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THE RITTER REACTION OF α-CHLOROCARBENIUM IONS; A SYNTHESIS OF CHLORO SUBSTITUTED 2-AZONIAALLENE SALTS

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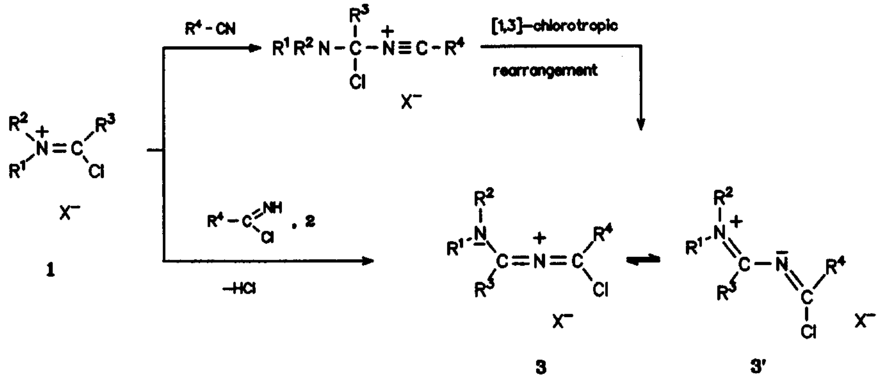
Abstract - α-Chlorocarbenium ions, **9**, stabilized by allylic resonance, react with nitriles, **10**, to give chloro substituted 2-azoniaallene salts, **12**. The cation **12k** abstracts chloride from the counterion $SbCl_6^-$ to furnish the chloroimine **13k** together with $SbCl_5$. The hexachloroantimonates **12** can be transformed into unpolar chlorides, **13b,l**, and **17**, with ammonium chlorides. Compounds **13** and **17** are hydrolyzed to give N-acyl imidoyl chlorides, **14a,b**, respectively the allophanate **18**. Electron-rich nitriles insert into the C-Cl bond of the 2-azoniaallene salts **12** to afford imidoyl chlorides, **15l-p,16**.

The reaction of α-chlorocarbenium ions, **1**, stabilized by an α-amino group, with nucleophiles may be referred to as generalized Vilsmeier-Arnold reaction.[1] The reaction of carbenium ions with nitriles is known as Ritter reaction.[2-4] Recently, the Vilsmeier-Arnold-Ritter reaction of reagents **1** with nitriles or their HCl adducts, **2**, to give amino substituted 2-azoniaallene salts,[5] **3** (with the most important canonical form **3'**), has found much recognition.[6]

Extension of this sequence to α-chlorocarbenium ions other than Vilsmeier-Arnold reagents, **1**, has little been studied. However, a reaction of α-chlorocarbenium ions, stabilized by an α-oxygen atom, with nitriles has found application in glycoside synthesis.[7,8] Furthermore, the reaction of certain α-acetoxycarbenium ions with benzonitrile to furnish heterocycles has been studied.[9]

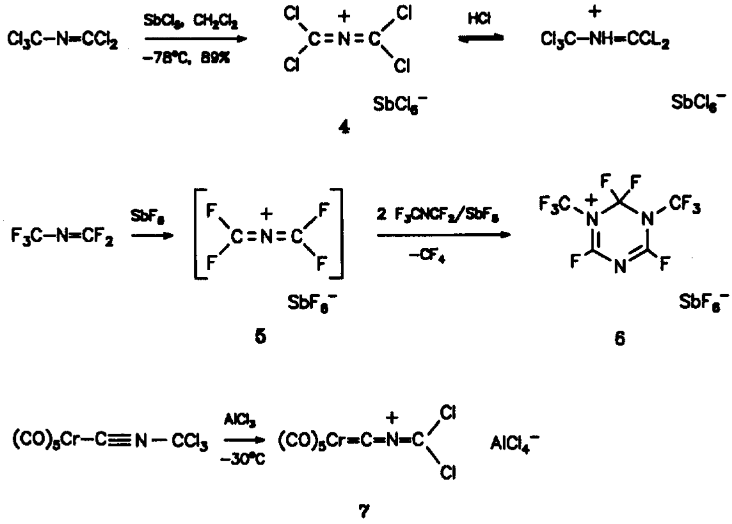
Herein we report the reaction of 1-chloro substituted carbocations, stabilized by allylic resonance, with nitriles to give chloro substituted 2-azoniaallene salts **12**.[5]

Only a few chloro substituted 2-azoniaallene salts, **12**, without a stabilizing amino substituent, have been reported in the literature. The hexachloroantimonate **4** has been obtained by Schmidt by chloride abstraction



