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THE REACTION OF 2,4,6-TRIS(TRIMETHYLSILOXY)-1,3,5-TRIAZINE WITH CHLOROCARBENIUM IONS: A NEW ACCESS TO 1-OXA-3-AZABUTATRIENIUM AND 2-AZAALLENIUM SALTS

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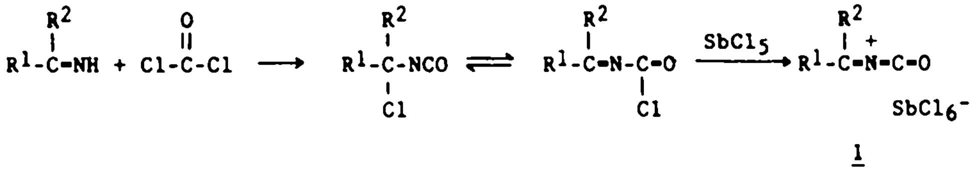
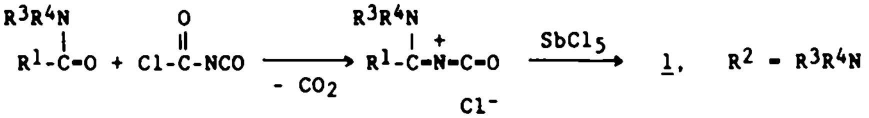
Abstract - Chlorocarbenium salts 2a-d of the Vilsmeier-Arnold type react with the silylated isocyanuric acid 3 to give 1-oxa-3-azabutatrienium salts 1 under mild conditions. From reactions of diarylchloromethenium salts 2h-l with 3 and ketones or tertiary carboxamides high yields of 2-azaallenium salts 9 were obtained. A few chloro substituted 2-azaallenium salts 5 were prepared from 1b and carbonyl compounds. The mechanisms of the new reactions are discussed.

We recently reported [1,2] on the preparation of certain 1-oxa-3-azabutatrienium salts 1, members of a new class of reactive heterocumulenes. Compounds 1 were prepared reacting either N-unsubstituted imines with phosgene or tertiary carboxamides with carbonyl chloride isocyanate in the presence of a Lewis acid.

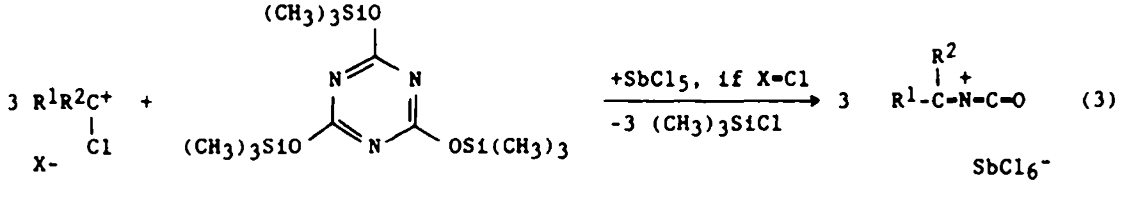


$$R^1\text{-}\overset{R^2}{\overset{|}{C}}\text{=NH} + \text{Cl-}\overset{O}{\overset{\|}{C}}\text{-Cl} \longrightarrow R^1\text{-}\underset{Cl}{\underset{|}{\overset{R^2}{\overset{|}{C}}}}\text{-NCO} \rightleftharpoons R^1\text{-}\overset{R^2}{\overset{|}{C}}\text{=N-}\underset{Cl}{\underset{|}{C}}\text{=O} \xrightarrow{SbCl_5} \underset{1}{R^1\text{-}\overset{R^2}{\overset{|}{C}}\text{=}\overset{+}{N}\text{=C=O}\;\; SbCl_6^-} \qquad (1)$$



$$R^1\text{-}\overset{R^3R^4N}{\overset{|}{C}}\text{=O} + \text{Cl-}\overset{O}{\overset{\|}{C}}\text{-NCO} \xrightarrow[-\,CO_2]{} R^1\text{-}\overset{R^3R^4N}{\overset{|}{C}}\text{=}\overset{+}{N}\text{=C=O}\;\; Cl^- \xrightarrow{SbCl_5} \underline{1},\quad R^2 = R^3R^4N \qquad (2)$$

We now found that reactions of the easily accessible triazine 3 [3-6] with chlorocarbenium ions constitute a third and cheaper method for the preparation of compounds 1. For instance, stirring three equivalents of the Vilsmeier-Arnold reagent 2a (X=Cl)$^{7)}$ with one equivalent of 3 in dichloromethane for four hours at room temperature gives after addition of antimony pentachloride the known $^{2)}$ hexachloroantimonate 1a in 91% yield. A much longer reaction time is required if one starts with the hexachloroantimonate 2a (X=$SbCl_6$) $^{8)}$ instead of the chloride. Similarly, the new butatrienium salts 1b,c were prepared, the constitutions of which follow from the spectral data (Table 1).



(3)

2 3 1a-c

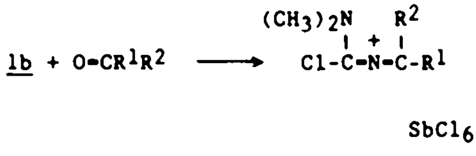
1,2	R^1	R^2
a	H	$(CH_3)_2N$
b	Cl	$(CH_3)_2N$
c	H	$C_6H_5(CH_3)N$
d	C_6H_5	$(CH_3)_2N$
e	$(CH_3)_2N$	$(CH_3)_2N$
f	$CH_3N\text{-}CH_2\text{-}CH_2\text{-}NCH_3$	
g	$(CH_3)_2N$	$(C_6H_5)_2N$
h	C_6H_5	C_6H_5
i	$4\text{-}(CH_3O)C_6H_4$	C_6H_5
j	$4\text{-}(CH_3O)C_6H_4$	$4\text{-}(CH_3O)C_6H_4$
k	$4\text{-}ClC_6H_4$	C_6H_5
l	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$

A related reaction of 2b (X=Cl) with trichloroisocyanuric acid has been described by Kukhar et al.$^{9)}$.

Rather little is known about the chemistry of the interesting triazine 3, which can be prepared simply by heating isocyanuric acid in hexamethyldisilazane. The well crystallizing 3 is soluble in most organic solvents and is only moderately moisture sensitive. The Russian authors $^{3,4)}$ who first prepared 3 found that this compound reacts with acyl chlorides to give N-acylated isocyanurates, but with trichloroacetyl chloride trichloroacetyl isocyanate was obtained $^{10)}$. With carbonyl chloride isocyanate a triazine is formed, which cycloreverses above 130°C to carbonyl diisocyanate $^{11)}$.

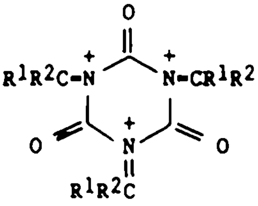
In the reaction described in this communication chlorides 2 (X=Cl) react faster with 3 than the corresponding hexachloroantimonates (X = $SbCl_6$). We believe therefore that the reaction starts with a nucleophilic attack of chloride on the silicon atoms of 3. The resulting anion reacts with 2 to give an electron deficient triazinium chloride, e.g 4, which decomposes to three molecules of 1.

1-Oxa-3-azabutatrienium salts react with ketones, aldehydes or tertiary carboxamides to form 2-azaallenium salts, e.g. 5 $^{2,12-14)}$. As may be expected, 1b is less reactive towards carbonyl compounds than 1a $^{2)}$. Thus, while 1a reacts with benzophenone in boiling chlorobenzene this reaction could not be achieved with 1b. On the other hand, a smooth reaction took place between 1b and the more nucleophilic 4,4'-dimethoxybenzophenone affording the 2-azaallenium salt 5a. With aldehydes without enolizable hydrogen atoms 15) and tertiary carboxamides the cumulenes 5b-g were obtained. On heating, the butatrienium salt 1c (NCO 2240 cm^{-1} in CH_2Cl_2) cyclized to the quinazolinium salt 6, from which the known 16) 1-methylquinazoline-4-one (7) was obtained with base.



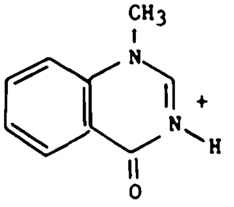
$$\underline{1b} + O{=}CR^1R^2 \longrightarrow Cl{-}\overset{(CH_3)_2N}{\overset{|}{C}}{=}\overset{+}{N}{=}\overset{R^2}{\overset{|}{C}}{-}R^1 \quad SbCl_6^-$$

5a-g



3 Cl^-

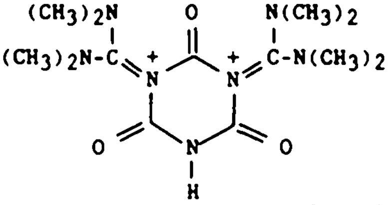
4



$SbCl_6^-$

6

5	R^1	R^2
a	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$
b	C_6H_5	H
c	$4\text{-}CH_3OC_6H_4$	H
d	$2,4,6\text{-}(CH_3O)_3C_6H_2$	H
e	$(E)\text{-}CH_3C{=}CHCH_3$	H
f	$(E)\text{-}HC{=}CHC_6H_5$	H
g	$(CH_3)_2N$	H

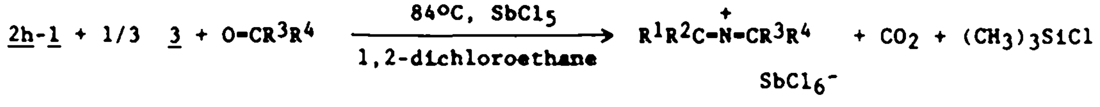


2 $SbCl_6^-$

8

Although the reaction mixture of 2d with 3 showed a strong N=C=O absorption at 2240 cm^{-1} (CH_2Cl_2) a pure butatrienium salt 1d was not isolated. On the other hand, no isocyanate bands were observed for the reaction mixtures of 2e-g with 3. In the case of 2e the heterocycle 8 was isolated in moderate yield. This compound may be formed by partial hydrolysis of an intermediate 4.

Recently, Volz and coworkers 17,18) described stable diarylchlorocarbenium salts. We examined reactions of 2h-l with the triazine 3 in the presence of $SbCl_5$. In boiling 1,2-dichloroethane N=C=O absorptions around 2240 cm^{-1} were observed in all cases. At the reaction temperature (83°C) the cumulenes 1 slowly decompose, but in the presence of ketones the 2-azaallenium hexachloroantimonates 9a-p were formed in high yields. No reaction took place between di- or trichlorophenylmethane and 3. Under the reaction conditions 2-azaallenium salts 9 derived from aldehydes proved to be unstable. With tertiary carboxamides mixtures of allenium salts 9 were isolated. Thus, from dimethylformamide and 2i (X = $SbCl_6$) a mixture of Gold's salt 9p 19) and the expected 2-azaallenium salt 9n was isolated.

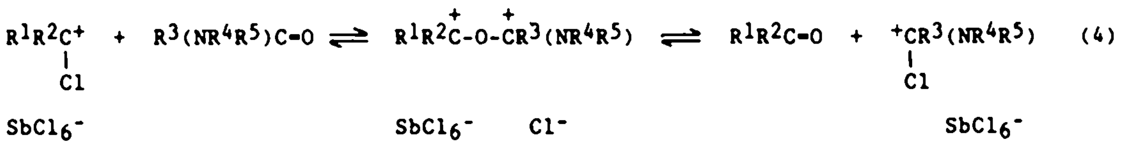


$$\underline{2h}\text{-}\underline{l} + 1/3\ \underline{3} + O{=}CR^3R^4 \xrightarrow[\text{1,2-dichloroethane}]{84^\circ C,\ SbCl_5} R^1R^2C{=}\overset{+}{N}{=}CR^3R^4 \quad SbCl_6^- + CO_2 + (CH_3)_3SiCl$$

9a-p

9	R^1	R^2	R^3	R^4
a	C_6H_5	C_6H_5	C_6H_5	C_6H_5
b	$4\text{-}(CH_3O)C_6H_4$	C_6H_5	C_6H_5	C_6H_5
c	$4\text{-}(CH_3O)C_6H_4$	$4\text{-}(CH_3O)C_6H_4$	C_6H_5	C_6H_5
d	$4\text{-}(CH_3O)C_6H_4$	C_6H_5	$4\text{-}(CH_3O)C_6H_4$	C_6H_5
e	$4\text{-}(CH_3O)C_6H_4$	$4\text{-}(CH_3O)C_6H_4$	$4\text{-}(CH_3O)C_6H_4$	C_6H_5
f	$4\text{-}(CH_3O)C_6H_4$	$4\text{-}(CH_3O)C_6H_4$	$4\text{-}(CH_3O)C_6H_4$	$4\text{-}(CH_3O)C_6H_4$
g	$4\text{-}ClC_6H_4$	C_6H_5	C_6H_5	C_6H_5
h	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	C_6H_5	C_6H_5
i	$4\text{-}ClC_6H_4$	C_6H_5	$4\text{-}ClC_6H_4$	C_6H_5
j	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	C_6H_5
k	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$
l	$4\text{-}(CH_3O)C_6H_4$	$4\text{-}(CH_3O)C_6H_4$	$4\text{-}ClC_6H_4$	C_6H_5
m	$4\text{-}(CH_3O)C_6H_4$	$4\text{-}(CH_3O)C_6H_4$	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$
n	$4\text{-}(CH_3O)C_6H_4$	C_6H_5	$(CH_3)_2N$	H
o	$4\text{-}(CH_3O)C_6H_4$	$4\text{-}(CH_3O)C_6H_4$	$(CH_3)_2N$	H
p	$(CH_3)_2N$	H	$(CH_3)_2N$	H

This latter result may be explained by the following exchange reaction of geminal dichlorides 2 (X = Cl) and tertiary carboxamides in the presence of antimony pentachloride 20):



$$\underset{\substack{|\\ Cl}}{R^1R^2C^+} + R^3(NR^4R^5)C{=}O \rightleftharpoons R^1R^2\overset{+}{C}\text{-}O\text{-}\overset{+}{C}R^3(NR^4R^5) \rightleftharpoons R^1R^2C{=}O + {}^+\underset{\substack{|\\ Cl}}{C}R^3(NR^4R^5) \qquad (4)$$

$SbCl_6^-$ $SbCl_6^-$ Cl^- $SbCl_6^-$

2 10 2'

For instance, 2h (X = Cl) and dimethylformamide react in the presence of antimony pentachloride to give the Vilsmeier-Arnold reagent 2a (X = $SbCl_6$) and benzophenone. The position of the equilibrium (4) lies on the side of the more stable cation (2 or 2'). Depending on the position of this equilibrium either 2 or 2' or both react with the triazine 3 and a carbonyl compound to form a 2-azaallenium salt 9. Thus, from the reaction of 2h with dimethylformamide only Gold's salt 9p and benzophenone were isolated. On the other hand, with the very stable salt 2j and dimethylformamide only the 2-azaallenium salt 9o was obtained, while with the intermediary stable cation 2i mixtures of 9n and 9p were formed resulting from reactions of both 2 and 2' with the triazine 3. The existence of dication ethers 10 has recently been demonstrated 21-23).

Table 1. Selected NMR and IR Data for Compounds 1 - 9.

Compound	^1H NMR [a]	^{13}C NMR [a]	IR (CH_2Cl_2) [cm^{-1}]
1a [b]	CH_3 3.41 (d, J = 1 Hz), 3.56 (d, J = 1 Hz), CH 8.51	CH_3 [c] 41.2, 45.4, C=O 132.7 (t, J = 4 Hz), C=N 157.8	2240, 1680
1b [b]	CH_3 3.62, 3.64	CH_3 46.3, 46.7, C=O 131.4, C=N 152.9	2250, 1650
1c [b]	CH_3 [c] 3.85, CH 8.81	CH_3 [c] 42.7, C=O 134.0, C=N 149.9, i-C 140.7, o,m,p-C 124.0, 131.3, 132.4	2240, 1650
2c [b,d]	CH_3 [c] 4.10 (d, J = 2 Hz), CH 9.36 (9.43)	CH_3 [c] 46.5 (52.4), =CCl 165.5 (162.9)	1620, 1585
2d [b]	CH_3 3.71, 3.89	CH_3 [c] 49.0, 50.0, =CCl 174.2, i-C 131.3, o,m,p-C 129.9, 130.3, 135.8	1620, 1590
2e [b]	CH_3 3.31	CH_3 44.9, =CCl 160.5	1640
2f [b]	CH_3 3.15, CH_2 3.98	CH_3 35.3, CH_2 50.9, =CCl 157.0	1625
2g [b]	CH_3 2.95, 3.52	CH_3 46.6, =CCl 158.3, i-C 143.2, p-C 130.4, o,m-C 127.2, 131.3	1610, 1585
3 [e]	CH_3 0.39	CH_3 0.2, C=N 171.4	
5a	NCH_3 3.57, 3.58, OCH_3 3.95	NCH_3 44.2, 44.7, OCH_3 56.9, C=N 158.8, 181.7, i-C 127.8, o-C 135.9, m-C 115.8, p-C 166.7	1585, 1610 [f]
5b	CH_3 3.76, 3.83, CH 9.16	CH_3 [g] 45.8, 46.4, HC=N 180.4, i-C 133.6, o,m,p-C 130.8, 134.6, 139.3	1555, 1580 [f], 1660 [f], 1700 [f]
5c	NCH_3 3.69, 3.80, OCH_3 4.00, CH 9.03	NCH_3 45.2, 45.7, OCH_3 57.4, HC=N 178.4, ClC=N 163.7, i-C 126.8, o-C 138.4, m-C 116.9, p-C 170.1	1500, 1530, 1560[f], 1600[f], 1660 [f]
5d	NCH_3 3.60, 3.68, OCH_3 3.99 (2 C), 4.00, CH 6.25 (2 H), 9.20	NCH_3 44.3, 44.5, OCH_3 57.8 (p), 58.0, HC=N 174.7, ClC=N 162.3 i-C 108.5, o-C 168.4, m-C 93.0, p-C 168.4	1540, 1550 [f], 1590 [f], 1620 [f]
5e	CH_3 [c] 1.97, 2.18 (d, J = 7 Hz), 3.68, 3.73, CH 7.39 (q, J = 7 Hz), 8.66	CH_3 [c] 11.0, 17.9, 45.2, 45.9, HC=N 183.4, ClC=N 164.6, C= 139.6, 166.8	1550, 1630, 1600 [f], 1660 [f]
5f	CH_3 3.68, 3.72, CH 7.39 (q, J = 10 and 16 Hz), 8.17 (d, J = 16 Hz), 8.88 (d, J = 10 Hz)	CH_3 [g] 45.3, 46.0, HC=N 180.9	1540, 1660, 1590 [f] 1620 [f]
5g	CH_3 [c] 3.27, 3.37, 3.44 (2 C), CH 8.30	CH_3 [c] 38.2, 42.9, 43.1, 43.6, HC=N 162.9, ClC=N 156.4	1590, 1650 [f]
6	CH_3 4.08, NCHN 8.90, NH 11.38	CH_3 41.7, C= 119.5, 121.9, 129.1, 131.6, 138.1, 139.2, 151.8, 157.5	1700, 1660 [h]
7	CH_3 3.73, NCHN 8.28		1700, 1640, 1600 [h]
8	CH_3 [c] 3.15, 3.37, NH 8.22	CH_3 [c] 42.1, 44.1, C= 143.7, 143.9 (2 C), 150.9 (2 C),	1670, 1740, 1770 [h]

Table 1 (continued).

Compound	^{1}H NMR a)	^{13}C NMR a)	IR (CH$_2$Cl$_2$) [cm^{-1}]
9a		C=N c) 157.2, phenyl 128.2, 130.9, 133.0, 136.7	1860, 1850 f), 1840 f), 1590
9b	OCH$_3$ e) 3.98	OCH$_3$ c) 56.4, C=N 156.2, 157.5, OC= 166.8	1850, 1820 f), 1590
9c	OCH$_3$ 3.94	OCH$_3$ 57.1, C=N 160.6, 158.0, OC= 167.2	1820, 1850 f), 1590
9d	OCH$_3$ e) 3.97	OCH$_3$ c) 56.3, C=N 156.9, OC= 166.2, aryl 116.2, 118.0, 128.6, 130.1, 130.7, 134.5, 135.0	1820, 1850 f), 1590
9e	OCH$_3$ e) 3.97	OCH$_3$ c) 56.2, C=N 158.3, 156.6, OC= 165.7	1820, 1850 f), 1590
9f	OCH$_3$ 3.92	OCH$_3$ 56.9, C=N 159.6 (t, J = 3 Hz), i-C 121.7, o-C 135.1, m-C 116.5, p-C 166.5	1820, 1850 f), 1590, 1570 f)
9g		C=N c) 156.2, 157.6	1860, 1840 f), 1585
9h		C=N c) 155.4, 158.3, aryl 126.8, 128.0, 130.9, 131.2, 133.1, 134.4, 136.9, 142.8	1860, 1840, 1580
9i		C=N c) 156.7, aryl 126.8, 127.9, 130.9, 131.1, 133.0, 134.7, 136.9, 142.7	1860, 1835, 1580
9j		C=N c) 155.8, 157.1	1860, 1830, 1580
9k		C=N 156.9, i-C 143.3, p-C 126.8, o,m-C 131.3, 134.5	1860, 1830, 1580
9l	OCH$_3$ 3.95	OCH$_3$ 57.1, C=N 160.7, 161.5, OC= 167.4	1820, 1840 f), 1850 f), 1780 f), 1590
9m	OCH$_3$ 3.95	OCH$_3$ c) 57.1, C=N 155.7, 161.5, OC= 167.2, aryl 116.6, 119.8 128.5, 130.9, 134.0, 136.3, 141.7	1820, 1850, 1585
9n	NCH$_3$ 3.45, 3.51 (d, J = 1 Hz), OCH$_3$ 3.94, CH 8.17	NCH$_3$ c) 39.3, 45.0, OCH$_3$ 56.9, C=N 164.3, 185.7, OC= 166.6	1710, 1640, 1590, 1500
9o	NCH$_3$ 3.46, 3.49 (d, J = 1 Hz), OCH$_3$ 3.94, CH 8.10	NCH$_3$ c) 39.0, 44.7, OCH$_3$ 56.8, C=N 163.9, 185.5, i-C 128.8, o-C 135.9, m-C 115.4, p-C 165.9	1640, 1590, 1570, 1490
9p	CH$_3$ c) 3.21, 3.26, CH 8.15	CH$_3$ c) 36.8, 43.0, C=N 166.5	1600

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a) Bruker WM-250 spectrometer; proton resonance at 250 MHz; internal reference tetramethylsilane; solvent CD$_3$CN; 303 K. b) X = SbCl$_6$. c) At 263 K. d) Mixture of (E,Z)-isomers. Signals of the minor compound in brackets. e) In CDCl$_3$ at 303 K. f) Shoulder. g) At 333 K. h) In KBr.

EXPERIMENTAL SECTION

IR spectra: Perkin-Elmer IR 299. The melting points are uncorrected. All experiments were carried out with exclusion of moisture in absolute solvents. The antimony pentachloride was distilled before use.

4-Dimethylamino-1-oxa-3-azabutatrienium Hexachloroantimonate (1a) 2): a) A solution of 3 (1.73 g, 5 mmol) in dichloromethane (15 ml) was added dropwise at 23°C to a stirred suspension of 2a (X=Cl) 7) (1.92 g, 15 mmol) in dichloromethane (20 ml). Stirring was continued for 4 h. Cooling to 0°C, slow addition of a solution of antimony pentachloride (4.49 g, 15 mmol) in dichloromethane (5 ml), stirring for 30 min at 0°C and precipitation with ether (25 ml) afforded a colourless moisture sensitive powder (5.91 g, 91%).

b) A mixture of 3 (1.73 g, 5 mmol) and 2a (X=$SbCl_6$) 8) (6.41 g, 15 mmol) in dichloromethane (60 ml) was stirred for 60 h at 23°C. The product (3.81 g, 88%) was filtered off.

4-Chloro-4-(dimethylamino)-1-oxa-3-azabutatrienium Hexachloroantimonate (1b): A mixture of 2b (X=Cl) 24) (9.75 g, 60 mmol) and 3 (6.91 g, 20 mmol) in 1,2-dichloroethane (120 ml) was stirred at 23°C for 20 h. After filtration and cooling to -20°C a solution of antimony pentachloride (17.94 g, 60 mmol) in 1,2-dichloroethane (12 ml) was added dropwise. The reaction mixture was stirred for 2 h at -20°C. Filtration and washing of the residue with dichloromethane (12 ml)/ether (12 ml) afforded a colourless powder (19.66 g, 70%), which can be recrystallized from 1,2-dichloroethane (30 ml)/acetonitrile (20 ml)/ether (20 ml) at -20°C giving a colourless powder (15.53 g); m.p. 196-200°C(dec).(Found: C, 10.23; H, 1.52; N, 5.96. Calc for $[C_4H_6ClN_2O]SbCl_6$ (MW= 468.0): C, 10.26; H, 1.29; N, 5.99%).

4-(N-Methylanilino)-1-oxa-3-azabutatrienium Hexachloroantimonate (1c): As described for 1b from 2c (X=Cl) 7) (9.50 g, 50 mmol) and 3 (6.22 g, 18 mmol) in dichloromethane (75 ml). Yield 19.08 g(77%) of a pale yellow moisture sensitive powder; m.p. 120-122°C (dec to 6). (Found: C, 20.77; H, 2.15; N, 5.60. Calc for $[C_9H_9N_2O]SbCl_6$ (MW = 495.7): C, 21.81; H, 1.83; N, 5.65%).

(Chloromethylene)(methylphenylammonium) Hexachloroantimonate (2c, X=$SbCl_6$): A solution of antimony pentachloride (2.99 g, 10 mmol) in dichloromethane (10 ml) was added dropwise to 2c (X=Cl) 7) (1.90 g, 10 mmol) at -30°C. After stirring for 2 h at -30°C the product was filtered off and washed with dichloromethane (10 ml). Yield 4.65 g (95%) of a colourless powder; m.p. 189-192°C (dec). (Found: C, 19.69; H, 1.67; N, 2.74. Calc for $[C_8H_9ClN]SbCl_6$ (MG = 489.1): C, 19.65; H, 1.86; N, 2.87%).

(Chlorophenylmethylene)(dimethylammonium) Hexachloroantimonate (2d, X=$SbCl_6$): As described for 2c from 2d (X=Cl) 25,26) (2.04 g, 10 mmol). Yield 4.38 g (87%) of colourless crystals; m.p. 129-131°C. (Found: C, 21.56; H, 1.90; N, 2.73. Calc for $[C_9H_{11}ClN]SbCl_6$ (MW = 503.1): C, 21.48; H, 2.20; N, 2.79%).

Chlorobis(dimethylamino)methenium Hexachloroantimonate (2e, X=$SbCl_6$): As described for 2c from 2e (X=Cl) 27) (1.71 g, 10 mmol). Yield 3.81 g (81%) of a colourless powder; dec above 283°C (ref. 26): 298°C (dec)). (Found: C, 13.01; H, 2.43; N, 5.92. Calc for $[C_5H_{12}ClN_2]SbCl_6$ (MW = 470.1): C, 12.77; H, 2.57; N, 5.96%).

2-Chloro-1,3-dimethylimidazolidinium Hexachloroantimonate (2f, X=$SbCl_6$): Oxalyl chloride (19.04 g, 150 mmol) in 1,2-dichloroethane (50 ml) was added dropwise to a solution of 1,3-dimethyl-2-imidazolidone (17.12 g, 150 mmol) in 1,2-dichloroethane (50 ml). After stirring for 30 min the temperature was raised to 70°C. After 3 h the reaction mixture was cooled and the solvent was removed under reduced pressure. The residue was washed with cyclohexane (50 ml)/dichloromethane (10 ml) and dried. Yield 20.29 g (80%) of colourless powdry 2f (X=Cl) 28), which was transformed to the hexachloroantimonate as described for 2c. Yield 52.52 g (94%) of a colourless powder; dec above 279°C. (Found: C, 13.05; H, 1.80; N, 5.96. Calc for $[C_5H_{10}ClN_2]SbCl_6$ (MW = 467.9): C, 12.83; H, 2.15; N, 5.99%).

Chloro(dimethylamino)(diphenylamino)methenium Hexachloroantimonate (2g, X=$SbCl_6$): A mixture of 2b (X=Cl) (1.63 g, 10 mmol) and diphenylamine (1.69 g, 10 mmol) in 1,2-dichloroethane (20 ml) was boiled under reflux for 3 h. After cooling to -30°C a solution of antimony pentachloride (2.99 g, 10 mmol) in 1,2-dichloroethane (10 ml) was added dropwise. The solution was concentrated to a volume of 15 ml and cooled to -15°C. Slow addition of pentane (20 ml) afforded a pale yellow precipitate (4.99 g, 84%), which after recrystallization from chloroform (30 ml) showed m.p.159-161°C (dec).(Found: C, 30.21; H, 2.37; N, 4.85. Calc for $[C_{15}H_{16}ClN_2]SbCl_6$ (MW = 594.2): C, 30.32; H, 2.71; N, 4.72%) 20).

2,4,6-Tris(trimethylsiloxy)-1,3,5-triazine (3)3,5,6): A suspension of dry isocyanuric acid (129.1 g, 1 mol) in hexamethyldisilazane (322.8 g, 2 mol) was boiled under reflux until a clear solution resulted (ca 50 h). Excess hexamethyldisilazane was removed under vacuum. The solid residue was dissolved in boiling hexane (1500 ml). Filtration and evaporation afforded a colourless powder (311.1 g,90%); m.p.93-95°C.

1-Chloro-1-(dimethylamino)-3,3-bis(4-methoxyphenyl)-2-azaallenium Hexachloroantimonate (5a): A mixture of 1b (2.34 g,5 mmol) and 4,4'-dimethoxybenzophenone (1.21g, 5 mmol) in dichloromethane (30 ml) was stirred at 23°C for 50 h. After addition of ether (60 ml) a yellow powder (2.40 g, 72%) was filtered off, which can be recrystallized from dichloromethane (8 ml)/ether (4 ml) at -20°C yielding yellow crystals (1.54 g); m.p. 164-166°C (dec). (Found: C, 32.13; H, 2.81; N, 4.13. Calc for $[C_{18}H_{20}ClN_2O_2]SbCl_6$ (MW = 666.3): C, 32.45; H, 3.03; N, 4.21%).

1-Chloro-1-(dimethylamino)-3-phenyl-2-azaallenium Hexachloroantimonate (5b): A solution of benzaldehyde (1.06 g, 10 mmol) in dichloromethane (15 ml) was added dropwise at -10°C to 1b (1.32 g, 10 mmol) in dichloromethane (15 ml). The reaction mixture was stirred for 15 h at 23°C. The yellow precipitate was filtered off and washed with dichloromethane (20 ml). Yield 3.98 g (75%), which was recrystallized from acetonitrile (20 ml) affording yellow prisms; m.p. 236-239°C (dec). (Found: C, 21.67; H, 2.03; N, 5.20. Calc for $[C_{10}H_{12}ClN_2]SbCl_6$ (MW = 530.1): C, 22.65; H 2.28; N, 5.29%).

1-Chloro-1-(dimethylamino)-3-(4-methoxyphenyl)-2-azaallenium Hexachloroantimonate (5c): As described for 5b from 4-methoxybenzaldehyde (0.68 g, 5 mmol) in 1,2-dichloroethane (40 ml). The product was precipitated with ether (80 ml) affording a yellow powder (2.63 g, 94%), which can be recrystallized from dichloromethane (25 ml)/ether (5 ml) at -20°C giving a yellow powder (2.11 g); m.p.177-179°C (dec). (Found: C, 23.58; H, 2.51; N, 4.99. Calc for $[C_{11}H_{14}ClN_2O]SbCl_6$ (MW = 560.2): C, 23.58; H, 2.52; N, 5.00%).

1-Chloro-1-(dimethylamino)-3-(2,4,6-trimethoxyphenyl)-2-azaallenium Hexachloroantimonate (5d): From 2,4,6-trimethoxybenzaldehyde (1.96 g, 10 mmol) as described for 5b. The product was precipitated with pentane (60 ml). Yield 5.89 g(95%) of a yellow powder; m.p. 196-199°C (dec). (Found: C, 25.26; H, 2.82; N, 4.67. Calc for $[C_{13}H_{18}ClN_2O_3]SbCl_6$ (MW = 620.2): C, 25.17; H, 2.93; N, 4.52%).

1-Chloro-1-(dimethylamino)-3-[(E)-1-methyl-1-propenyl]-2-azaallenium Hexachloroantimonate (5e): From tiglic aldehyde (0.42 g, 5 mmol) as described for 5b. Precipitation with ether (100 ml) at -50°C afforded a brown powder (1.98 g, 78%); m.p. 95-96°C (dec). (Found: C, 19.08; H, 2.78; N, 5.43. Calc for $[C_8H_{14}ClN_2]SbCl_6$ (MW = 508.1): C, 18.91; H, 2.78; N, 5.51%).

1-Chloro-1-(dimethylamino)-3-[(E)-2-phenylethenyl]-2-azaallenium Hexachloroantimonate (5f): From cinnamic aldehyde (1.32 g, 10 mmol) as described for 5b. Yield 5.01 g (90%) of a yellow powder, which crystallized from acetonitrile (80 ml) giving yellow leaflets; dec above 211°C. (Found:C, 26.11; H, 2.69; N, 4.93. Calc for $[C_{12}H_{14}ClN_2]SbCl_6$ (MW = 556.2): C, 25.91; H, 2.54; N, 5.04%).

1-Chloro-1,3-bis(dimethylamino)-2-azaallenium Hexachloroantimonate (5g) 29): A mixture of N,N-dimethylformamide (0.73 g, 10 mmol) and 1b (4.68 g, 10 mmol) in 1,2-dichloroethane (25 ml) was stirred at 23°C for 130 h. Slow addition of ether (50 ml) to the reaction mixture afforded a pale yellow precipitate (3.48 g, 70%), which was dissolved in dichloroethane (10 ml). Filtration and addition of ether (5 ml) at -20°C afforded a pale yellow powder; m.p. 185-189°C. (Found: C, 14.58; H, 2.77; N, 8.35. Calc for $[C_6H_{13}ClN_3]SbCl_6$ (MW = 497.1): C, 14.50; H, 2.64; N, 8.46%).

1-Methyl-4-oxoquinazolinium Hexachloroantimonate (6): A solution of 1c (0.46 g, 1 mmol) in chlorobenzene (5 ml) was boiled under reflux for 1 h. Evaporation of the solvent and stirring of the residue in dichloromethane (5 ml) yielded a greenish-grey powder (0.38 g, 76%); m.p. 258-261°C (dec). (Found: C, 21.80; H, 1.64; N, 5.54. Calc for $[C_9H_9N_2O]SbCl_6$ (MW = 495.7): C, 21.81; H, 1.83; N, 5.65%).

1-Methylquinazoline-4-one (7) 16): A suspension of 6 (1.49 g, 3 mmol) in dichloromethane (20 ml) and triethylamine (1 ml) was stirred for 12 h. Addition of chloroform and extraction with aqueous sodium carbonate yielded after work-up a colourless powder (0.36 g, 75%). The picrate showed m.p. 246-250°C (dec) (ref.16): 249-250°C (dec)).

1,3-Bis[bis(dimethylamino)methylene]hexahydro-2,4,6-trioxo-1,3,5-triazine-1,3-diylium Bis(hexachloroantimonate) (8): A mixture of 2e (X=Cl) 26) (3.54 g, 20 mmol) and 3 (3.46 g, 10 mmol) in acetonitrile (30 ml) was boiled under reflux for 3 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (40 ml). A solution of antimony pentachloride (5.98 g, 20 mmol) in dichloromethane (10 ml) was added dropwise at -50°C. The mixture was stirred for 30 min at -50°C. After filtration the residue was washed with dichloromethane (20 ml) affording a colourless powder (5.11 g, 51%), which was suspended in acetonitrile (20 ml). After filtration from an impurity the solvent was removed and the residue was suspended in dichloromethane (30 ml). Boiling under reflux for 30 min, filtration and reprecipitation of the residue from acetonitrile (10 ml/dichloromethane (30 ml) gave a colourless powder; m.p. 233-238°C (dec). (Found: C, 15.88; H, 2.31; N, 9.74. Calc for $[C_{13}H_{25}N_7O_3]2SbCl_6$ (MW = 996.4): C, 15.67; H, 2.53; N, 9.84%).

Tetraphenyl-2-azaallenium Hexachloroantimonate (9a) 12): To antimony pentachloride (2.99 g, 10 mmol) in 1,2-dichloroethane (10 ml) a solution of 2h (X=Cl)30)(2.37 g, 10 mmol) in 1,2-dichloroethane (10 ml) was added dropwise at -10°C. A orange-red precipitate was formed. The suspension was warmed up to +23°C and a solution of 3 (1.38 g, 4 mmol) and benzophenone (1.82 g, 10 mmol) in 1,2-dichloroethane (20 ml) was added. The reaction mixture was boiled under reflux for 3 h. Evaporation of the solvent and chromatography of the residue on silica gel (40 cm,∅ 4 cm) with dichloromethane as eluent afforded a pale yellow powder, which was recrystallized from dichloromethane/pentane at -20°C giving pale yellow needles (3.47 g,51%); m.p. 213-215°C (ref.12): 185-189°C (dec)).

1-(4-Methoxyphenyl)-1,3,3-triphenyl-2-azaallenium Hexachloroantimonate (9b) 31): From 2h (2.37 g, 10 mmol) and 4-methoxybenzophenone (2.12 g, 10 mmol) as described for 9a. The reaction mixture was boiled under reflux for 15 h. Evaporation of the solvent and stirring the residue under ether (100 ml) afforded a yellow powder (6.61 g, 93%); m.p. 144-146°C (dec) (ref.31): 155-157°C).

1,1-Bis(4-methoxyphenyl)-3,3-diphenyl-2-azaallenium Hexachloroantimonate (9c) 12): From 2h (2.37 g, 10 mmol) and 4,4'-dimethoxybenzophenone (2.42 g, 10 mmol) as described for 9a. The crude product was dissolved in dichloromethane (30 ml). Slow addition of ether (80 ml) afforded a dark yellow precipitate (5.19 g, 70%); m.p. 201-203°C (dec) (ref.12): 202-205°C (dec)).

1,3-Bis(4-methoxyphenyl)-1,3-diphenyl-2-azaallenium Hexachloroantimonate (9d): From 2i [32] (2.76 g, 10 mmol) and 4-methoxybenzophenone (2.12 g, 10 mmol) as described for 9a. The crude product was recrystallized from dichloromethane (15 ml)/carbon tetrachloride (25 ml) affording a yellow powder (5.98 g, 81%); m.p. 173-175°C. (Found: C, 45.54; H, 3.46; N, 1.90. Calc for $[C_{28}H_{24}NO_2]SbCl_6$ (MW = 741.0): C, 45.39; H, 3.27; N, 1.89%).

Tris(4-methoxyphenyl)phenyl-2-azaallenium Hexachloroantimonate (9e): From 2i(X=Cl) (2.67 g, 10 mmol) and 4,4'-dimethoxybenzophenone (2.42 g, 10 mmol) as described for 9a. The reaction mixture was boiled under reflux for 1 h. Evaporation of the solvent and recrystallization of the residue (7.09 g, 92%) from dichloromethane (140 ml)/ether (700 ml) at -20°C afforded yellow needles; m.p.133-135°C (dec). (Found: C, 45.21; H, 3.22; N, 1.99. Calc for $[C_{29}H_{26}NO_3]SbCl_6$ (MW = 771.0): C, 45.18; H, 3.40; N, 1.82%).

Tetrakis(4-methoxyphenyl)-2-azaallenium Hexachloroantimonate (9f): From 2j [33] (X=Cl) (2.97 g, 10 mmol) and 4,4'-dimethoxybenzophenone (2.42 g, 10 mmol) as described for 9a. After evaporation of the solvent the residue crystallized on treatment with pentane (50 ml)/ether (50 ml). Recrystallization from dichloromethane (20 ml)/pentane (10 ml)/ether (10 ml) at -20°C afforded reddish-yellow prisms (6.57 g, 82%); m.p. 189-192°C (dec). (Found: C, 44.74; H, 3.22; N, 2.04. Calc for $[C_{30}H_{28}NO_4]SbCl_6$ (MW = 801.0): C, 44.98; H, 3.52; N, 1.75%).

(4-Chlorophenyl)triphenyl-2-azaallenium Hexachloroantimonate (9g): From 2k [34] (X=Cl) (2.72 g, 10 mmol) and benzophenone (1.82 g, 10 mmol) as described for 9a. After evaporation of the solvent the residue was recrystallized from acetonitrile (20 ml) affording a nearly colourless powder (4.29 g, 60%); m.p. 185-187°C. (Found: C, 43.54; H, 2.77; N, 1.97. Calc. for $[C_{26}H_{19}ClN]SbCl_6$ (MW = 715.3): C, 43.65; H, 2.68; N, 1.96%).

1,1-Bis(4-chlorophenyl)-3,3-diphenyl-2-azaallenium Hexachloroantimonate (9h): From 2h (X=Cl) (2.37 g, 10 mmol) and 4,4'-dichlorobenzophenone (2.51 g, 10 mmol) as described for 9a. After evaporation of the solvent the residue was recrystallized from acetonitrile (20 ml)/ether (15 ml) at -20°C affording orange prisms (4.20 g, 56%); m.p. 213-216°C (dec). (Found: C, 41.56; H, 2.43;N, 1.95). Calc for $[C_{26}H_{18}Cl_2N]SbCl_6$ (MW = 749.8): C, 41.65; H, 2.42; N, 1.87%).

1,3-Bis(4-chlorophenyl)-1,3-diphenyl-2-azaallenium Hexachloroantimonate (9i): From 2k (X=Cl) (2.72 g, 10 mmol) and 4-chlorobenzophenone (2.17 g, 10 mmol) as described for 9a. After boiling under reflux for 18 h the reaction was complete. Evaporation of the solvent and recrystallization of the residue from acetonitrile (20 ml) afforded a nearly colourless powder (4.06 g, 54%); m.p. 174-176°C. (Found: C, 41.58; H, 2.43; N, 1.70. Calc for $[C_{26}H_{18}Cl_2N]SbCl_6$ (MW = 749.8): C, 41.65; H, 2.42; N, 1.87%).

Tris(4-chlorophenyl)phenyl-2-azaallenium Hexachloroantimonate (9j): From 2k (X=Cl) (2.72 g, 10 mmol) and 4,4'-dichlorobenzophenone (2.51 g, 10 mmol) as described for 9i. Crystallizing the crude product from acetonitrile (25 ml)/ether (15 ml) at -20°C afforded a pale yellow powder (5.89 g, 75%); m.p. 224-227°C (dec). (Found: C, 39.61; H, 2.14 ; N, 1.69. Calc for $[C_{26}H_{17}Cl_3N]SbCl_6$ (MW = 784.2): C, 39.82; H, 2.19; N, 1.79%).

Tetrakis(4-chlorophenyl)-2-azaallenium Hexachloroantimonate (9k): From 2l(X=Cl)[35] (3.06 g, 10 mmol) and 4,4'-dichlorobenzophenone (2.51 g, 10 mmol) as described for 9i. The product crystallized from the reaction mixture on cooling to -20°C in form of yellow prisms (5.81 g, 71%), which can be recrystallized from acetonitrile; dec above 230°C. (Found: C, 38.13; H, 1.91; N, 1.89. Calc for $[C_{26}H_{16}Cl_4N]SbCl_6$ (MW = 818.7): C, 38.14; H, 1.97; N, 1.71%).

1-(4-Chlorophenyl)-1-phenyl-3,3-bis(4-methoxyphenyl)-2-azaallenium Hexachloroantimonate (9l): From 2k (X=Cl) (2.72 g, 10 mmol) and 4,4'-dimethoxybenzophenone

(2.42 g, 10 mmol) as described for 9a. After evaporation of the solvent the residue was recrystallized from dichloromethane (35 ml)/carbon tetrachloride (50 ml) giving a yellowish powder (4.57 g, 59%); m.p. 184-188°C (dec). (Found: C, 43.78; H, 3.12; N, 2.24. Calc for $[C_{28}H_{23}ClNO_2]SbCl_6$ (MW = 775.4): C, 43.37; H, 2.99; N, 1.81%).

1,1-Bis(4-chlorophenyl)-3,3-bis(4-methoxyphenyl)-2-azaallenium Hexachloroantimonate (9m): From 21 (X=Cl) (3.06 g, 10 mmol) and 4,4'-dimethoxybenzophenone (2.42 g, 10 mmol) as described for 9a. After boiling for 8 h under reflux the reaction mixture was evaporated under reduced pressure and the residue was recrystallized from acetonitrile (15 ml) affording a yellowish powder (5.64 g, 70%); m.p. 211-214°C (dec). (Found: C, 41.47; H, 2.83; N, 1.79. Calc for $[C_{28}H_{22}Cl_2NO_2]SbCl_6$ (MW = 809.9): C, 41.52; H, 2.74; N, 1.73%).

1-(Dimethylamino)-3-(4-methoxyphenyl)-3-phenyl-2-azaallenium Hexachloroantimonate (9n) and 1,3-Bis(dimethylamino)-2-azaallenium Hexachloroantimonate (9p) 2): To a mixture of 2i (X=Cl) (2.67 g, 10 mmol) and 3 (1.38 g, 4 mmol) in dichloromethane (50 ml) a solution of antimony pentachloride (2.99 g, 10 mmol) in dichloromethane (15 ml) was added dropwise at -78°C. After 30 min a solution of dimethylformamide (0.73 g, 10 mmol) in dichloromethane (15 ml) was added dropwise. The reaction mixture was stirred for 12 h at +23°C. