1,3-Diaza-2-azoniaallene Salts, Novel N_3-Building Blocks: Preparation and Cycloadditions to Olefins

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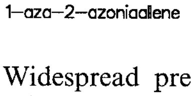
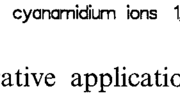
Introduced are 1,3-diaza-2-azoniaallene salts $R^1-N=N^+=N-R^2\ X^-$ (**6**) representing a new functional group. The reactive intermediates **6** are prepared by reaction of *N*-chlorotriazenes $R^1-N=N-NCl-R^2$ (**8**) with Lewis acids. The salt **6a** is stable below −50 °C. It shows a strong IR band at 2018 cm^{-1}, equivalent aryl groups in the ^1H and ^{13}C NMR spectra, and gives a correct elemental analysis. The allenes **6** undergo $[4\pi + 2\pi]$ cycloadditions to both electron-rich and electron-deficient olefins affording 4,5-dihydro-1,2,3-triazolium salts **11** ("1,3-dipolar cycloadditions with inverse electron demand"). The cycloadditions proceed with complete conservation of the stereochemistry of the olefins. Cycloadducts **11w,11ai** of dibutyl maleate rearrange in solution into the respective more stable *trans*-isomers **11v,11ah**. The structure of **11m** was determined by X-ray structural analysis.

Five types of monocations **2**–**6** can be conceived by replacing the carbon atoms of allenes **1** by nitrogen atoms. Only a few keteniminium salts **2** have been isolated. According to X-ray crystallographic analysis they are isosteric to allenes.[1] The C=N=C unit of the remarkably stable 2-azoniaallene salts **3** is rather flexible.[2,3] Depending on the substituents, allene type local D_{2d} symmetries,[3] allyl cation type local C_{2v} symmetries,[4,5] and, most often, geometries in between these two extremes were found by crystal structural analyses.[6,7] Only recently, 1-aza-2-azoniaallene salts **4** have become known as reactive intermediates.[8-13] Calculations suggest them to be geometrically related to ketenimines. X-ray crystallographic analysis of a salt **5** revealed a linear NCN unit and bond lengths characteristic for a cyanamidium structure.[14]



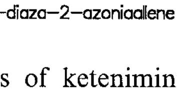
1

allenes



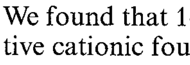
2

keteniminium ions



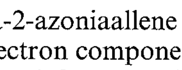
3

2–azoniaallene ions



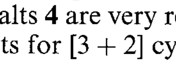
4

1–aza–2–azoniaallene ions



5

cyanamidium ions



6

1,3–diaza–2–azoniaallene ions

Widespread preparative applications of keteniminium salts **2**, e.g. [2 + 2] cycloadditions with olefins and azomethines, have been discovered, especially by Ghosez and his group.[15-17] For 2-azoniaallene salts **3** cycloadditions, ene and other reactions have been reported.[18-22] We found that 1-aza-2-azoniaallene salts **4** are very reactive cationic four-electron components for [3 + 2] cycloadditions to nitriles, olefins, acetylenes, carbodiimides, and isocyanates.[8-13] The salts **4** were obtained by chlorination of hydrazones with *tert*-butyl hypochlorite and treatment of the resulting (chloroalkyl) azo compounds with Lewis acids such as antimony pentachloride.

In this study, we set out to extend this approach to the synthesis of heterocumulenes **6**, which might be termed 1,3-diaza-2-azoniaallene salts, to our knowledge a hitherto unknown class of compounds. Oxidation of the triazene **7a**[23] with *tert*-butyl hypochlorite afforded a stable *N*-chlorotriazene **8a**. In contrast to **7a**, compound **8a** is very soluble in organic solvents like chloroform. The structure of **8a** was determined from its NMR and IR data (Table 2). Compounds **8ad–ag,aj,ak** are less stable than **8a**. Occasionally, they exploded on attempted isolation (caution!). For further transformation into cumulenes **6** isolation of compounds **8** is not required.

Stable open-chain *N*-chlorotriazenes seem to be unreported in the literature.[24] On the other hand, cyclic compounds **8**, e.g. 1-chlorobenzotriazole, are well documented.[25,26]

On addition at −60 °C of antimony pentachloride to a solution of **8a** in dichloromethane a red-orange solid **6a** precipitated, which at −50 °C was isolated by filtration. At −80 °C the compound can be stored for months but it decomposes quickly above −25 °C. In acetonitrile, decomposition of **6a** affords essentially (> 95 %) two products in equal amounts, namely the diazonium salt **9a**,[27] which remains in solution, and the azo compound **10a**,[28] which precipitates. The ^1H NMR spectrum of **6a** (at −35 °C in CD_3CN) shows only one singlet at 7.93 ppm for aromatic protons. In the ^{13}C NMR spectrum four resonances for two equivalent aryl substituents are found. The IR spectrum (at −50 °C in MeCN) is dominated by a very strong band at 2018 cm^{-1}, which may be assigned to the asymmetric stretching vibration of the $N=N^+=N$ unit. At room temperature this band faded away over the course of the next five minutes. These data together with a correct elemental analysis are in accord with the structure of a 1,3-diaza-2-azoniaallene salt **6a**. The AM1-calculated[29] geometry for the cation **6a** is shown in Figure 1. The N=N=N unit is calculated to be bent (155°), the planes through C15–N1–N2 and C4–N3–N2 are almost perpendicular with respect to each other (C15–N1–N3–N4 = 107°) as are the planes through the two aryl rings (C16–C15–C4–C9 = 122°).

Cumulenes **6** can be regarded as N3 substituted azides. The question as to the site of protonation and alkylation of hydrazoic acid and alkyl azides was first answered by Schmidt, who prepared rather stable N1 protonated and alkylated hexachloroantimonates of hydrazoic acid and methyl azide.[30] Later IR and Raman spectroscopic studies confirmed Schmidt's structural proposals.[31] According to ab initio calculations an isolated cation $\mathrm{H{-}N{=}N^{+}{=}N{-}H}$ is about 200 $\mathrm{kJmol^{-1}}$ less stable than the tautomer $\mathrm{H_2N{-}N^{+}{\equiv}N}$.[32,33]

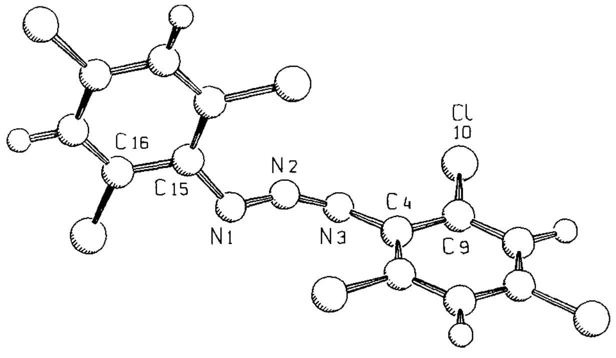


Figure 1. AM1-calculated geometry for the cation **6a**.

Other classes of triazenium salts have been reported in the literature, e.g. compounds $\mathrm{R^1N{=}N{-}N^{+}R^2{=}CR^1R^2}$,[34] obtained by the reaction of imines with aryldiazonium salts,[35] and triazenium salts $\mathrm{R^1R^2N^{+}{=}N{-}NR^3R^4}$.[36] In contrast to the 1-aza-2-azoniaallene salts **4** the salt **6a** is neither especially moisture sensitive nor does it react with methanol. While even at $-60\,^{\circ}\mathrm{C}$ ions **4** undergo fast cycloadditions to nitriles to afford 1,2,4-triazolium salts[8] no reaction with nitriles could be achieved with cumulene **6a**. Similarly, **6a** does not react with isocyanates (methyl isocyanate, phenyl isocyanate), isothiocyanates (methyl isothiocyanate, isopropyl isothiocyanate), or azo compounds (2,3-diazabicyclo[2.2.1]hept-2-ene).

However, the heterocumulenes **6** undergo smooth cycloadditions to many olefins. Thus, **6a** reacts with ethene between $-60\,^{\circ}\mathrm{C}$ and $-25\,^{\circ}\mathrm{C}$ to give the 4,5-dihydro-1,2,3-triazolium salt **11a** (83 %). Similarly, the other salts **11** were obtained (Scheme). Olefins with up to three substituents react. However, no reaction occurred with 2,3-dimethylbut-2-ene or tetraphenylethene. Spiro compounds (e.g. **11j**) as well as bicyclic 1,2,3-triazolium salts (e.g. **11p,q,r**) can be made. Electron-rich olefins such as 2-methylbut-2-ene or vinyl acetate react equally well as do electron-deficient olefins, e.g. ethyl acrylate, dibutyl maleate, dibutyl fumarate, or *N*-phenylmaleimide. However, no reaction could be induced between **6a** and maleic anhydride or coumarin. The reaction of **6a** with vinyl chloride furnished the triazolium salt **12**. Obviously, the primarily formed salt **11g** lost HCl under the experimental conditions. No reactions could be achieved with 1-chlorobenzotriazole and olefins in the presence of antimony pentachloride.

