C(5)–N(6)–C(61)	0.8(9)	1
N(6)–C(61)–C(62)	91.9(4)	89
C(3)–N(2)–N(1)–C(11)	−148.2(6)	178
C(5)–N(1)–C(11)	−38.5(9)	5
N(2)–N(1)–C(11)–C(12)	77.2(6)	93

(lowest minimum found: $\Delta H_f^0 = 1194$ kJmol^{-1}) than the conformation found ($\Delta H_f^0 = 1230$ kJmol^{-1}) in the crystal. The differences between the experimental and the calculated bond lengths should be noted. The dihedral angle C(11)–N(1)–C(5)–N(6) [found −38.5(9)°, calculated +5°] was calculated to be easily deformed. Packing effects in the crystal may be responsible for the discrepancy between the calculated and measured dihedral angle.

Regarding the reaction mechanism for the formation of compounds **7** the following questions seemed of interest: a) Is the cycloaddition of the heterocumulene **3** to the carbodiimide **4** a concerted or a two-step process? b) What is the mechanism of the rearrangement **6** → **7**?

While we have no expermimental arguments at hand, AM1 calculations for the formation of **7l** support the mechanism shown in Scheme 1. For **6l** a rather long N(1)–C(5) bond (161 pm) was calculated indicating facile bond dissociation. Ring opening to **5l** [with the distance N(1)–C(5) as reaction coordinate] requires almost no activation enthalpy ($\Delta H_f^{\neq} = 6$ kJmol^{-1}). For the reverse reaction (**5l** → **6l**) an activation enthalpy of $\Delta H_f^{\neq} = 107$ kJmol^{-1} was calculated. The activation enthalpy for the dissociation of the cyanamidium ion[29,30] **5l** into the carbodiimide **4l** and the 1-aza-2-azoniaallene ion **3a** [distance C(3)–N(4) as reaction coordinate] is $\Delta H_f^{\neq} = 71$ kJmol^{-1}; that for the reverse reaction (**3a** + **4l** → **5l**) is even smaller ($\Delta H_f^{\neq} = 46$ kJmol^{-1}). In

Scheme 2. AM1-calculated heats of formation [kJmol^{-1}] for the reaction **3a** + **4l** → **7l**, relative to $\Delta H_f^0 = 1174$ kJmol^{-1} of **5l**



contrast, the concerted ring opening (**6l** → **3a** + **4l**) requires $\Delta H_f^{\neq} = 102$ kJmol^{-1} [distance C(3)–N(4) as reaction coordinate], and the concerted cycloaddition $\Delta H_f^{\neq} = 178$ kJmol^{-1}. Thus, on the basis of AM1 calculations the concerted cycloaddition **3a** + **4l** → **6l** is disfavored by 96 kJmol^{-1} compared to the two-step pathway via **5l**.

Additions of nucleophiles to the nitrilium triple bond proceed stereoelectronically controlled in such a way that in the product the nitrilium *N* substituent and the nucleophile are *cis*-oriented with respect to each other[31,32]. Such a conformation (phenyl and trichlorophenyl *cis*) is in fact observed for **7l**. This may be taken as an experimental argument in favor of a nitrilium intermediate **5l** (AM1: phenyl and trichlorophenyl *cis* with respect to each other: $\Delta H_f^0 = 1275$ kJmol^{-1}; *trans* form: $\Delta H_f^0 = 1269$ kJmol^{-1}).

In agreement with the X-ray results AM1 calculates a preferred shift of C(21)H$_3$ to N(2). With the distance C(3)–C(21) as reaction coordinate a high activation enthalpy of $\Delta H_f^0 = 189$ kJmol^{-1} was calculated. In the transition structure the positivated and almost planar C(21)H$_3$ is located above the C(3)–N(2) bond [dihedral angle C(21)–C(3)–N(2)–N(1) = 110°]. Experimentally, the [1,2] methyl shift was found to be fast at room temperature. An intermediate **6** has never been observed. It should be rememered that a heterolytic bond cleavage in an isolated molecule is an unfavorable process. In the gas phase homolytic bond breaking predominates. However, in solution heterolysis may be supported by solvatation. Thus, it may well be that the activation enthalpy for the polar [1,2] methyl shift **6l** → **7l** is much lower in solution than calculated for the isolated cation.