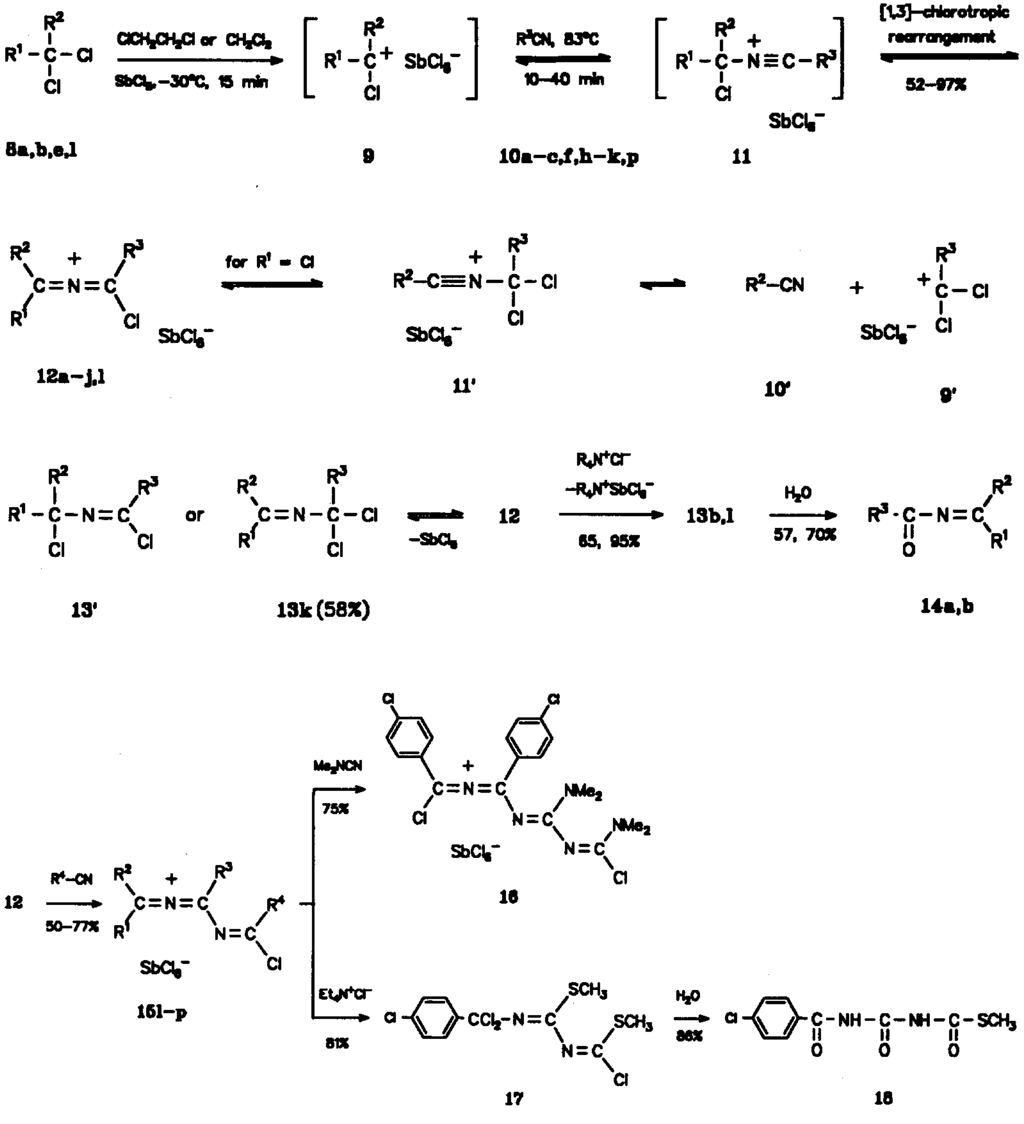
Scheme 1.

from 2-aza-pentachloropropene with $SbCl_5$.[10] Correspondingly, the tetrafluoro-2-azoniaallene salt **5**,[11-13] and the complex **7**[14] have been prepared. Compound **5** is unstable. Depending on the experimental conditions it reacts with starting material to give *inter alia* the triazinium salt **6**.[11-13] Complex **7** decomposes slowly at -30°C.[14]



Scheme 2.

If 4-chlorobenzotrichloride, **8b**, is treated with $SbCl_5$ at -30°C in



8–15	R¹	R²	R³	8–15	R¹	R²	R³	8–15	R¹	R²	R³	R⁴
a	Cl	Ph	Ph	g	Cl	$Cl_2C{=}CCl$	$4\text{-}ClC_6H_4$	l	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	MeS	MeS
b	Cl	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	h	Cl	$Cl_2C{=}CCl$	Me_2N	m	Cl	Ph	MeS	MeS
c	Cl	Ph	$2\text{-}ClC_6H_4$	i	Cl	$Cl_2C{=}CCl$	$i\text{-}Pr_2N$	n	Cl	$4\text{-}ClC_6H_4$	MeS	MeS
d	Cl	$4\text{-}ClC_6H_4$	$2\text{-}ClC_6H_4$	j	Cl	$Cl_2C{=}CCl$	MeS	o	Cl	$4\text{-}ClC_6H_4$	Me_2N	Me_2N
e	Cl	$Cl_2C{=}CCl$	Ph	k	Cl	$4\text{-}ClC_6H_4$	Cl_3C	p	Cl	$Cl_2C{=}CCl$	Cl	Cl
f	Cl	$Cl_2C{=}CCl$	$4\text{-}MeC_6H_4$									

Scheme 3.

1,2-dichloroethane the orange carbenium salt **9b** precipitates.[15-17] After addition of 4-chlorobenzonitrile, **10b**, and warming up to room temperature the precipitate dissolves. However, the formation of the salt **12b** requires higher temperatures (83°C for 10 minutes). Evaporation of the solvent affords a very moisture sensitive brown powder, which can be crystallized from acetonitrile to furnish brownish prisms of **12b**.

In the ^{13}C-NMR spectrum (CD_2Cl_2, 263 K) four signals for equivalent p-disubstituted aryl groups and one signal for C=N (167.9 ppm, broad) are observed. The IR spectrum (CH_2Cl_2) shows a very broad and strong absorption for the antisymmetrical C=N=C stretching vibration at 1682 cm^{-1} with shoulders at 1663, 1740, 1790 and 1852 cm^{-1}.[18-21] The intensities of the shoulders change somewhat with the concentration of the solution.

The other salts **12** are prepared and characterized correspondingly. All compounds **12** are very moisture sensitive. They are moderately stable in the solid state if kept cool (5°C) and dry. However, solutions of the well crystallizing vinyl derivatives **12e-j** in acetonitrile turn black within a few minutes. Because of their low solubility in other solvents like dichloromethane we were not able to obtain ^{13}C-NMR spectra for some of the salts **12**.

A mechanism rationalizing our results is presented in Scheme 3. Several side reactions determine scope and limitation of the reaction.

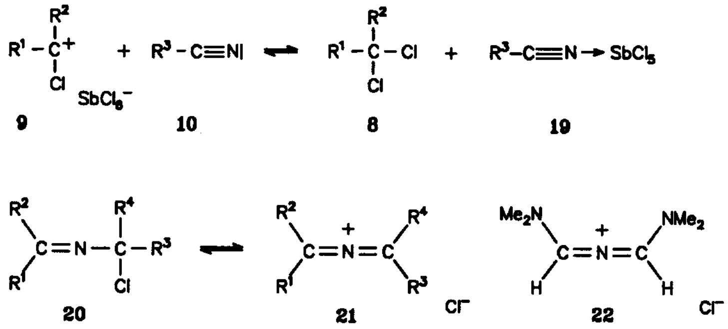
1) The reaction of a carbenium salt **9** with a nitrile requires temperatures above 50°C, conditions which carbenium salts may not survive. For instance, the reaction of CCl_4 with benzonitrile in the presence of $SbCl_5$ gave mixtures of compounds. Recently, Olah et al reported that the ion CCl_3^+ decomposes above of -50°C.[22] In our hand, only carbenium ions, which are stabilized by allylic resonance, give salts **12**.

2) Nitriles form stable complexes of variable stoichiometry with Lewis acids.[23-26] Unfavourable equilibria between **9** and the nitrile-$SbCl_5$ complexes **19** are responsible for the high reaction temperatures required for the formation of **12** (Scheme 4). For instance, for the formation of salts **12** from electron-rich cyanamides long reaction times are needed (e.g. 40 minutes at 83°C for **12h,i**, and 40 hours for **15o**). No reactions could be achieved between hexachloroethane and nitriles in the presence of $SbCl_5$. Till now, no salts **12** were obtained with Lewis acids other than $SbCl_5$. In contrast, alkenes are alkylated by polychloroalkanes in the presence of diverse Lewis acids under mild conditions.[27]

3) The salts **12** decompose at higher temperatures. For instance, a whole cascade of compounds is formed from **12j** at temperatures above 50°C.[28] Attempts to prepare salts **12** with R^1=Cl, R^2=R^3=4-$CH_3C_6H_4$ or with R^2=Ph, R^3= 4-CH C H met with failure. The reaction mixtures show strong C=N=C

bands around 1700 cm^{-1}, but turn black during evaporation of the solvent. Electron-withdrawing substituents R^2,R^3 seem to stabilize salts **12**.

4) Symmetrically substituted salts **12** are more stable than those with $R^1 \neq Cl$ or with $R^2 \neq R^3$. Obviously, the formation of the salts **12** is reversible. For R^1=Cl this may cause an exchange of the substituents R^2 and R^3 via **11'**. Combinations of either nitrile **10** or **10'** with each of the carbenium ions **9** and **9'** lead to mixtures of allenes **12**.[28]



Scheme 4.

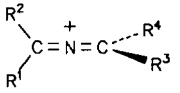
5) Compounds **12** are themselves α-chlorocarbenium salts, which may react with nitriles. Thus, the salt **12l** reacts with methyl thiocyanate to give the imine **15l**. Attempts to add methyl thiocyanate to **15l** failed. The addition of a nitrile to an α-chlorocarbenium ion results in the formation of a new α-chlorocarbenium ion, in which the positive charge is more effectively delocalized than in the starting ion. Therefore, a polymerization of electron-rich nitriles with α-chlorocarbenium ions as starter is not feasible. From the reactions of **8a,b,e** with methyl thiocyanate, N,N-dimethylcyanamide or cyanogen chloride the 1:2 adducts **15m-p** are obtained in good yields. Notably, the 2-azoniaallene **12b** reacts with two molecules of N,N-dimethylcyanamide to furnish the pale yellow polymethine salt **16**. Attempts to add a further molecule of N,N-dimethylcyanamide to **16** failed. With cyanogen chloride, **10p**, hexachloropropene, **8e**, reacts in the presence of $SbCl_5$ to give a rather unstable orange salt, for which a ^{13}C-NMR spectrum could not be obtained. The structural proposal **15p** is based on the elemental analysis and a broad and strong C=N=C IR absorption at 1659 cm^{-1} with shoulders at 1645, 1690, 1713 and 1900 cm^{-1} (in CH_2Cl_2).

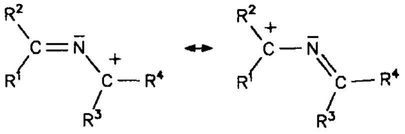
6) Findeisen and Wagner reported Lewis acid catalyzed additions of geminal dichloro and trichloro compounds to "activated nitriles".[29,30] If **8a** is

treated with $SbCl_5$ and trichloroacetonitrile, **10k**, a salt **12k** is not formed. Instead, the chloride **13k** is obtained, which formerly has been prepared from other precursors.[31,32] The constitution of **13k** was proven by Drach et al by means of nuclear quadrupole resonance.[33] The cation **12k** is a stronger Lewis acid than $SbCl_5$ abstracting Cl^- from the hexachloroantimonate ion. The equilibrium **12k** $\rightleftharpoons$ **13k** is shifted completely to the site of **13k**. Findeisen's "activated nitriles" are extremely electron deficient nitriles, for which the equilibria **12** $\rightleftharpoons$ **13** lie far on the side of **13**. Compound **13k** is readily soluble in CCl_4. In the ^{13}C-NMR spectrum signals for CCl_2 and CCl_3 are observed at 103.9 and 107.1 ppm (in CD_3CN). In conclusion, for compound **13k** the equilibrium between the covalent form **20** and the ionic structure **21** lies far on the left side (Scheme 4).

The chlorides **13a,b,l** and **17** are prepared from **12a,b,l**, respectively **15n** by anion exchange with tetraalkylammonium chlorides. The resulting chlorides are extremely moisture sensitive. Even under "rigorously dry" conditions **13a** was always contaminated with large portions of the hydrolysis product **14a**. Compounds **13b,l** show ^{13}C-NMR signals for CCl_2 at 97.1 ppm (in C_6D_6) and 86.7 (in $CDCl_3$), respectively. With traces of water **13b** is hydrolyzed to give **14b**. For the chloride **17** very broad ^{13}C-NMR resonances are observed at 99.9 and 146.8 ppm ($CDCl_3$, 273 K). The signal at 99.9 ppm can be assigned to CCl_2. The line widths of about 180 Hz for both signals seem to indicate a fast equilibration between an ionic and an unpolar form. On addition of $SbCl_5$ to **17** the hexachloroantimonate **15n** is formed back. With water the allophanate **18** is obtained. In conclusion, in **13a,b,l,k**, and **17** the chlorine atoms are essentially covalently bonded. However, the pronounced sensitivity against moisture indicates tendencies for heterolytic cleavage of the C-Cl bonds.

It should be recalled that Gold's chloride **22** is a typical salt.[34-36] 2-Azoniaallene salts are known to assume in the crystal either a geometry with (local) allene (D_{2d}, **A**) or azaallylium (C_{2v}, **B**) symmetry or, in most cases, a geometry intermediate between these extremes.[5,37,38]





A: D_{2d} symmetry for $R^1=R^2=R^3=R^4=H$
$\alpha = 180^\circ$, $\beta = 90^\circ$

B: C_{2v} symmetry for $R^1=R^2=R^3=R^4=H$
$\alpha \approx 120^\circ$, $\beta = 0^\circ$

α: bond angle C=N=C
β: angle between the planes through $N-C-R^1-R^2$ and $N-C-R^3-R^4$

The 2-azaallylium structure **B** is stabilized by conjugative interaction of the formal cumulenic unit with electron-releasing substituents. Electron-withdrawing substituents, on the other hand, stabilize the allenic structure **A**.[37,38] Increasing D_{2d} character of the chlorides shifts the equilibrium **20** **21** towards the left side. 2-Azaallylium chlorides are salts, 2-azoniaallene chlorides are not.

EXPERIMENTAL SECTION

All solvents are dried by standard methods and $SbCl_5$ is distilled before use. All experiments are carried out with exclusion of moisture. The melting points are uncorrected. IR: Mattson Polaris FT-IR spectrometer; solutions in CH_2Cl_2 if not stated otherwise; absorptions in cm^{-1}; sh = shoulder. ^1H- and ^{13}C-NMR: Bruker WM-250 and Bruker AC-250 spectrometers; solutions in CD_3CN at 295 K if not stated otherwise; tetramethylsilane as internal standard; δ-scale; chemical shifts in ppm, coupling constants in Hz; br = broad.

1,3-Dichloro-1,3-diphenyl-2-azoniaallene Hexachloroantimonate (**12a**): A solution of $SbCl_5$ (2.99 g, 10 mmol) in $ClCH_2CH_2Cl$ (10 ml) is added dropwise with stirring to a cold (-30°C) solution of **8a** (1.96 g, 10 mmol) in $ClCH_2CH_2Cl$ (40 ml). An orange precipitate is formed. Stirring is continued for 15 min at -30°C. A solution of **10a** (1.03 g, 10 mmol) in $ClCH_2CH_2Cl$ (10 ml) is added. After warming to 25°C in the course of 30 min the mixture is boiled under reflux for 10 min. After cooling the mixture is ready for reactions with nucleophiles. If isolation of the salt is desired the solvent is evaporated under reduced pressure and the residue (5.97g, 100%) is crystallized at -20°C from CH_3CN (7.5 ml)/CCl_4 (7.5 ml) to afford very moisture sensitive brownish prisms (3.12 g, 52%); mp 140-145°C (dec)(ref[5]: 135-145°C (dec)). IR: 1575, 1660(sh), 1682, 1736(sh), 1809(sh), 1864(sh). ^1H-NMR(CD_2Cl_2): 7.86(m,m-H), 8.15(m,p-H), 8.36(m,o-H). ^{13}C-NMR(CD_2Cl_2, 263 K): 128.4, 143.2(i,p-C), 131.5, 134.8(o,m-C), 167.4(C=N,br).

1,3-Dichloro-1,3-bis(4-chlorophenyl)-2-azoniaallene Hexachloroantimonate (**12b**): From **8b** (2.29 g, 10 mmol) and **10b** (1.38 g, 10 mmol) as described for **12a**. The crude product (6.66 g, 100%), which is pure enough for most applications, can be crystallized at -20°C from CH_3CN (10 ml)/CCl_4 (10 ml) yielding a very moisture sensitive pale brown powder (3.71 g, 56%); mp 144-147°C (dec). IR: 1582, 1663(sh), 1680, 1740(sh), 1790(sh), 1852(sh).

^1H-NMR(CD_2Cl_2): 7.83(m), 8.33(m)(aryl). ^{13}C-NMR(CD_2Cl_2, 263 K): 127.6, 151.5(i,p-C), 132.0, 136.2(m,o-C), 168.2(C=N,br). (Found: C, 25.60; H, 1.39; N, 2.27. Calc for $[C_{14}H_8Cl_4N]SbCl_6$ (MW = 666.5): C, 25.23; H, 1.21; N, 2.10%).

1,3-Dichloro-1-(2-chlorophenyl)-3-phenyl-2-azoniaallene Hexachloroantimonate **(12c)**: From **8a** (1.96 g, 10 mmol) and **10c** (1.38 g, 10 mmol) as described for **12a**. However, after addition of the nitrile the reaction mixture is boiled under reflux for 15 min. Yield: 6.15 g (97%) of a very moisture sensitive dark powder, which can be crystallized at -20°C from CH_3CN (10 ml); mp 130-133°C (dec). IR: 1582, 1733, 1760(sh), 1800(sh), 1860(sh). ^{13}C-NMR(CD_2Cl_2, 263 K): 125.4, 127.6, 129.9, 131.6, 133.7, 135.1, 138.6, 139.2, 142.0, 143.2 (aryl), 157.7, 163.8(C=N). (Found: C, 26.69; H, 1.71; N, 2.17. Calc for $[C_{14}H_9Cl_3N]SbCl_6$ (MW = 632.0): C, 26.60; H, 1.44; N, 2.22%).

1,3-Dichloro-1-(2-chlorophenyl)-3-(4-chlorophenyl)-2-azoniaallene Hexachloroantimonate **(12d)**: From **8b** (2.30 g, 10 mmol) and **10c** (1.38 g, 10 mmol) as described for **12a**. Yield: 6.28 g (94%) of a dark powder, which is crystallized at -20°C from CH_3CN (20 ml) to give very moisture sensitive yellow prisms (3.98 g, 60%); mp 149-151°C (dec). IR: 1574, 1705(sh), 1732, 1794(sh), 1856(sh). ^{13}C-NMR(CD_2Cl_2, 263 K): 125.6, 126.3, 130.0, 132.2, 133.8, 136.2, 138.9, 139.5, 142.3, 151.1(aryl), 159.1, 162.8(C=N). (Found: C, 25.41; H, 1.85; N, 2.11. Calc for $[C_{14}H_8Cl_4N]SbCl_6$ (MW = 666.5): C, 25.23; H, 1.21; N, 2.10%).

1,3,4,5,5-Pentachloro-1-phenyl-2-azonia-1,2,4-pentatriene Hexachloroantimonate **(12e)**: From **8e** (2.49 g, 10 mmol) and **10a** (1.03 g, 10 mmol) as described for **12a**. After cooling to 23°C the reaction mixture is concentrated under reduced pressure to a volume of about 10 ml. Very moisture sensitive orange prisms (4.00 g, 62%) are filtered off. The compound is sparingly soluble in CH_2Cl_2 and $ClCH_2CH_2Cl$ and decomposes within a few min in CH_3CN; mp 154-156°C (dec). IR: 1555, 1586, 1660(sh), 1694, 1728(sh), 1770(sh), 1825(sh), 1879(sh). ^1H-NMR(CD_3CN): 7.85(m, m-H), 8.20(m, p-H), 8.36(m, o-H). (Found: C, 18.59; H, 1.07; N, 2.22. Calc for $[C_{10}H_5Cl_5N]SbCl_6$ (MW = 650.9): C, 18.45; H, 0.77; N 2.15%).

1,3,4,5,5-Pentachloro-1-(4-methylphenyl)-2-azonia-1,2,4-pentatriene Hexachloroantimonate **(12f)**: From **10f** (1.17 g, 10 mmol) as described for **12e**. Yield: 4.92 g (74%) of very moisture sensitive red crystals, which decompose within a few min in CH_3CN; mp 160-164°C (dec). IR: 1551(sh), 1590, 1686, 1721(sh), 1767(sh). ^1H-NMR(CD_2Cl_2): 2.72(CH_3), 7.76(m), 8.32(m) (aryl). ^{13}C-NMR(CD_2Cl_2): 24.4(CH_3), 133.6, 137.7(o,m-C), 125.2, 126.2, 146.9, 153.5, 164.0, 174.1(i,p-C,C=N,C=C). (Found: C, 19.79; H, 1.21; N, 2.19. Calc for[C H Cl N]SbCl (MW = 664.9): C, 19.87; H, 1.06; N, 2.11%).

1,3,4,5,5-Pentachloro-1-(4-chlorophenyl)-2-azonia-1,2,4-pentatriene Hexachloroantimonate **(12g)**: From **10b** (1.38 g, 10 mmol) as described for **12e**. Yield: 4.45 g (65%) of a moisture sensitive orange-yellow powder, which is sparingly soluble in CH_2Cl_2 or $ClCH_2CH_2Cl$ and decomposes within a min in CH_3CN; mp 171-175°C (dec). IR: 1551(sh), 1574, 1655, 1694(sh), 1732 (sh), 1771(sh). ^{1}H-NMR(CD_2Cl_2): 7.89(m), 8.33(m)(aryl). ^{13}C-NMR (CD_2Cl_2): 133.0, 137.6 (o,m-C). (Found: C, 17.57; H, 0.75; N, 2.00. Calc for $[C_{10}H_4Cl_6N]SbCl_6$ (MW = 685.3): C, 17.52; H, 0.59; N, 2.04%).

1,3,4,5,5-Pentachloro-1-(dimethylamino)-2-azonia-1,2,4-pentatriene Hexachloroantimonate **(12h)**: From **10h** (7.01 g, 10 mmol) as described for **12e**. However, the reaction mixture is boiled under reflux for 40 min. Evaporation of the solvent affords an oil, which is dissolved in CH_2Cl_2 (10 ml). On slow addition of ether (30 ml) a colourless powder precipitates (4.63 g, 75%); mp 142-145°C. IR: 1501, 1652. ^{1}H-NMR: 3.57, 3.75(CH_3). ^{13}C-NMR(273 K): 46.2, 46.6(CH_3), 125.3, 136.8, 155.7, 159.9 (C=N,C=C). (Found: C, 11.68; H, 0.97; N, 4.54. Calc for $[C_6H_6Cl_5N_2]SbCl_6$ (MW = 617.9): C, 11.66; H, 0.98; N, 4.53%).

1,3,4,5,5-Pentachloro-1-(diisopropylamino)-2-azonia-1,2,4-pentatriene Hexachloroantimonate **(12i)**: From **10i** (1.26 g, 10 mmol) as described for **12h**. Yield: 4.89 g (73%) of a yellow powder; mp 165-168°C. IR: 1505, 1644(br). ^{1}H-NMR: 1.45(d,J=6.8), 1.60(d,J=6.9,br)(CH_3), 4.59(sept,J=6.8), 4.82(br)(CH). ^{13}C-NMR(273K): 19.7(CH_3), 60.7(CH,br), 125.1, 137.1, 154.6(br), 159.1(br)(C=N,C=C). (Found: C, 17.86; H, 2.12; N, 3.96. Calc for $[C_{10}H_{14}Cl_5N_2]SbCl_6$ (MW = 674.0): C, 17.82; H, 2.09; N, 4.16%).

1,3,4,5,5-Pentachloro-1-(methylthio)-2-azonia-1,2,4-pentatriene Hexachloroantimonate **(12j)**: A solution of $SbCl_5$ in CH_2Cl_2 (10 ml) is added to a cold (-30°C) mixture of **8e** (2.49 g, 10 mmol) and **10j** (0.73 g, 10 mmol) in CH_2Cl_2 (30 ml). The temperature is raised to 23°C in the course of 10 min. The mixture is boiled under reflux for 20 min. After keeping at -20°C for 24 h red-orange crystals are filtered off (4.52 g, 73%), which are sparingly soluble in CH_2Cl_2 and $ClCH_2CH_2Cl$ and decompose in CH_3CN; dec above 110°C. IR: 1478, 1648(br), 1733(sh). ^{1}H-NMR: 3.11(br) (CH_3). (Found: C, 9.63; H, 0.60; N, 2.17. Calc for $[C_5H_3Cl_5NS]SbCl_6$ (MW = 620.9): C, 9.67; H, 0.49; N, 2.26%).

3-Chloro-1,1-bis(4-chlorophenyl)-3-methylthio-2-azoniaallene Hexachloroantimonate **(12l)**: From **8l** (3.06 g, 10 mmol) and **10j** (0.73 g, 10 mmol) as described for **12a**. The crude product is crystallized at -20°C from CH_3CN (8 ml) to furnish pale brown prisms (5.22 g, 77%); mp 158-161°C (dec). IR: 1578, 1628(sh), 1667(sh), 1767, 1856. ^{1}H-NMR(263 K): 2.73(CH_3). ^{13}C-NMR(263 K): 20.7(CH_3), 131.5, 136.6(o,m-C), 129.0, 145.9(i,p-C), 165.5, 172.9(C=N). (Found: C, 26.41; H, 1.72; N, 2.15. Calc for

$[C_{15}H_{11}Cl_3NS]SbCl_6$ (MW = 678.1): C, 26.56; H, 1.64; N, 2.07%).

[Dichloro(4-chlorophenyl)methyl][chloro(4-chlorophenyl)methylene]amine **(13b)**: To a solution of **12b** (6.67 g, 10 mmol, prepared without isolation in $ClCH_2CH_2Cl$ (60 ml)) benzyltriethylammonium chloride (2.27 g, 10 mmol) in CH_2Cl_2 (10 ml) is added. The red colour of the mixture fades and a precipitate is formed. The solvent is evaporated and the residue is extracted with CCl_4 (4x20 ml). Filtration and evaporation of the solvent yields a solid, which crystallizes at -20°C from CH_3CN (10 ml) to give a very moisture sensitive colourless powder (2.39 g, 65%); mp 133-135°C (dec). IR: 1590, 1632. ^{13}C-NMR(C_6D_6): 97.1(CCl_2), 152.3(C=N). (Found: C, 45.99; H, 2.36; N, 3.87. Calc for $C_{14}H_8Cl_5N$ (MW = 367.5): C, 45.75; H, 2.19; N, 3.81%).

[Chloro(4-chlorophenyl)methylene](pentachloroethyl)amine **(13k)**: From **8b** (2.29 g, 10 mmol) and **10k** (1.44 g, 10 mmol) as described for **12a**. However, the reaction mixture is boiled under reflux for 30 min. The crude product crystallizes at -20°C from CH_3CN (5 ml) furnishing pale brown crystals (3.91 g, 58%); mp 79-82°C (dec)(ref[32]: 83-84°C). IR: 1590, 1644. ^1H-NMR($CDCl_3$): 7.45(m), 8.08(m)(aryl). ^{13}C-NMR($CDCl_3$): 103.0 (CCl_3), 106.4(CCl_2), 129.1, 131.0(o,m-C), 133.7, 140.7(i,p-C), 156.1(C=N). (Found: C, 29.17; H, 1.21; N, 3.78. Calc for $C_9H_4Cl_7N$ (MW = 374.3): C, 28.88; H, 1.08; N, 3.74%).

[Dichloro(methylthio)methyl][bis(4-chlorophenyl)methylene]amine **(13l)**: A solution of tetraethylammonium chloride (0.83 g, 5 mmol) in CH_2Cl_2 (10 ml) is added to a solution of **12l** (3.39 g, 5 mmol) in CH_2Cl_2 (50 ml). A precipitate is formed. The solvent is evaporated under reduced pressure and the residue is repeatedly extracted with CCl_4 (4x20ml). The solvent of the combined extracts is evaporated to furnish a colourless residue, which is crystalized at -20°C from CH_3CN (8 ml) to afford moisture sensitive pale yellow crystals (1.80 g, 95%); mp 96-98°C. IR: 1544, 1625. ^1H-NMR($CDCl_3$): 2.62(CH_3). ^{13}C-NMR($CDCl_3$, 263 K): 17.8(CH_3), 86.7(CCl_2), 128.2, 128.4(o,m-C), 133.9, 142.9(i,p-C), 150.8(C=N). (Found: C, 47.39; H, 2.96; N, 3.63. Calc for $C_{15}H_{11}Cl_4NS$ (MW = 379.1): C, 47.52; H, 2.92; N, 3.70%).

N-(chlorophenylmethylene)benzamide **(14a)**: From **12a** (2.99 g, 5 mmol) in CH_2Cl_2 (20 ml) as described for **13l**. Work-up yields an oily mixture of compounds according to the ^1H-NMR spectrum. Crystallization at -20°C from obviously moist CH_3CN (5 ml) affords colourless prisms (0.69 g, 57%); mp 81-83°C (dec). IR(CCl_4): 1655, 1706. ^{13}C-NMR: 128.7, 128.8, 129.6, 129.7, 131.5, 133.4, 133.5, 133.9(phenyl), 144.9, 176.0(C=N, C=O). (Found: C, 68.73; H, 4.24; N, 5.78. Calc for $C_{14}H_{10}ClNO$ (MW = 243.7): C, 69.00; H, 4.14; N, 5.75%).

N-[Chloro(4-chlorophenyl)methylene]-4-chlorobenzamide **(14b)**: A solution of **13b** (2.21 g, 6 mmol) + H_2O (0.11 g, 6 mmol) in $ClCH_2CH_2Cl$ (15 ml) is stirred for 15 min. The solvent is evaporated under reduced pressure and the residue is crystallized at -20°C from CH_3CN (10 ml) to furnish colourless crystals (1.32 g, 70%); mp 109-112°C (dec). IR(CCl_4): 1490, 1547, 1590, 1655, 1706. ^{13}C-NMR(C_6D_6): 144.2(C=N), 174.2(C=O). (Found: C, 54.20; H, 2.80; N, 4.51. Calc for $C_{14}H_8Cl_3NO$ (MW = 312.6): C, 53.79; H, 2.58; N, 4.48%).

3-[Chloro(methylthio)methyleneamino]-1,1-bis(4-chlorophenyl)-3-(methylthio)-2-azoniaallene Hexachloroantimonate **(15l)**: From **8l** (3.06 g, 10 mmol) and **10j** (1.46 g, 20 mmol) as described for **12a**. However, after addition of **10j** the reaction mixture is stirred at 25°C for 30 min. The solvent is evaporated and the oily residue is dissolved in CH_2Cl_2 (10 ml). Slow addition of ether (50 ml) affords a yellow precipitate, which crystallizes at -20°C from CH_3CN (10 ml) forming yellow prisms (5.26 g, 70%); mp 137-140°C (dec). IR: 1582. ^1H-NMR: 2.45, 2.68(CH_3). ^{13}C-NMR: 17.7, 19.4(CH_3), 130.9, 131.3, 134.5, 142.7(aryl), 163.9, 170.3, 183.5 (C=N). (Found: C, 27.24; H, 1.94; N, 3.71. Calc for $[C_{17}H_{14}Cl_3N_2S_2]SbCl_6$ (MW = 751.3): C, 27.18; H, 1.88; N, 3.73%).

1-Chloro-3-[chloro(methylthio)methyleneamino]-3-methylthio-1-phenyl-2-azoniaallene Hexachloroantimonate **(15m)**: From **8a** (0.98 g, 5 mmol) and **10j** (0.73 g, 10 mmol) in $ClCH_2CH_2Cl$ (30 ml) as described for **12a**. However, after warming to 23°C the reaction mixture is boiled under reflux for 15 min. Evaporation of the solvent and crystallization of the residue at -20°C from CH_2Cl_2 (10 ml) affords yellow prisms (2.26 g, 71%); mp 131-133°C. IR(KBr): 1551, 1636. ^1H-NMR: 2.79, 2.89(CH_3), 7.67(m,m-H), 7.86(m,p-H), 8.21(m,o-H). ^{13}C-NMR: 18.8, 20.5(CH_3), 130.6, 132.1, 132.5, 138.1(phenyl), 157.5, 169.6(br), 191.0(C=N). (Found: C, 20.52; H, 1.77; N 4.32. Calc for $[C_{11}H_{11}Cl_2N_2S_2]SbCl_6$ (MW = 640.7): C, 20.62; H, 1.73; N, 4.37%).

1-Chloro-3-[chloro(methylthio)methyleneamino]-1-(4-chlorophenyl)-3-(methylthio)-2-azoniaallene Hexachloroantimonate **(15n)**: a) From **8b** (1.15 g, 5 mmol) and **10j** (0.73 g, 10 mmol) in $ClCH_2CH_2Cl$ (40 ml) as described for **12a**. The solvent is evaporated under reduced pressure. The residue crystallizes at -20°C from $ClCH_2CH_2Cl$ (10 ml) affording yellow needles (2.13 g, 63%), which can be recrystallized from CH_2Cl_2 (30 ml); mp 164-166°C (dec). IR(KBr): 1543, 1590(sh), 1636. ^1H-NMR(323 K): 2.80, 2.90(CH_3), 7.66(m), 8.16(m)(aryl). ^{13}C-NMR(323 K): 18.9, 20.6(CH_3), 130.9, 131.0, 133.9, 144.4(phenyl), 156.6, 170.0, 190.9(C=N). (Found: C, 19.44; H, 1.57; N, 4.03. Calc for $[C_{11}H_{10}Cl_3N_2S_2]$ $SbCl_6$ (MW = 675.2): C, 19.57; H, 1.49; N, 4.15%).

b) A solution of $SbCl_5$ (0.90 g, 3 mmol) in CH_2Cl_2 (10 ml) is added to a cold (-10°C) solution of **17** (1.13 g, 3 mmol) in CH_2Cl_2 (15 ml). The ^1H-NMR spectrum of the yellow precipitate (1.50 g, 74%) is identical with that of product a).

1-Chloro-3-[chloro(dimethylamino)methyleneamino]-1-(4-chlorophenyl)-3-(dimethylamino)-2-azoniaallene Hexachloroantimonate (**15o**): From **8b** (2.29 g, 10 mmol) and **10h** (1.40 g, 20 mmol) as described for **12a**. However, the mixture is boiled under reflux for 40 h. The solvent is removed under reduced pressure and the yellow residue is crystallized at -20°C from CH_2Cl_2 (20 ml) to afford colourless prisms (5.13 g, 77%); mp 168-171°C. IR: 1586, 1640(sh). ^1H-NMR: 3.15, 3.33, 3.36, 3.37(CH_3). ^{13}C-NMR: 39.8, 40.2, 42.9, 43.0(CH_3), 130.4, 132.2, 132.7, 142.2(aryl), 150.7(br), 153.5, 159.6(br,C=N). (Found: C, 23.11; H, 2.42; N 8.17. Calc for $[C_{13}H_{16}Cl_3N_4]SbCl_6$ (MW = 669.1): C, 23.33; H, 2.41; N, 8.38%).

1,1,3,5,6,7,7-Heptachloro-4-aza-2-azonia-1,2,4,6-heptatetraene Hexachloroantimonate (**15p**): A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (5 ml) is added to a cold (-30°C) mixture of **8e** (2.49 g, 10 mmol) and **10p** (1.22 g, 20 mmol) in CH_2Cl_2 (20 ml). A yellow precipitate is formed. The temperature is raised to 25°C in the course of 20 min, and the mixture is stirred at 23°C for 5 h. After keeping at -20°C for 12 h an orange-yellow crystalline powder is filtered off (3.35 g, 50%); mp 131-135°C (dec). IR: 1559, 1645(sh), 1659, 1713(sh), 1900. (Found: C, 9.04; H, 0.25; N, 4.15. Calc for $[C_5Cl_7N_2]SbCl_6$ (MW = 670.7): C, 8.95; H,0.00; N, 4.18%).

[1,7-Dichloro-5,7-bis(4-chlorophenyl)-3-(dimethylamino)-2,4,6-triaza-2,4,6-heptatrien-1-ylidene]dimethylammonium Hexachloroantimonate (**16**): To a solution of **12b** (6.67g, 10 mmol, prepared without isolation in $ClCH_2CH_2Cl$ (60 ml)) a solution of **10h** (1.40 g, 20 mmol) is added dropwise. After stirring at 25°C for 2.5 h the solvent is removed under reduced pressure and the residue is purified by flash-chromatography (silica gel, CH_2Cl_2 as eluent) affording 6.08 g (75%), which are stirred for 30 min under CH_2Cl_2 (15 ml)/ether (40 ml) to give 5.60 g (69%) of pale yellow crystals; mp 130-133°C (dec). IR: 1570(sh), 1586, 1636, 1650(sh). ^1H-NMR(263 K): 2.97, 3.24, 3.30, 3.31(CH_3). ^{13}C-NMR(263 K): 39.7, 40.0, 42.3, 42.5(CH_3), 129.4, 130.5, 130.6, 131.8, 132.0, 132.4, 141.4, 141.8 (aryl), 148.9, 149.4, 161.1, 162.6(C=N). (Found: C, 29.66; H, 2.44; N; 8.63. Calc for $[C_{20}H_{20}Cl_4N_5]SbCl_6$ (MW = 806.7): C, 29.78; H, 2.50; N, 8.68%).

1-[Chloro(methylthio)methylene]-3-[dichloro(4-chlorophenyl)methyl]-2-methylisothiourea (**17**): Tetraethylammonium chloride (0.83 g, 5 mmol) in CH_2Cl_2 (10 ml) is added to a solution of the hexa-chloroantimonate **15n** (3.38 g, 5 mmol) in CH Cl (30 ml). A precipitate is formed and the yellow colour of the mixture fades. The solvent is evaporated and the residue is extracted with CCl_4 (50 ml). After filtration the solvent is removed under reduced pressure and the residue is crystallized at -20°C from CH_3CN (8 ml) to give large pale yellow prisms (1.53 g, 81%); mp 79-81°C. IR(CCl_4): 1594, 1632. ^{1}H-NMR($CDCl_3$, 273K)): 2.53, 2.56(CH_3), 7.37 (m), 7.95(m)(aryl). ^{13}C-NMR($CDCl_3$, 273K): 15.3, 17.6(CH_3), 99.9(very br,CCl_2), 128.2(o,m-C?), 135.4, 143.8, 146.8(very br), 169.3(i,p-C?,C=N). (Found: C, 35.33; H, 2.40; N, 7.70. Calc for $[C_{11}H_{10}Cl_3N_2S_2]Cl$ (MW = 376.2): C, 35.12; H, 2.68; N, 7.45%).

S-Methyl 4-(4-Chlorobenzoyl)thioallophanate (**18**): a) Crude **15n** (6.75 g, 10 mmol) is dissolved in CH_3CN (40 ml) containing H_2O (0.54 g, 30 mmol). After stirring for 12 h at 23°C colourless crystals (2.35 g, 86%) are filtered off; mp 212-215°C (dec). IR(KBr): 1463, 1532, 1594, 1659, 1710. ^{1}H-NMR(D_6-DMSO, 323K)): 2.31(CH_3), 7.60(m), 7.96(m)(aryl), 11.20, 11.27(NH). ^{13}C-NMR(D_6-DMSO, 323K): 12.1(CH_3), 128.7, 130.1(o,m-C), 130.9, 138.3(i,p-C), 149.2, 166.9, 169.5(C=O). (Found: C, 44.02; H, 3.33; N, 10.16. Calc for $C_{10}H_9ClN_2O_3S$ (MW = 272.7): C, 44.04; H, 3.33; N, 10.28%).
b) Crude **17** (3.76 g, 10 mmol) is dissolved in CH_3CN (15 ml) containing H_2O (0.54 g, 30 mmol). After stirring for 10 min the colourless crystals are filtered off (1.85 g, 68%); mp 212-215°C (dec).

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