Only a few 4,5-dihydro-1,2,3-triazolium salts have been reported in the literature.[36]

The structural assignments of the new compounds are based on their NMR and IR spectra (Table 2). The structure of **11m** was confirmed by X-ray crystallographic analysis (Figure 2, Table 1).

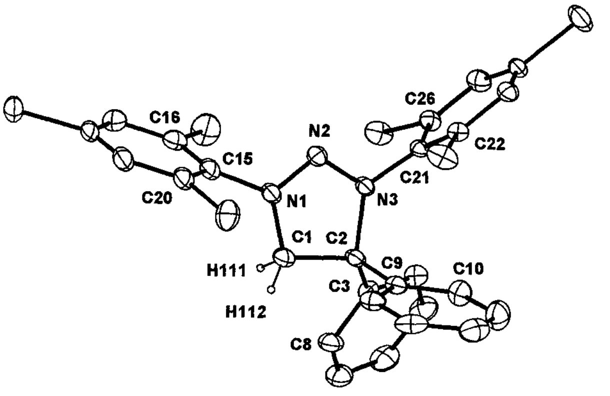


Figure 2. ORTEP Plot of the Cation **11m**.

1,3-Diaza-2-azoniaallene salts **6** react with olefins stereoselectively with complete retention of the configuration of the olefin. Thus, from **6a** and (*E*)-hex-3-ene exclusively the *trans*-form **11n** was obtained, and (*Z*)-hex-3-ene afforded the pure *cis*-form **11o**. Corresponding stereoselectivities were observed for cycloadditions of **6a** to (*E*)- and (*Z*)-1,4-dichlorobut-2-ene (**11s, 11t**), dibutyl fumarate and dibutyl maleate (**11v, 11w**), and for the reaction of **6ag** with dibutyl fumarate and dibutyl maleate (**11ah, 11ai**). This points to a concerted [$4\pi + 2\pi$]-cyclo-

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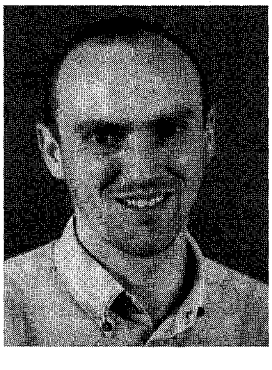
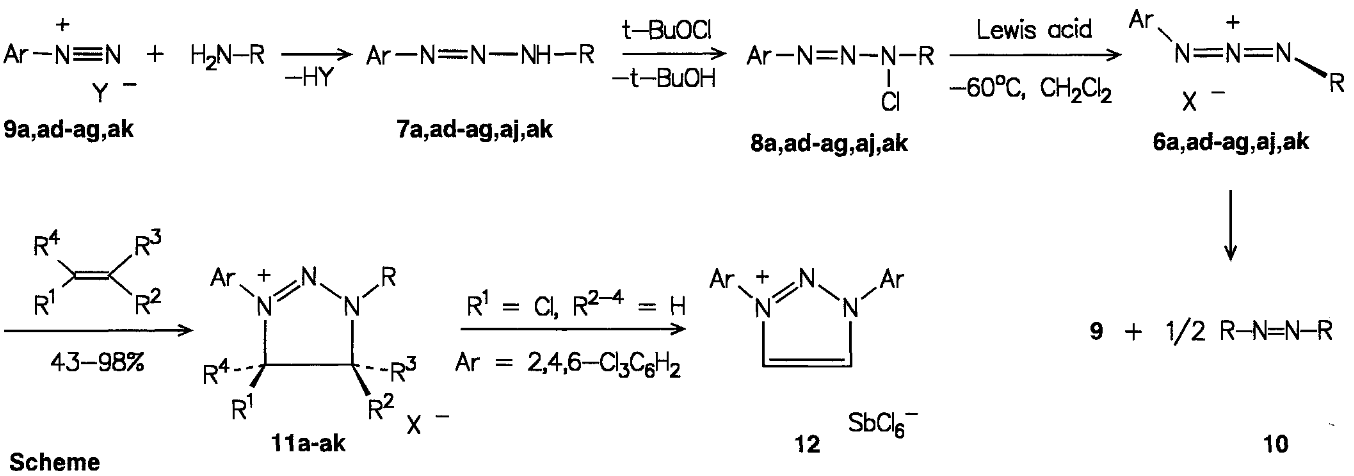
Biographical Sketch



Wolfgang Wirschun was born 1967 in Albstadt, Germany. In 1988 he went to the University of Konstanz, where he finished his graduate education in chemistry in 1994. At the present he's working on his Ph.D. project on cationic heterocumulenes under the supervision of Prof. Dr. J.C. Jochims in Konstanz.



Scheme

[a]	Ar	R	R^1	R^2	R^3	R^4
a	[b]	[b]	H	H	H	H
b	[b]	[b]	Bu	H	H	H
c	[b]	[b]	OAc	H	H	H
d	[b]	[b]	CH_2Cl	H	H	H
e	[b]	[b]	CH_2CN	H	H	H
f	[b]	[b]	Ph	H	H	H
g	[b]	[b]	Cl	H	H	H
h	[b]	[b]	CO_2Et	H	H	H
i	[b]	[b]	CH_3	H	H	CH_3
j	[b]	[b]	H	$(CH_2)_4$		H
k	[b]	[b]	CH_2Cl	H	H	CH_3
l	[b]	[b]	CH_2Cl	H	H	CH_2Cl
m	[b]	[b]	Ph	H	H	Ph
n	[b]	[b]	Et	H	Et	H
o	[b]	[b]	Et	Et	H	H
p	[b]	[b]	[l]		H	H
q	[b]	[b]	$(CH_2)_3$		H	H
r	[b]	[b]	$(CH_2)_4$		H	H
s	[b]	[b]	CH_2Cl	H	CH_2Cl	H
t	[b]	[b]	CH_2Cl	CH_2Cl	H	H
u	[b]	[b]	O=CNPhC=O		H	H
v	[b]	[b]	CO_2Bu	H	CO_2Bu	H
w	[b]	[b]	CO_2Bu	CO_2Bu	H	H
x	[b]	[b]	CH_3	CH_3	CH_3	H
y	[b]	[b]	CH_3	Cl	H	CH_3
z	[b]	[b]	$(CH_2)_3$		H	H[h]
aa	[b]	[b]	$(CH_2)_3$		H	H[i]
ab	[b]	[b]	$(CH_2)_3$		H	H[j]
ac	[b]	[b]	$(CH_2)_3$		H	H[k]
ad	[c]	[c]	Bu	H	H	H
ae	[d]	[d]	$(CH_2)_3$		H	H
af	[e]	[e]	$(CH_2)_3$		H	H
ag	[f]	[f]	CH_2Cl	H	H	H
ah	[f]	[f]	CO_2Bu	H	CO_2Bu	H
ai	[f]	[f]	CO_2Bu	CO_2Bu	H	H
aj	[b]	[f]	$(CH_2)_3$		H	H
ak	[g]	CH_3	$(CH_2)_3$		H	H[m]

[a] X: $SbCl_6$, if not noted otherwise.
[b] 2,4,6-$Cl_3C_6H_2$.
[c] 2,4,6-$Br_3C_6H_2$.
[d] 4-ClC_6H_4.
[e] 2,4,6-$Me_3C_6H_2$.
[f] 4-$NO_2C_6H_4$.
[g] 4-MeC_6H_4.
[h] X: $AlCl_4$.
[i] X: $TiCl_6^-$.
[j] X: $SnCl_6^-$.
[k] ClO_4.
[l]

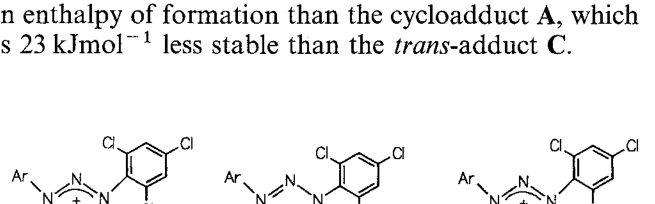
[m] X:Cl.