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Experimental

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

Cyclopentanone (2,4,6-Trichlorophenyl)hydrazone (**1f**): A mixture of cyclopentanone (10.02 g, 100 mmol) and (2,4,6-trichlorophenyl)-hydrazine (21.15 g, 100 mmol) was boiled for 5 h in ethanol (80 ml) containing acetic acid (1 ml). The reaction mixture was kept at −18°C for crystallization. Yield: 17.93 g (65%) of colorless prisms; m.p. 44–45°C. – $C_{11}H_{11}Cl_3N_2$ (277.6): calcd. C 47.59, H 4.00, N 10.09; found C 47.65, H 3.98, N 10.18.

(1-Chlorocyclopentane)azo(2,4,6-trichlorobenzene) (**2f**): The reaction was carried out in the dark. *tert*-Butyl hypochlorite (13.03 g, 120 mmol) was added dropwise to a cold (−10°C) solution of **1f** (27.76 g, 100 mmol) in chloroform (120 ml). After stirring at 0°C for 3 h the solvent was removed under reduced pressure. The orange oily residue (29.33 g, 94%) was used without further purification. – $C_{11}H_{10}Cl_4N_2$ (312.0): calcd. C 42.34, H 3.23, N 8.98; found C 42.02, H 3.21, N 9.00.

Formation of the Triazolium Salts **7** *from (α-Chloroalkyl)azo Compounds* **2** *and Carbodiimides* **4**. *General Procedure:* A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 ml) was added dropwise

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

No. IR[b]	^{1}H NMR (CD_3CN,295 K)[a] δ,J[Hz]	^{13}C NMR (CD_3CN,295 K)[a] δ
1f 1475, 3338[d]	6.68 (NH), 7.28 (aryl)[c]	24.9, 25.0, 27.0, 33.1 (CH_2), 127.2, 127.8, 128.6, 139.1 (aryl), 162.9 (C=N)[c]
2f 1578, 1737[d]	7.37 (aryl)[c]	24.3, 41.6 (CH_2), 102.6 (CH), 127.0, 128.8, 133.4, 145.8 (aryl)[c]
7a 1717	0.88 (d, J=6.1), 1.66 (d, J=6.9), 2.90, 3.51 (CH_3), 3.05 (sept, J= 6.1), 4.64 (sept, J= 6.9)(CH), 7.60 137.9, (aryl)[c]	12.6, 19.3 (2C), 24.2 (2C), 34.0 (CH_3), 48.0, 50.8 (CH), 128.4, 130.2, 135.1, 139.7, 155.4 (aryl, C=N)[b,d]
7b 1721[f]	0.87 (d, J=6.1), 1.58 (d, J=6.9), 2.58, 3.29 (CH_3), 3.12 (sept, J= 6.1), 4.59 (sept, J= 6.9) (CH), 7.78 (aryl)	12.3, 19.0(2C), 24.6 (2C), 34.2 (CH_3), 48.7, 51.5 (CH), 129.7, 131.4, 137.4, 138.7, 140.1, 157.6 (aryl, C=N)
7c 1713	0.84 (d, J=6.1), 1.20 (t, J=7.3), 1.58 (d, J=7.0), 2.60 (CH_3), 3.16 (sept, J=6.1), 3.70 (q, J=7.3), 4.53 (sept, J=6.9)(CH), 7.78 (aryl)	12.0, 14.3, 18.9 (2C), 24.7 (2C)(CH_3), 43.8, 48.6, 51.4 (CH_2, CH), 130.2, 131.5, 137.2, 138.7, 139.7, 157.3 (aryl, C=N)[e]
7d 1721[f]	0.85 (d, J=6.1), 1.20 (t, J=7.3), 1.58 (d, J=6.9), 2.61 (CH_3), 3.17 (sept, J=6.1), 3.71 (q, J=7.3), 4.57 (sept, J=6.9)(CH), 7.78 (aryl)	12.1, 14.2, 19.0 (2C), 24.7, (2C)(CH_3), 43.9, 48.7, 51.6 (CH_2, CH), 130.3, 131.6, 137.6, 138.9, 140.2, 157.4 (aryl, C=N)
7e 1706	0.83 (d, J=6.1), 1.39 (d, J=7.1), 1.58 (d, J= 6.9), 2.67 (CH_3), 3.16 (sept, J= 6.1), 4.01 (sept, J=7.1), 4.53 (sept, J=6.9) (CH), 7.79 (aryl)	13.0, 18.8 (2C), 21.0 (2C), 24.7 (2C), 48.5, 51.3, 55.2 (CH), 130.9, 131.6, 137.2, 139.0, 140.1, 157.4 (aryl, C=N)
7f 1713	0.85 (d, J=6.1), 1.56 (d, J=6.9)(CH_3), 3.12 (sept, J=6.1), 4.45 (sept, J=6.9)(CH), 1.97 (m, 4H), 2.99 (m, 2H), 3.47 (m, 2H)(CH_2), 7.80 (aryl)[g]	17.8, 18.8, 21.3, 22.8, 24.7, 45.7, 48.9, 50.5 (CH_3, CH_2, CH), 129.8, 131.3, 137.6[h], 138.6, 139.7, 157.1 (aryl, C=N)[g]
7g 1710	2.60, 3.29 (CH_3), 2.81 (m), 4.11 (m)(NCH), 7.78 (aryl)	12.3, 24.8, 25.7, 28.8, 34.4, 35.0, 59.1 (CH_3, CH_2, CH 130.1, 131.3, 137.5 138.9, 140.0, 157.5 (aryl, C=N)
7h 1717	1.22 (t, J=7.2), 2.64 (CH_3), 3.72 (q, J=7.2, CH_2), 2.87 (m), 4.10 (m) (NCH), 7.79 (aryl)	12.2, 14.2, 24.8, 25.7, 26.2, 26.3, 28.7, 35.1, 44.0, 56.3, 59.2 (CH_3, CH CH), 130.5, 131.5, 137.7, 138.9, 140. 157.5 (aryl, C=N)
7i 1710	2.81 (m), 4.02 (m)(CH), 3.02 (m), 3.47 (m) (CH_2), 7.78 (aryl)[e]	17.9, 21.3, 22.9, 24.8, 25.7, 26.2, 35.1, 45.8, 55.7, 58.0 (CH_2, CH), 13 131.3, 137.9[h], 1 139.7, 157.2 (aryl C=N)[e]
7l 1710	1.68 (d, J=6.9), 2.68, 3.33 (CH_3), 4.70 (sept, J=6.9, CH), 7.36 (aryl)	12.5, 19.1 (2C), 3 (CH_3), 51.9 (CH), 121.1, 124.2, 127. 129.5, 130.5, 138. 139.0, 139.8, 145. 156.5 (aryl, C=N)
7m 1710	2.49, 3.46 (CH_3), 7.68 (aryl)	13.0, 34.6 (CH_3), 121.1, 124.6, 126. 129.1, 129.6, 130. 131.4, 131.6, 132. 139.0, 140.2, 140. 144.7, 156.7 (aryl C=N)
7n 1717[f]	2.48, 3.45 (CH_3), 7.66 (aryl)	13.0, 34.5 (CH_3), 121.0, 124.5, 126. 129.1, 129.5, 130. 131.4, 131.6, 132. 139.0, 140.1, 140. 144.8, 156.7 (aryl C=N)
8 1620, 3438, 3411	1.27 (d, J=6.5), 1.43 (d, J=6.5), 1.51 (d, J= 7.1), 2.57 (CH_3), 3.85 (m, J=6.5 and 7.0), 4.44 (sept, J=7.1), 4.61 (sept, J=6.5) (CH), 5.04 (d, J=7.0, NH)	11.1, 20.2 (2C), 2 (2C), 22,4 (2C)(CH 47.2, 50.0, 53.1 (146.4, 153.1 (C=N)
9 1617, 3361	1.50 (9H), 2.74, 3.65 (CH_3), 5.21 (NH), 7.72 (aryl)[c]	14.1, 28.9 (3C), 3 56.0 (CH_3, CH), 12 131.1, 137.5, 142. 155.2, 160.1 (aryl C=N)[c]

[a] TMS as internal standard. – [b] KBr pellets; cm^{-1}. – [c] In $CDCl_3$. – [d] In CCl_4. – [e] At 273 K. – [f] In CH_2Cl_2. – [g] At 263 K. – [h] Broad.

to a cold solution of the compound **2** (10 mmol) and the carbodiimide **4** (12 mmol) in CH_2Cl_2 (20 ml). Alternatively, a solution of **2** (10 mmol) and **4** (12 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (−60°C) suspension of $AlCl_3$ (1.33 g, 10 mmol) in CH_2Cl_2 (20 ml). The colored mixture was first stirred at −60°C for 1 h and then at 0°C for 1 h, during which time the color faded to yellow. The solvent was evaporated under reduced pressure and the residue purified by crystallization or precipitation.

4,5-Dihydro-4-isopropyl-5-(isopropylimino)-2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7a**): From **2a**[6,9] (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and **4a** (1.51 g, 12 mmol). The yellow residue was precipitated from CH_2Cl_2 (10 ml)/pentane (80 ml). Crystallization at −20°C from CH_2Cl_2 (30 ml)/ether (200 ml) afforded fine yellow needles (4.62 g, 65%); m.p. 163−165°C (dec.). − $C_{16}H_{22}Cl_9N_4Sb$ (711.2): calcd. C 27.00, H 3.22, N 7.53; found C 27.02, H 3.12, N 7.88.

4,5-Dihydro-4-isopropyl-5-(isopropylimino)-2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Tetrachloroaluminate (**7b**): From **2a** (2.86 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4a** (1.26 g, 10 mmol). The brown oil solidified when treated with pentane (20 ml) to afford a moisture-sensitive pale yellow powder (4.56 g, 84%); m.p. 118−120°C (dec.). − $C_{16}H_{22}AlCl_7N_4$ (545.5): calcd. C 35.23, H 4.06, N 10.27; found C 34.94, H 4.23, N 10.19.

2-Ethyl-4,5-dihydro-4-isopropyl-5-(isopropylimino)-3-methyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7c**): From **2c**[9] (3.00g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and **4a** (1.51 g, 12 mmol). Ether (100 ml) was added to the yellow solution. Filtration and precipitation of the residue from CH_2Cl_2 (25 ml)/ether (100 ml) afforded fine yellow leaflets (5.14 g, 71%); m.p. 176−178°C (dec.). − $C_{17}H_{24}Cl_9N_4Sb$ (725.2): calcd. C 28.16, H 3.34, N 7.73; found C 28.24, H 3.37, N 7.70.

2-Ethyl-4,5-dihydro-4-isopropyl-5-(isopropylimino)-3-methyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Tetrachloroaluminate (**7d**): From **2c** (3.00 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4a** (1.26 g, 10 mmol) as described for **7b**. Yield: 5.46 g (98%) of a moisture-sensitive brownish powder; m.p. 126−128°C (dec.). − $C_{17}H_{24}AlCl_7N_4$ (559.6): calcd. C 36.49, H 4.32, N 10.01; found C 36.30, H 4.53, N 9.88.

4,5-Dihydro-2,4-diisopropyl-5-(isopropylimino)-3-methyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7e**): From **2e**[9] (3.14 g, 10 mmol) as described for **7c**. Yield: 6.16 g (83%) of a yellow powder, which was crystallized at −18°C from hot acetonitrile (30 ml) to furnish pale yellow needles (5.30 g); m.p. 183 to 185°C (dec.). − $C_{18}H_{26}Cl_9N_4Sb$ (739.3): calcd. C 29.25, H 3.55, N 7.58; found C 29.31, H 3.49, N 7.60.

2,3,5,6,7,8-Hexahydro-1-isopropyl-2-(isopropylimino)-3-(2,4,6-trichlorophenyl)-1H-[1,2,4]triazolo[2,3-a]pyridinium Hexachloroantimonate (**7f**): From **2f** (3.12 g, 10 mmol) as described for **7c**. Yield: 6.00 g (81%) of a yellow powder, which was precipitated from CH_2Cl_2 (30 ml)/ether (120 ml) to furnish pale yellow leaflets (5.82 g); m.p. 142−143°C (dec.). − $C_{18}H_{24}Cl_9N_4Sb$ (737.3): calcd. C 29.33, H 3.28, N 7.60; found C 29.31, H 3.28, N 7.58.

4-Cyclohexyl-5-(cyclohexylimino)-4,5-dihydro-2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7g**): From **2a** (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and **4g** (2.48 g, 12 mmol). Precipitation at −20°C from CH_2Cl_2 (20 ml)/ether (100 ml) afforded yellow leaflets (6.60 g, 83%); m.p. 157−159°C (dec.). − $C_{22}H_{30}Cl_9N_4Sb$ (791.3): calcd. C 33.39, H 3.82, N 7.08; found C 33.37, H 3.81, N 6.97.

4-Cyclohexyl-5-(cyclohexylimino)-2-ethyl-4,5-dihydro-3-methyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7h**): From **2c** (3.00 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and **4g** (2.48 g, 12 mmol). Precipitation at −20°C with pentane (60 ml) afforded an orange oil, which solidified in vacuo to give a yellow powder (6.14 g, 76%). Crystallization at −20°C from hot acetonitrile (6 ml) afforded pale yellow fine crystals (4.50 g); m.p. 164−167°C (dec.). − $C_{23}H_{32}Cl_9N_4Sb$ (805.4): calcd. C 34.30, H 4.00, N 6.96; found C 34.27, H 4.08, N 6.88.

1-Cyclohexyl-2-(cyclohexylimino)-2,3,5,6,7,8-hexahydro-3-(2,4,6-trichlorophenyl)-1H-[1,2,4]triazolo[2,3-a]pyridinium Hexachloroantimonate (**7i**): From **2f** (3.12 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and **4g** (2.48 g, 12 mmol). Yellow prisms (7.00 g, 86%) were precipitated at −20°C from the reaction mixture by slow addition of ether (100 ml). Crystallization at −20°C from hot acetonitrile (40 ml) afforded yellow cubes (5.60 g); m.p. 147−148°C (dec.). − $C_{24}H_{32}Cl_9N_4Sb$ (817.4): calcd. C 35.27, H 3.95, N 6.85; found C 35.36, H 3.98, N 6.93.

4,5-Dihydro-4-isopropyl-2,3-dimethyl-5-(phenylimino)-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7l**): From **2a** (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and **4l**[33] (1.92 g, 12 mmol). After stirring at −60°C for 4 h and at 25°C for 3 h the solvent was evaporated under reduced pressure. The residue was precipitated from CH_2Cl_2 (20 ml)/ether (100 ml) to afford a brown powder (6.68 g, 90%). Crystallization from hot dichloromethane (60 ml) afforded yellow prisms (4.02 g); m.p. 163−165°C (dec.). − $C_{19}H_{20}Cl_9N_4Sb$ (745.2): calcd. C 30.62, H 2.71, N 7.52; found C 30.58, H 2.75, N 7.44.

X-Ray Diffraction Analysis of **7l**[26]: $[C_{19}H_{20}Cl_3N_4]SbCl_6 \cdot CH_2Cl_2$, crystal size 0.3 × 0.3 × 0.3 mm^3, monoclinic, space group $P2_1c$, $Z = 4$, $a = 1903.3(9)$, $b = 951.8(3)$, $c = 1996.3(8)$ pm, $\beta = 115.61(3)°$, $V = 3261(2) \cdot 10^6$ pm^3, $d_{calc} = 1.69$ Mgm^{-3}, $T = 296$ K, $\mu_{Mo\text{-}K\alpha} = 12.5$ cm^{-1}, ω scan, $2.0 \leq \omega \leq 29.3°min^{-1}$, $4.0 \leq 2T \leq 54.0°$, 7783 collected reflections, 6528 independent reflections [$I > 1\,\sigma(I_0)$]. The cell constants and the intensities of the reflections were measured on a Siemens R3m/V diffractometer with a graphite monochromator, $\lambda_{Mo\text{-}K\alpha} = 71.073$ pm. The structure was solved by the Patterson method using the program Siemens SHELXTL PLUS. Hydrogen atoms were fixed on calculated geometrically ideal positions (riding model, fixed isotropic U). The aryl rings were treated as rigid groups. The anisotropic refinement led to agreement factors $R_1 = 0.079$, $R_2 = 0.081$.

4,5-Dihydro-2,3-dimethyl-4-phenyl-5-(phenylimino)-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**7m**): From **2a** (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and **4m**[34] (2.14 g, 11 mmol). After stirring at −60°C for 1 h and at 0°C for 1 h ether (100 ml) was added to the reaction mixture. A blue oil precipitated, which solidified to a green powder (7.78 g, 100%) on drying. Precipitation from CH_2Cl_2 (30 ml)/pentane (200 ml) afforded a pale green powder (7.01 g); m.p. 172−174°C (dec.). − $C_{22}H_{18}Cl_9N_4Sb$ (779.2): calcd. C 33.91, H 2.33, N 7.19; found C 34.30, H 2.44, N 6.99.

4,5-Dihydro-2,3-dimethyl-4-phenyl-5-(phenylimino)-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Tetrachloroaluminate (**7n**): From **2a** (2.86 g, 10 mmol), $AlCl_3$ (1.33 g, 10 mmol), and **4m** (2.14 g, 11 mmol). The product was precipitated from CH_2Cl_2 (10 ml)/pentane (60 ml) to give a moisture-sensitive blue oil, which solidified to a pale green powder (6.10 g, 99%) on drying; m.p. 196−198°C (dec.). − $C_{22}H_{18}AlCl_7N_4$ (613.6): calcd. C 43.07, H 2.96, N 9.13; found C 43.29, H 3.25, N 9.03.

1,4-Diisopropyl-3-(isopropylamino)-5-methyl-4H-1,2,4-tirazolium Hexachloroantimonate (**8**): From **2j** (1.91 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and **4a** (1.26 g, 10 mmol). The product was precipitated

from CH_2Cl_2 (20 ml)/ether (120 ml) to give a yellow powder (5.02 g, 90%). Reprecipitation from CH_2Cl_2 (50 ml)/ether (200 ml) afforded a yellow powder (4.62 g); m.p. 199–201°C. – $C_{12}H_{25}Cl_6N_4Sb$ (559.8): calcd. C 25.75, H 4.50, N 10.01; found C 25.61, H 4.43, N 9.94.

5-(tert-Butylamino)-2,3-dimethyl-1-(2,4,6-trichlorophenyl)-1H-1,2,4-triazolium Hexachloroantimonate (**9**)

a) From **2a** (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and **4k**[35] (1.85 g, 12 mmol). After stirring the reaction mixture at 25°C for 2 h, the solvent was evaporated under reduced pressure. The remaining orange oil was precipitated from CH_2Cl_2 (15 ml)/ether (100 ml). The resulting oil solidified at –20°C to give a pale brown powder (4.78 g, 70%). Crystallization at –20°C from CH_2Cl_2 (20 ml)/ether (40 ml) afforded a colorless powder (4.49 g); m.p. 182–184°C. – $C_{14}H_{18}Cl_9N_4Sb$ (683.2): calcd. C 24.61, H 2.66, N 8.20; found C 24.62, H 2.70, N 8.43.

b) From **2a** (2.86 g, 10 mmol), $SbCl_5$ (2.99 g, 10 mmol), and *tert*-butylcyanamide[36] (1.18 g, 12 mmol) according to the General Procedure. Slow addition of ether (120 ml) to the reaction mixture afforded pale yellow fine prisms (5.38 g, 79%), which can be recrystallized from hot chloroform or precipitated from CH_2Cl_2/ether; m.p. 182–184°C.

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