Table 1. Selected Bond Lengths (pm), Bond Angles, and Torsional Angles (°) of the Cation **11m**[37]

N1–N2	128.8(4)	C2–C1–N1	103.6(3)	N3–C2–C1–N1	−13.7(3)
N2–N3	129.1(4)	C1–N1–N2	113.3(3)	C2–C1–N1–N2	13.6(4)
N3–C2	156.2(4)	N2–N3–C21	114.1(3)	C1–N1–N2–N3	−5.9(4)
C2–C1	154.8(4)	N3–C2–C3	115.9(3)	N1–N2–N3–C21	−174.8(3)
C1–N1	147.2(4)	N3–C2–C9	107.4(3)	N2–N3–C21–C22	79.3(4)
N1–C15	143.0(4)	N2–N1–C15	120.1(3)	N2–N3–C2–C3	127.8(3)
N3–C21	144.7(4)	C1–C2–C3	109.5(3)	N2–N3–C2–C9	−108.1(3)
C2–C3	152.2(5)	C1–C2–C9	116.1(3)	N2–N1–C15–C16	68.9(4)
C2–C9	153.1(5)	C1–N1–C15	124.2(3)	N3–C2–C3–C8	−145.7(3)
N1–N2–N3	110.5(3)	C2–N3–C21	131.5(3)	N3–C2–C9–C10	−79.5(4)
N2–N3–C2	113.4(2)	N1–N2–N3–C2	−4.8(4)	C8–C3–C2–C9	91.8(3)
N3–C2–C1	97.0(2)	N2–N3–C2–C1	12.1(3)	C10–C9–C2–C3	47.8(4)

addition mechanism (1,3-dipolar cycloaddition with inverse electron demand).[12] AM1 calculations for the cycloaddition of **6a** to ethene support this view. The cycloaddition was calculated to be exothermic by 167 kJmol^{-1} with an activation enthalpy $\Delta H^{\neq}$ of 74 kJmol^{-1}. In the transition structure the forming CN-bonds are of equal lengths (210 pm) in agreement with a synchronous reaction. The important orbital interaction is that of LUMO of **6a** (LUMO −6.13 eV, HOMO −13.41 eV) with HOMO of ethene (LUMO +1.44 eV, HOMO −10.55 eV).

Cycloadditions of **6a** to the more electron-deficient olefins, dimethyl maleate and dimethyl fumarate, were calculated to be much less exothermic (81 kJmol^{-1}, resp. 89 kJmol^{-1}). Experimentally, it was found that the cycloadduct **11w** of dibutyl maleate with **6a** rearranges at 23 °C in solution (CD_3CN) into the *trans*-isomer **11v** with a half-life of about 50 minutes. For this isomerization AM1 calculations suggest an anchimeric assistance of one of the *ortho*-chlorine atoms. The chloronium intermediate **B** was calculated to be only 59 kJmol^{-1} higher in enthalpy of formation than the cycloadduct **A**, which is 23 kJmol^{-1} less stable than the *trans*-adduct **C**.



A **B** **C**

Ar: 2,4,6-$Cl_3C_6H_2$

The cycloadduct **11ai** of **6ag** and dibutyl maleate was also observed to rearrange in solution to the more stable *trans*-form **11ah**. In this case a neighboring effect is excluded. Under comparable conditions, the transformation **11ai** → **11ah** was slower by a factor of ca 50 than the rearrangement **11w** → **11v**. AM1 calculations suggest heterolysis of one of the C–N bonds of **11ai**, rotation around the RO_2CC^+–C bond followed by ring closure to **11ah**.

All solvents were dried by standard methods. The experiments were carried out with exclusion of moisture. The melting points are uncorrected. IR spectra: Perkin-Elmer FTIR 1600. ^1H and ^{13}C NMR spectra: Bruker AC-250 spectrometer; internal reference TMS; δ-scale. X-Ray diffraction analysis of **11m**: Enraf-Nonius-CAD4 diffractometer (graphite monochromator, $\lambda_{Mo\text{-}K\alpha} = 71.069$ pm). The structure (monoclinic, space group $P\,21/n$) was solved by the Patterson method with subsequent difference-Fourier synthesis using the programs SHELXS-86 and SHELXL-93. The hydrogen atoms H5, H13, H23, H25 were fixed in calculated positions (d(C–H) = 0.95 pm). The other hydrogen atoms were found by difference-Fourier synthesis. The anisotropic refinement led to agreement factors $R_1 = 0.031$ and $R_2 = 0.070$ ($I > 2$sigma (I)).[37]

1,3-Bis(2,4,6-trichlorophenyl)-1,3-diaza-2-azoniaallene Hexachloroantimonate (6a):

A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (40 mL) was added dropwise under stirring to a cold (−60 °C) suspension of **8a** (4.38 g, 10 mmol) in CH_2Cl_2 (20 mL). After stirring at −60 °C for 5 min an orange-red powder was isolated by filtration through a cooled (−50 °C) frit and dried at −50 °C in vacuo. Yield. ca 7.37 g (100 %). The product decomposes above −25 °C but can be stored at −80 °C for several months. Decomposition in solution (MeCN) gives **10a**, which precipitates, plus **9a**, which remains in solution, as well as traces (< 5 %) of unidentified products.

1,3-Bis(4-nitrophenyl)triazene (7ag):

Isoamyl nitrite (23.43 g, 200 mmol) was added dropwise to a cold (0 °C) solution of *p*-nitroaniline (13.81 g, 100 mmol) in Et_2O (200 mL). After stirring at 23 °C for 2 h, then at 0 °C for 30 min, filtration afforded a yellow powder (13.50 g, 94 %); mp 230–232 °C [Lit.[38] 234 °C (dec)].

3-(4-Nitrophenyl)-1-(2,4,6-trichlorophenyl)triazene (7aj):

p-Nitroaniline (1.38 g, 10 mmol) was added to a cold (0 °C) suspension of **9a** (Y: $SbCl_6$)[27] (5.43 g, 10 mmol) in EtOH (100 mL). The mixture was stirred at 23 °C for 1 h. Filtration and washing of the residue with EtOH afforded a yellow powder (2.80 g, 81 %, decomposing at 23 °C); mp 142–146 °C (dec).

1-Chloro-1,3-bis(2,4,6-trichlorophenyl)triazene (8a):

tert-Butylhypochlorite[39] (1.30 g, 12 mmol) was added dropwise with exclusion of light to a cold (−10 °C) suspension of **7a**[23] (4.04 g, 10 mmol) in CH_2Cl_2 (20 mL). Stirring at 0 °C for 1 h afforded a clear yellow solution. Evaporation of the solvent furnished an analytically pure yellow powder (4.37 g, 100 %); mp 108–110 °C (dec). Crystallization of 0.70 g at −80 °C from pentane (10 mL)/CH_2Cl_2 (2 mL) afforded a pale yellow powder (0.61 g); mp 108–110 °C (dec).

MS (EI, 105 °C): *m/e* 402 (1 %, aryl-N=N$^+$=N-aryl), 388 (1 %, aryl-N=N-aryl$^+$), 207 (80 %, aryl-N_2^+), 179 (100 %, aryl$^+$).

1-Chloro-1,3-bis(2,4,6-tribromophenyl)triazene (8ad):

Me_3COCl (1.30 g, 12 mmol) was added dropwise with exclusion of light to a cold (−20 °C) suspension of **7ad**[23,40] (6.71 g, 10 mmol) in CH_2Cl_2 (200 mL). The mixture was stirred at −20 °C for 2 h, then at 23 °C for 1 h. Evaporation to a volume of ca 40 mL and filtration afforded an analytically pure yellow powder (5.22 g, 74 %); mp: explosion at 106 °C; caution! The product can be kept at −15 °C but decomposes at 23 °C.

1-Chloro-1,3-bis(4-nitrophenyl)triazene (8ag):

From **7ag** (4.04 g, 10 mmol) as described for **8a**. Stirring at −10 °C for 1 h and at 23 °C for 1 h afforded a yellow suspension. Evaporation of the solvent furnished an analytically pure yellow powder (3.21 g, 100 %), which underwent explosive decomposition in one case; mp: explosion at 125 °C; caution! The compound is stable at 0 °C for weeks.

1-Chloro- and 3-chloro-3-(4-nitrophenyl)-1-(2,4,6-trichlorophenyl)triazene (8aj):

From a cold (−40 °C) suspension of **7aj** (3.46 g, 10 mmol) in CH_2Cl_2 (100 mL) as described for **8a**. Stirring at −40 °C for 30 min, then at 23 °C for 1 h afforded an orange solution. Evaporation of the solvent furnished an orange powder (3.76 g, 99 %), which was crystallized at −40 °C from CH_2Cl_2 to give a yellow-orange powder; mp: explosive decomposition at 105 °C; caution!

Reaction of 1,3-Diaza-2-azoniaallene Hexachloroantimonates with Olefins; General Procedure:

A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a cold (−60 °C) suspension or solution of **8** (10 mmol) and the olefin (12 mmol or an excess in the case of gaseous olefins) in CH_2Cl_2 (40 mL). The color of the mixture changed and a precipitate was formed in most cases. The mixture was stirred between −60 °C and −30 °C for 1 h, then at 0 °C for 30 min, and finally at 23 °C for 15 min. Workup with separation of small amounts of aryldiazonium salts **9** afforded **11** as analytically pure powders, which could be reprecipitated.

4,5-Dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11a**):

From **8a** (4.38 g, 10 mmol) and ethene (excess). Filtration of the mixture and slow addition of CCl_4 (120 mL) to the cold (0 °C) filtrate afforded a colorless powder (6.32 g, 83 %), which was dissolved in CH_2Cl_2 (20 mL)/MeCN (4 mL). On addition of Et_2O (40 mL) a small amount of **9a** precipitated. The mixture was filtered with charcoal. Slow addition of Et_2O (40 mL) to the filtrate furnished a colorless crystalline powder (5.48 g, 72 %); mp 217–219 °C (dec).

4-Butyl-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11b**):

From **8a** (4.38 g, 10 mmol) and hex-1-ene (1.01 g, 12 mmol). Filtration of the mixture and slow addition of CCl_4 (160 mL) furnished a colorless powder (5.68 g, 69 %), which was dissolved in CH_2Cl_2 (40 mL). Slow addition of Et_2O (40 mL), filtration with charcoal, and slow addition of Et_2O (120 mL) to the filtrate afforded a colorless crystalline powder (5.24 g, 64 %); mp 183–185 °C (dec).

4-Acetoxy-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11c**):

From **8a** (4.38 g, 10 mmol) and vinyl acetate (1.18 g, 12 mmol). Addition of CCl_4 (20 mL) to the mixture, filtration and slow addition of further CCl_4 (60 mL) to the filtrate furnished a yellow powder (5.60 g, 68 %), which was reprecipitated from CH_2Cl_2 (80 mL)/Et_2O (80 mL) to furnish a colorless crystalline powder (5.27 g, 64 %); mp 181–184 °C (dec).

4-Chloromethyl-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11d**):

From **8a** (4.38 g, 10 mmol) and allyl chloride (0.92 g, 12 mmol). The mixture was filtered. Slow addition of CCl_4 (80 mL) afforded a colorless precipitate (6.16 g, 76 %), which was dissolved in CH_2Cl_2 (80 mL). Filtration with charcoal and slow addition of Et_2O (200 mL) to the filtrate afforded a colorless powder (4.80 g, 59 %); mp 218–220 °C (dec).

4-Cyanomethyl-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-dihydro-1,2,3-triazolium Hexachloroantimonate (**11e**):

From **8a** (4.38 g, 10 mmol) and allyl cyanide (0.81 g, 12 mmol). Filtration of the mixture and slow addition of CCl_4 (80 mL) to the filtrate afforded 7.64 g (95 %) of a pale yellow powder, which was reprecipitated from MeCN (3 ml)/Et_2O (20 mL) to furnish a colorless powder (6.12 g, 76 %); mp 218–220 °C (dec).

4,5-Dihydro-4-phenyl-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11f**):

From **8a** (4.38 g, 10 mmol) and distilled styrene (1.25 g, 12 mmol). The mixture was evaporated and the residue was suspended in CH_2Cl_2 (40 mL). Filtration and slow addition of CCl_4 (120 mL) to the filtrate afforded a beige precipitate (5.39 g, 64 %), which was dissolved in CH_2Cl_2 (40 mL)/MeCN (2 mL). Addition of CCl_4 (20 mL), filtration, and addition of CCl_4 (80 mL) to the filtrate furnished a colorless powder (3.62 g, 43 %); mp 216–218 °C (dec).

4-Ethoxycarbonyl-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11h**):

From **8a** (4.38 g, 10 mmol) and ethyl acrylate (1.20 g, 12 mmol). Slow addition of CCl_4 (200 mL) to the mixture, filtration, and slow addition at -20 °C of further CCl_4 (120 mL) to the filtrate afforded a colorless powder (6.96 g, 83 %), which was dissolved in CH_2Cl_2 (30 mL). Slow addition of Et_2O (100 mL) gave a colorless crystalline powder (6.16 g, 70 %); mp 140–143 °C (dec).

4,5-Dihydro-4,4-dimethyl-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11i**):

From **8a** (4.38 g, 10 mmol) and excess of isobutene. Addition of CCl_4 (200 mL) to the mixture afforded a colorless precipitate (6.96 g, 88 %), which was suspended in CH_2Cl_2 (20 mL)/MeCN (20 mL). Addition of Et_2O (80 mL) and filtration afforded a colorless powder (6.44 g, 81 %); mp 230–232 °C (dec).

FAB MS: m/e 458 (100 %).

1,3-Bis(2,4,6-trichlorophenyl)-2,3-diaza-1-azoniaspiro[4.4]non-1-ene Hexachloroantimonate (**11j**):

From **8a** (4.38 g, 10 mmol) and methylenecyclopentane (0.99 g, 12 mmol). The mixture was filtered after addition of CCl_4 (40 mL). Slow addition of further CCl_4 (100 mL) to the filtrate afforded a pale red powder (4.32 g, 53 %), which was reprecipitated from CH_2Cl_2 (40 mL)/Et_2O (80 mL) to give a colorless powder (4.12 g, 50 %); mp 207–209 °C (dec).

4-Chloromethyl-4,5-dihydro-4-methyl-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11k**):

From **8a** (4.38 g, 10 mmol) and methallyl chloride (1.09 g, 12 mmol). Addition of CCl_4 (40 mL), filtration, and slow addition of further CCl_4 (120 mL) to the filtrate afforded a pale yellow powder (4.92 g, 59 %), which was dissolved in CH_2Cl_2 (20 mL). Addition of Et_2O (20 mL), filtration, and addition of further Et_2O (40 mL) to the filtrate afforded a colorless powder (3.64 g, 44 %); mp 216–218 °C (dec).

4,4-Bis(chloromethyl)-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11l**):

From **8a** (4.38 g, 10 mmol) and 3-chloro-2-chloromethylprop-1-ene (1.50 g, 12 mmol). Addition of CCl_4 (80 mL), filtration, and slow addition at -20 °C of further CCl_4 (140 mL) to the filtrate afforded a pale yellow powder (6.96 g, 81 %), which was reprecipitated from CH_2Cl_2 (40 mL)/MeCN (8 mL)/Et_2O (160 mL) to afford a colorless crystalline powder (6.08 g, 71 %); mp 201–203 °C (dec).

4,5-Dihydro-4,4-diphenyl-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11m**):

From **8a** (4.38 g, 10 mmol) and 1,1-diphenylethene (2.16 g, 12 mmol). Filtration of the mixture followed by slow addition of Et_2O (200 mL) to the filtrate afforded a colorless powder (6.48 g, 71 %); mp 136–140 °C (dec). Crystallization at -20 °C from MeCN furnished colorless prisms suitable for X-ray structural analysis.

MS (FAB): m/e 582 (M^+, 80 %), 374 (M^+-aryl-N_2, 20 %), 207 (aryl-N_2^+, 100 %).

(E)-4,5-Diethyl-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11n**):

From **8a** (4.38 g, 10 mmol) and (*E*)-hex-3-ene (1.01 g, 12 mmol). The solvent of the mixture was evaporated. The ^1H NMR spectrum (CD_3CN) of the brown solid residue (8.14 g, 100 %) showed the presence of **11n** (95 %), the diazonium salt **9a** (5 %), and traces of impurities but no trace of **11o**. Dissolution in CH_2Cl_2 (40 mL), filtration from insoluble **9a** and slow addition of Et_2O (120 mL) to the filtrate afforded a colorless precipitate (5.92 g, 72 %), which was reprecipitated from CH_2Cl_2 (30 mL)/Et_2O (100 mL) to give a colorless powder (5.35 g, 65 %); mp 186–188 °C (dec).

(Z)-4,5-Diethyl-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11o**):

From **8a** (4.38 g, 10 mmol) and (*Z*)-hex-3-ene (1.01 g, 12 mmol). The solvent of the mixture was evaporated. The brown solid residue (8.12 g, 99 %) showed the presence of **11o** (95 %), the diazonium salt **9a** (5 %), and traces of impurities but no trace of **11n** (^1H NMR). Workup as described for **11n**. Yield: 6.08 g (74 %) of a colorless powder; mp 217–219 °C (dec). Refluxing a solution of **11o** either in $ClCH_2CH_2Cl$ or MeCN for 3 h did not effect isomerization.

(1S,R,2R,S,6S,R,7R,S)-3,5-Bis(2,4,6-trichlorophenyl)4,5-diaza-3-azoniatricyclo[5.2.1.$0^{2,6}$]dec-2-ene Hexachloroantimonate (**11p**):

From **8a** (4.38 g, 10 mmol) and norbornene (1.13 g, 12 mmol). Slow addition of Et_2O (120 mL) to the red mixture afforded a colorless precipitate (4.74 g, 57 %), which was reprecipitated from CH_2Cl_2 (20 mL)/Et_2O (40 mL) to furnish a colorless powder (3.83 g, 46 %); mp 241–243 °C (dec).

3,3a,4,5,6,6a-Hexahydro-1,3-bis(2,4,6-trichlorophenyl)-cyclopenta-[d]-1,2,3-triazolium Hexachloroantimonate (**11q**):

From **8a** (4.38 g, 10 mmol) and cyclopentene (0.82 g, 12 mmol). The mixture was filtered. Slow addition of CCl_4 (80 mL) to the filtrate afforded a pale yellow powder (5.72 g, 71 %). Crystallization from CH_2Cl_2 (60 mL)/Et_2O (700 mL) furnished colorless needles (5.26 g, 65 %); mp 279–281 °C (dec).

3a,4,5,6,7,7a-Hexahydro-1,3-bis(2,4,6-trichlorophenyl)-cyclohexa-[d]-1H-1,2,3-triazolium Hexachloroantimonate (**11r**):

From **8a** (4.38 g, 10 mmol) and cyclohexene (0.99 g, 12 mmol). Slow addition of CCl$_4$ (80 mL) to the clear red mixture afforded pale yellow leaflets (6.08 g, 74%), which were reprecipitated from CH$_2$Cl$_2$ (20 mL)/Et$_2$O (60 mL) to give a colorless powder (5.16 g, 63%); mp 236–237 °C (dec).

(E)-4,5-Bis(chloromethyl)-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11s**):

From **8a** (4.38 g, 10 mmol) and (*E*)-1,4-dichlorobut-2-ene (1.50 g, 12 mmol, containing 14% of the (*Z*)-form). The solvent of the mixture was evaporated. The ^{1}H NMR spectrum (CD$_3$CN) of the brown solid residue (8.62 g, 100%) showed the presence of **11s** (80%), the (*E*)-form **11t** (14%), the diazonium salt **9a** (5%), and traces of impurities. Precipitation from CH$_2$Cl$_2$ (60 mL)/CCl$_4$ (80 mL) afforded a pale yellow crystalline powder (7.52 g, 87%); mp 186–188 °C (dec).

(Z)-4,5-Bis(chloromethyl)-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11t**):

From **8a** (4.38 g, 10 mmol) and (*Z*)-1,4-dichlorobut-2-ene (1.50 g, 12 mmol, containing 2% of the (*E*)-form). The solvent of the mixture was evaporated. The ^{1}H NMR spectrum (CD$_3$CN) of the brown solid residue (8.61 g, 100%) showed the presence of **11t** (92%), the (*Z*)-form **11s** (2%), the diazonium salt **9a** (5%), and traces of impurities. The product was suspended in CH$_2$Cl$_2$ (60 mL). Addition of CCl$_4$ (20 mL), filtration and slow addition of CCl$_4$ (60 mL) to the filtrate afforded a colorless crystalline powder (6.24 g, 72%), which was reprecipitated from CH$_2$Cl$_2$ (40 mL)/MeCN (4 mL)/Et$_2$O (100 mL) to give a colorless crystalline powder (5.56 g, 64%); mp 246–248 °C (dec).

3,3a,4,5,6,6a-Hexahydro-4,6-dioxo-5-phenyl-1,3-bis(2,4,6-trichlorophenyl)pyrrolo[3,4-d]-1,2,3-triazolium Hexachloroantimonate (**11u**):

From **8a** (4.38 g, 10 mmol) and *N*-phenylmaleimide (1.73 g, 10 mmol). Addition of CCl$_4$ (40 mL) to the mixture, filtration, and slow addition of further CCl$_4$ (80 mL) to the filtrate afforded a pale yellow powder (7.48 g, 82%), which was reprecipitated from CH$_2$Cl$_2$ (40 mL)/MeCN (8 mL)/Et$_2$O (120 mL) to give a pale yellow powder (6.60 g, 72%); mp 221–223 °C (dec).

(E)-4,5-Bis(butoxycarbonyl)-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11v**):

From **8a** (4.38 g, 10 mmol) and dibutyl fumarate^{41} (2.74 g, 12 mmol). The solvent of the mixture was evaporated. The ^{1}H NMR spectrum (CD$_3$CN) of the brown solid residue (9.05 g, 100%) showed the presence of **11v**, small amounts of the diazonium salt **9a**, and impurities, but no trace of **11w**. The product was suspended in CH$_2$Cl$_2$ (40 mL). Filtration after addition of CCl$_4$ (40 mL) and slow addition of further CCl$_4$ (240 mL) to the filtrate afforded a colorless crystalline powder (7.92 g, 82%); mp 127–129 °C (dec).

(Z)-4,5-Bis(butoxycarbonyl)-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11w**):

From **8a** (4.38 g, 10 mmol) and dibutyl maleate (2.74 g, 12 mmol). The solvent of the mixture was evaporated. The ^{1}H NMR spectrum (CD$_3$CN) of the pale brown semi-solid residue (8.79 g, 91%) showed the presence of **11v** and **11w** (ca 1 : 5), small amounts of the diazonium salt **9a**, and impurities. The product rearranged in CD$_3$CN at 23 °C into **11v** with a half-life of ca 50 min.

4,5-Dihydro-1,3-bis(2,4,6-trichlorophenyl)-4,4,5-trimethyl-1,2,3-triazolium Hexachloroantimonate (**11x**):

From **8a** (4.38 g, 10 mmol) and 2-methylbut-2-ene (0.84 g, 12 mmol). Slow addition of CCl$_4$ (120 mL) to the mixture afforded a pale yellow solid precipitate (5.81 g, 72%), which was reprecipitated from CH$_2$Cl$_2$ (60 mL)/MeCN (8 mL)/Et$_2$O (120 mL) to give a colorless crystalline powder (4.85 g, 60%); mp 249–251 °C (dec).

5-Chloro-4,5-dihydro-4,4-dimethyl-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11y**):

From **8a** (4.38 g, 10 mmol) and 1-chloro-2-methylpropene (1.09 g, 12 mmol). Addition of CCl$_4$ (80 mL) to the mixture, filtration with charcoal, and slow addition of CCl$_4$ (80 mL) to the filtrate afforded a colorless solid precipitate (6.46 g, 78%), which was reprecipitated from CH$_2$Cl$_2$ (20 mL)/Et$_2$O (40 mL) to give a colorless crystalline powder (6.21 g, 75%); mp 233–235 °C (dec).

3,3a,4,5,6,6a-Hexahydro-1,3-bis(2,4,6-trichlorophenyl)cyclopenta-[d]-1,2,3-triazolium Perchlorate (**11ac**):

a) A solution of **8a** (4.38 g, 10 mmol) and cyclopentene (0.82 g, 12 mmol) in CH$_2$Cl$_2$ (40 mL) was added dropwise to a cold (– 60 °C) suspension of AlCl$_3$ (1.34 g, 10 mmol) in CH$_2$Cl$_2$ (20 mL). After stirring as described in the general procedure the solvent was evaporated. The brown residue was dissolved in CH$_2$Cl$_2$ (60 mL) and pentane (200 mL) was added. Stirring at – 20 °C for 1 h afforded **11z** as a hygroscopic brown powder, which was dissolved in MeCN (40 mL). Addition of NaClO$_4$ · H$_2$O (1.69 g, 12 mmol) in MeCN (20 mL), stirring for 1 h, evaporation of the solvent furnished a solid, which was suspended in CHCl$_3$ (40 mL). Filtration with charcoal and evaporation of the solvent afforded a brownish foam, which solidified when stirred in Et$_2$O (80 mL) to give a pale yellow powder (**11ac**, 3.59 g, 63%); mp 221–223 °C (dec).

b) Hygroscopic **11aa** was prepared from **8a** (4.38 g, 10 mmol), cyclopentene (0.82 g, 12 mmol), and SnCl$_4$ (1.31 g, 5 mmol) as described for a). Transformation into **11ac** afforded a colorless powder (3.25 g, 51%); mp 209–216 °C (dec).

c) Hygroscopic **11ab** was prepared from **8a** (4.38 g, 10 mmol), cyclopentene (0.82 g, 12 mmol), and TiCl$_4$ (0.95 g, 5 mmol) as described for a). Transformation into **11ac** afforded a colorless powder (4.85 g, 85%); mp 213–215 °C (dec).

4-Butyl-4,5-dihydro-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (11ad):

From crude **8ad** (7.05 g, 10 mmol) and hex-1-ene (1.01 g, 12 mmol). The intermediate **6ad** was identified by its IR spectrum (CH$_3$CN, – 20 °C): 1960(sh), 1992, 2006(sh). The mixture was cooled to – 30 °C and CCl$_4$ (50 mL) was added. After filtration at – 30 °C CCl$_4$ (200 mL) was added to the filtrate. Stirring was continued for 10 min and further CCl$_4$ (50 mL) was added. Filtration afforded a grey powder (7.40 g, 68%), which was reprecipitated at – 20 °C from CH$_2$Cl$_2$ (25 mL)/Et$_2$O (150 mL) to furnish a colorless powder (5.77 g, 52%); mp 196–197 °C (dec).

3,3a,4,5,6,6a-Hexahydro-1,3-bis(4-chlorophenyl)cyclopenta[*d*]-1,2,3-triazolium Hexachloroantimonate (11ae):

Me$_3$COCl (1.30 g, 12 mmol) was added dropwise with exclusion of light to a cold (–60 °C) suspension of **7ae**^{38} (2.66 g, 10 mmol) and cyclopentene (0.82 g, 12 mmol) in CH$_2$Cl$_2$ (60 mL). The resulting clear red solution was stirred between –60 and –30 °C for 1 h, then at 0 °C for 30 min, and at 23 °C for 15 min. The solvent was evaporated and the yellow solid residue was precipitated from CHCl$_3$ (40 mL)/Et$_2$O (100 mL) to afford the chloride **11ae** as a yellow powder (3.29 g, 89%); mp 235–237 °C (dec). A solution of SbCl$_5$ (2.99 g, 10 mmol) in CH$_2$Cl$_2$ (20 mL) was added dropwise to a cold (–20 °C) suspension of the chloride **11ae** (3.69 g, 10 mmol) in CH$_2$Cl$_2$ (130 mL). The clear orange solution was stirred at –20 °C for 15 min, then at 0 °C for 10 min, and at 23 °C for 10 min. The solvent was evaporated and the residue was precipitated from CH$_2$Cl$_2$ (130 mL)/MeCN (20 mL)/Et$_2$O (130 mL) to furnish an orange crystalline powder (4.82 g, 64%) containing 1 mol of crystal CH$_2$Cl$_2$; mp 228–230 °C (dec).

3,3a,4,5,6,6a-Hexahydro-1,3-bis(4-chlorophenyl)cyclopenta-[d]-1,2,3-triazolium Hexachloroantimonate (**11af**):

The chloride **11af** was prepared from **7af**^{40} (2.81 g, 10 mmol) as described for **11ae**. Evaporation of the solvent afforded a dark brown residue, which was dissolved in CH$_2$Cl$_2$ (40 mL). At –20 °C a solution of SbCl$_5$ (2.99 g, 10 mmol) in CH$_2$Cl$_2$ (20 mL) was added. After warming to 23 °C the product was precipitated by very slow addition of CCl$_4$ (200 mL) to afford a pale brown powder, which

Table 2. Selected NMR and IR Data for the New Compounds Prepared

Product	Molecular Formula[a]	^{1}H NMR[b] δ, J (Hz)	^{13}C NMR[b] δ	IR[c] ν (cm^{-1})
6a	$C_{12}H_4Cl_{12}N_3Sb$ (737.4)	7.93 (aryl)[d]	123.3, 132.5, 138.4, 144.4 (aryl)[d]	2018 (vs), 1976 (sh), 1275, 1202, 1144[e]
7ag	$C_{12}H_9N_5O_4$ (287.3)	7.63, 8.23 (AA′MM′, aryl), 13.18 (NH)[f]		1594, 1609, 3282[g]
7aj	$C_{12}H_7Cl_3N_4O_2$ (345.6)	7.44 ($Cl_3C_6H_2$), 7.47 (m), 8.18 (m) ($O_2NC_6H_4$), 13.19 (NH)[h]		1511, 1525, 1601, 3300
8a	$C_{12}H_4Cl_7N_3$ (438.4)	7.37, 7.47 (aryl)[i]	128.8, 129.0, 129.1, 132.5, 137.1, 137.5, 138.2, 141.3 (aryl)[i]	1445, 1485, 1569
8ad	$C_{12}H_4Br_6ClN_3$ (705.1)	7.78, 7.89 (aryl)[j]	117.7, 120.6, 126.1, 126.6, 135.4, 136.0, 141.2, 144.4 (aryl)[j]	1481, 1561[j]
8ag	$C_{12}H_8ClN_5O_4$ (321.7)	7.64, 8.23 (AA′MM′, aryl)[f]	118.3 (br), 125.1, 144.6, 150.5 (br) (aryl)[f]	1588, 1606[g]
8aj	$C_{12}H_6Cl_4N_4O_2$ (380.0)	7.49, 7.56 ($Cl_3C_6H_2$), 7.74 (m), 7.87 (m), 8.29 (m), 8.32 (m) ($O_2NC_6H_4$)[k]	16 aryl signals[k]	1525, 1553, 1569, 1591, 1609
11a	$C_{14}H_8Cl_{12}N_3Sb$ (765.4)	5.05 (CH_2), 7.81 (aryl)	57.6 (CH_2), 130.4 (*i*-C), 130.9, 135.0 (*m*,*o*-C), 140.6 (*p*-C)	1559, 1571
11b	$C_{18}H_{16}Cl_{12}N_3Sb$ (821.5)	0.88 (m, CH_3), 1.33 (m, 4H), 2.03 (m, 2H) (CH_2), 4.75 (q, J = 10.4, 14.1), 5.16 (t, J = 14.0) (ring-CH_2), 5.48 (m, CH), 7.81, 7.83 (aryl)	14.0, 22.8, 27.8, 32.3, 61.4, 71.8 (CH_3, CH_2, CH)	1558, 1571
11c	$C_{16}H_{10}Cl_{12}N_3O_2Sb$ (823.5)	2.12 (CH_3), 5.14 (q, J = 3.7, 17.3), 5.38 (q, J = 9.4, 17.3), (H5, 5′), 7.49 (q, J = 3.7, 9.3, H4), 7.81, 7.85 (aryl)	20.4 (CH_3), 62.3, 86.5 (CH_2, CH), 169.4 (C=O)	1560, 1570, 1783
11d	$C_{15}H_9Cl_{13}N_3Sb$ (813.9)	4.09 (d, J = 4.4, CH_2), 5.07 (q, J = 10.3, 15.0), 5.26 (t, J = 15.0) (H5, 5′), 5.99 (m, CH), 7.82, 7.83 (aryl)	42.8, 59.9, 71.0 (CH_2, CH)	1559, 1570
11e	$C_{16}H_9Cl_{12}N_4Sb$ (804.5)	3.30 (d, J = 5.6, CH_2), 5.01 (q, J = 10.3, 15.2), 5.37 (t, J = 15.2) (H5, 5′), 5.87 (m, H4), 7.82, 7.86 (aryl)	22.0, 61.2, 66.6 (CH_2, CH), 115.4 (CN)	1559, 1569
11f	$C_{20}H_{12}Cl_{12}N_3Sb$ (841.5)	5.31 (q, J = 11.5, 15.4), 5.51 (t, J = 15.2) (CH_2), 6.71 (q, J = 11.5, 14.8, CH), 7.86 ($Cl_3C_6H_2$)	61.6, 73.9 (CH_2, CH)	1558, 1571
11h	$C_{17}H_{12}Cl_{12}N_3O_2Sb$ (837.5)	1.15 (t, J = 7.2, CH_3), 4.27 (m, OCH_2), 5.30 (t, J = 14.9), 5.48 (q, J = 9.5, 15.0) (H5, 5′), 6.08 (q, J = 14.8, 9.6, H4), 7.83, 7.84 (aryl)	13.9 (CH_3), 60.0, 66.0, 69.3 (CH_2, CH), 163.0 (C=O)	1561, 1571, 1759
11i	$C_{16}H_{12}Cl_{12}N_3Sb$ (793.5)	1.91 (CH_3), 4.97 (CH_2), 7.89, 7.92 (aryl)[m]	26.3 (CH_3), 67.3, 82.3 (CH_2, C)[m]	1559, 1570[g]
11j	$C_{18}H_{14}Cl_{12}N_3Sb$ (819.5)	1.82 (m, 4H), 2.36 (m, 4H), 4.86 (CH_2), 7.81, 7.84 (aryl)	22.1, 37.8, 66.9, 88.0 (CH_2, C)	1558, 1571
11k	$C_{16}H_{11}Cl_{13}N_3Sb$ (827.9)	2.04 (CH_3), 4.27, 5.04 (AB-q, J = 15.2) (CH_2), 7.82, 7.84 (AB-q, J = 2.4) (aryl)	22.8, 48.3, 65.5, 83.4 (CH_3, CH_2, C), 128.8, 130.2, 131.0, 131.5, 131.6, 134.8, 136.5, 136.6, 140.8, 141.0 (aryl)	1559, 1571
11l	$C_{16}H_{10}Cl_{14}N_3Sb$ (862.4)	4.52 (AB-q, J = 12.9, 4H), 5.21 (2H) (CH_2), 7.83, 7.84 (aryl)	44.8 (2C), 64.0, 84.1 (CH_2, C), 129.8, 129.9, 131.0, 131.5, 134.7, 136.3, 141.2, 141.3 (aryl)	1560, 1570
11m	$C_{26}H_{16}Cl_{12}N_3Sb$ (917.6)	5.83 (CH_2), 7.53, 7.84 ($Cl_3C_6H_2$)[l]	68.2, 90.2 (CH_2, C)[l]	1557, 1568
11n	$C_{18}H_{16}Cl_{12}N_3Sb$ (821.5)	1.02 (t, J = 7.4, CH_3), 2.07 (m, CH_2), 5.10 (m, CH), 7.83 (aryl)	9.2 (CH_3), 26.2 (CH_2), 76.4 (CH), 129.3, 131.2, 135.2, 140.6 (aryl)	1557, 1571
11o	$C_{18}H_{16}Cl_{12}N_3Sb$ (821.5)	0.94 (t, J = 7.4, CH_3), 2.08 (m, CH_2), 5.50 (m, CH), 7.82 (aryl)	11.2 (CH_3), 20.5 (CH_2), 75.1 (CH), 130.2, 131.3, 135.1, 140.6 (aryl)	1557, 1570
11p	$C_{19}H_{14}Cl_{12}N_3Sb$ (831.5)	3.01 (m, br, H6, 9), 5.37 (br, H1, 5), 7.80 (aryl)	24.6, 36.0, 43.8, 78.7 (CH_2, CH), 130.1 (*p*-C), 131.2 (*m*-C), 135.0 (*o*-C), 140.5 (*i*-C)	1558, 1571
11q	$C_{17}H_{12}Cl_{12}N_3Sb$ (805.5)	2.10 (m, 4H), 2.42 (m, 2H) (CH_2), 5.86 (m, CH), 7.82 (aryl)	25.2, 34.9, 77.3 (CH_2, CH), 129.8, 131.3, 135.3, 140.5 (aryl)	1557, 1572
11r	$C_{18}H_{14}Cl_{12}N_3Sb$ (819.5)	1.51 (m, 2H), 1.73 (m, 2H), 2.06 (m, 4H) (CH_2), 5.58 (m, CH), 7.82 (aryl)	20.0, 23.2, 69.7 (CH_2, CH), 129.2, 131.3, 135.0, 140.4 (aryl)	1557, 1571
11s	$C_{16}H_{10}Cl_{14}N_3Sb$ (862.4)	4.18 (m, CH_2), 5.97 (m, CH), 7.85 (aryl)	42.3 (CH_2), 73.3 (CH), 128.9, 131.5, 135.1 (br), 141.0 (aryl)	1557, 1569
11t	$C_{16}H_{10}Cl_{14}N_3Sb$ (862.4)	4.27 (m, CH_2), 6.07 (m, CH), 7.84 (aryl)	38.8 (CH_2), 72.7 (CH), 129.7, 131.3, 135.1 (br), 141.0 (aryl)	1560, 1569
11u	$C_{22}H_{11}Cl_{12}N_4O_2Sb$ (910.5)	6.49 (CH)	70.4 (CH), 127.3, 128.6, 131.0, 131.1, 131.4, 131.7, 135.1 (br), 141.9 (aryl), 165.4 (C=O)	1561, 1570, 1746

Table 2. (continued)

Product	Molecular Formula[a]	^{1}H NMR[b] δ, J (Hz)	^{13}C NMR[b] δ	IR[c] ν (cm^{-1})
11v	$C_{24}H_{24}Cl_{12}N_3O_4Sb$ (965.7)	0.85 (t, J = 7.4, CH_3), 1.14 (m), 1.50 (m), 4.25 (m) (CH_2), 6.52 (CH), 7.89 (aryl)	13.8 (CH_3), 19.6, 30.6, 70.2 (CH_2), 72.1 (CH), 129.5, 131.2, 135.0, 141.2 (aryl), 161.9 (C=O)	1560, 1569, 1757
11w	$C_{24}H_{24}Cl_{12}N_3O_4Sb$ (965.7)	0.86 (t, J = 7.3, CH_3), 1.16 (m), 1.52 (m), 4.18 (m) (CH_2), 6.62 (CH), 7.87 (aryl)[n]	13.9, 19.6, 30.6, 69.5, 71.2 (CH_3, CH_2, CH), 129.4, 131.2, 135.0 (br), 140.9 (aryl), 161.9 (CO)[n]	1560, 1569, 1767
11x	$C_{17}H_{14}Cl_{12}N_3Sb$ (807.5)	1.55 (d, J = 7.0), 1.73, 1.90 (CH_3), 5.27 (q, J = 7.0, CH), 7.83, 7.84 (aryl)	12.5, 20.2, 27.3 (CH_3), 75.2, 83.8 (C4, 5), 128.5, 129.1, 131.3, 131.6, 135.5 (br), 136.5, 140.6, 140.7 (aryl)	1557, 1571
11y	$C_{16}H_{11}Cl_{13}N_3Sb$ (827.9)	1.97, 2.04 (CH_3), 7.07 (CH), 7.86, 7.89 (q, J = 2.0) (aryl)	19.9, 27.1 (CH_3), 85.3, 85.9 (C4, 5), 127.8, 128.6, 131.5, 131.8, 131.9, 135.4, 135.8, 136.5, 140.9, 141.4 (aryl)	1557, 1569
11ac	$C_{17}H_{12}Cl_7N_3O_4$ (570.5)	1.89–2.47 (m, 6H, CH_2), 6.23 (m, CH), 7.65 (aryl)[i]	24.8, 33.8, 76.8 (CH_2, CH), 128.6, 130.1, 134.4, 140.1 (aryl)[i]	1558, 1572
11ad	$C_{18}H_{16}Br_6Cl_6N_3Sb$ (1088.2)	0.88 (t, J = 6.9, CH_3), 1.33 (m, 4H), 2.07 (m, 2H) (CH_2), 4.71 (q, J = 10.7, 14.1), 5.13 (t, J = 14.0) (NCH_2), 5.50 (m, CH), 8.11, 8.13 (aryl)	14.0, 22.8, 28.0, 32.8, 61.3, 71.8 (CH_3, CH_2, CH)	1547, 1559
11ae	$C_{17}H_{16}Cl_8N_3Sb \cdot CH_2Cl_2$ (752.6)	1.68 (m, 1H), 1.87 (m, 1H), 2.30 (m, 4H) (CH_2), 5.45 (CH_2Cl_2), 5.79 (m, CH), 7.71 (AA′BB′, aryl)	24.6, 35.0 (CH_2), 55.3 (CH_2Cl_2), 72.8 (C4, 5), 122.0, 131.4, 134.8, 136.5 (aryl)	1460, 1489, 1585
11af	$C_{23}H_{30}Cl_6N_3Sb$ (683.0)	1.73–2.31 (m, 6H, CH_2), 2.34 (12H), 2.35 (6H) (CH_3), 5.63 (m, CH), 7.16 (aryl)	18.6, 21.2 (CH_3), 25.6, 34.5 (CH_2), 75.8 (C4, 5), 131.4, 136.3, 143.3 (aryl)	1451, 1609
11ag	$C_{15}H_{13}Cl_7N_5O_4Sb$ (697.2)	4.12 (m), 5.25 (m) (CH_2), 6.19 (m, CH)	44.0, 57.7, 67.9 (CH_2, CH), 121.6, 122.7, 126.8, 127.1, 139.5, 140.6, 149.7, 149.8 (aryl)	1539, 1615
11ah	$C_{24}H_{28}Cl_6N_5O_8Sb$ (849.0)	0.82 (t, J = 7.3, CH_3), 1.19 (m), 1.51 (m), 4.22 (m) (CH_2), 6.62 (CH), 8.10, 8.49 (AA′MM′, aryl)	13.8, 19.6, 30.7, 69.4, 69.9 (CH_3, CH_2, CH), 122.8, 126.5, 141.4, 149.5 (aryl), 163.9 (C=O)	1539, 1760
11ai	$C_{24}H_{28}Cl_6N_5O_8Sb$ (849.0)	0.86 (t, J = 7.4, CH_3), 1.25 (m), 1.56 (m), 4.20 (m) (CH_2), 6.66 (CH), 8.04, 8.51 (AA′MM′, aryl)	13.8, 19.5, 30.8, 69.7, 70.3 (CH_3, CH_2, CH), 122.4, 127.0, 140.3, 149.9 (aryl), 163.1 (C=O)	1539, 1760
11aj	$C_{17}H_{14}Cl_9N_4O_2Sb \cdot \frac{1}{2}CH_2Cl_2$ (789.6)	1.79–2.47 (m, CH_2), 5.99 (m, CH), 7.83 (2,4,6-$Cl_3C_6H_2$), 7.96, 8.45 (AA′BB′, $O_2NC_6H_4$)	24.9, 34.7, 34.9, 74.1, 76.4 (CH_2, CH), 122.1, 126.8, 130.1, 131.4, 135.0, 140.1, 149.5, 169.9 (aryl)	1538
11ak	$C_{13}H_{18}ClN_3 \cdot H_2O$ (269.8)	1.47 (m, 2H), 1.94–2.52 (m, 4H) (CH_2), 2.39, 4.03 (CH_3), 6.13 (m, CH), 7.30, 7.45 (AA′BB′, aryl)[i]	21.1, 23.7, 33.3, 34.0, 38.9 (CH_3, CH_2), 71.0, 74.5 (CH), 118.7, 130.7, 132.5, 139.7 (aryl)[i]	1509
12	$C_{14}H_6Cl_{12}N_3Sb$ (763.4)	7.91 (aryl), 9.06 (H4, 5)	129.9, 130.9, 134.5, 136.5, 141.4 (aryl, CH)	1551, 1566

[a] Satisfactory microanalyses obtained: C ±0.38, H ±0.34, N ±0.33.

[b] In CD_3CN at 295–303 K with TMS as internal standard.

[c] In CH_2Cl_2.

[d] At 238 K.

[e] In MeCN at 223 K.

[f] In $CDCl_3$/D_6-DMSO (1 : 1).

[g] In KBr.

[h] In $CDCl_3$/D_6-DMSO (4 : 1).

[i] In $CDCl_3$.

[j] At 253 K in CD_2Cl_2; IR in CCl_4.

[k] At 253 K in CD_2Cl_2; 1 : 1 mixture of the 1- and the 3-chloro isomer.

[l] In CD_3CN/CD_2Cl_2 (1 : 1).

[m] At 323 K in CD_3CN/D_6-DMSO (4 : 1).

[n] At 263 K.

was reprecipitated from CH_2Cl_2 (40 mL)/Et_2O (200 mL) to give a pale yellow powder (4.78 g, 70 %); dec above 172 °C.

4-Chloromethyl-4,5-dihydro-1,3-bis(4-chlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11ag**):

From **8ag** (3.22 g, 10 mmol) and allyl chloride (0.92 g, 12 mmol). At the end of the reaction MeCN (20 mL) was added. The product was precipitated from the clear red solution by slow addition of Et_2O (160 mL). The brown semi-solid precipitate was suspended in CH_2Cl_2 (40 mL). After stirring for 10 min Et_2O (80 mL) was added to furnish an orange solid precipitate (5.04 g, 72 %); mp 221–225 °C (dec).

(E)-4,5-Bis(butoxycarbonyl)-4,5-dihydro-1,3-bis(4-chlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11ah**):

From **8ag** (3.22 g, 10 mmol) and dibutyl fumarate (2.74 g, 12 mmol). The solvent of the mixture was evaporated. The ^{1}H NMR spectrum (CD_3CN) of the pale brown semi-solid residue (8.49 g, 100 %) showed the presence of **11ah** and impurities but no trace of **11ai**. After 1 week at 23 °C in CD_3CN the spectrum showed an equilibrium mixture of **11ah** and **11ai** containing ca 3 % of **11ai**. Dissolution in CH_2Cl_2 (80 mL)/MeCN (8 mL) and slow addition of Et_2O (200 mL) at −20 °C afforded a yellow powder (5.52 g, 65 %), which was reprecipitated from CH_2Cl_2 (40 mL)/MeCN (4 mL)/Et_2O (100 mL) to give a yellow powder (5.01 g, 59 %); mp 122–125 °C (dec).

(Z)-4,5-Bis(butoxycarbonyl)-4,5-dihydro-1,3-bis(4-chlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**11ai**):

From **8ag** (3.22 g, 10 mmol) and dibutyl maleate (2.74 g, 12 mmol). The solvent of the clear orange solution was evaporated. The ^{1}H NMR spectrum (CD_3CN) of the pale brown semi-solid residue (8.49 g, 100 %) showed the presence of **11ai** and impurities but no trace of **11ah**. The product rearranged at 23 °C in CD_3CN with a half-life of ca 40 h into the *trans*-form **11ah**. Crude **11ai** was suspended in CH_2Cl_2 (60 mL). After addition of Et_2O (40 mL) and filtration the solution was cooled to −20 °C. Slow addition of Et_2O (160 mL) and stirring at 23 °C for 3 h afforded a yellow powder (5.94 g, 70 %); mp 126–128 °C (dec).

3,3a,4,5,6,6a-Hexahydro-3-(4-nitrophenyl)-1-(2,4,6-trichlorophenyl)-cyclopenta[d]-1,2,3-triazolium Hexachloroantimonate **(11aj)**:

From **8aj** (3.80 g, 10 mmol) in CH_2Cl_2 (80 mL) and cyclopentene (0.82 g, 12 mmol). Slow addition of CCl_4 (160 mL) to the mixture afforded a pale yellow powder (4.86 g, 65 %), which was reprecipitated from CH_2Cl_2 (40 mL)/MeCN (4 mL)/Et_2O (50 mL) to furnish a yellow powder (3.44 g, 44 %) of **11aj** · ½ CH_2Cl_2; mp 235–237 °C (dec).

3,3a,4,5,6,6a-Hexahydro-3-methyl-1-(4-methylphenyl)-cyclopenta-[d]-1,2,3-triazolium Chloride **(11ak)**:

Me_3COCl (1.30 g, 12 mmol) was added dropwise with exclusion of light to a cold (−50 °C) suspension of **7ak** (FLUKA) (1.49 g, 10 mmol) and cyclopentene (0.82 g, 12 mmol) in CH_2Cl_2 (40 mL). The yellow solution was stirred at −30 °C for 1 h, then at 0 °C for 30 min, and at 23 °C for 15 min. Evaporation of the solvent afforded a yellow sirup, which was dissolved in $CHCl_3$ (20 mL). Addition of Et_2O (120 mL) afforded a hygroscopic pale yellow precipitate (2.40 g, 89 % (hydrate)); mp 202–204 °C (dec).

1,3-Bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (12):

From **8a** (4.38 g, 10 mmol) and excess of vinyl chloride. Filtration of the mixture and slow addition of CCl_4 (200 mL) to the filtrate gave a pale yellow powder (7.48 g, 98 %), which was crystallized from CH_2Cl_2 (90 mL)/MeCN (25 mL)/Et_2O (220 mL) to afford a colorless crystalline powder; mp 238–241 °C (dec).

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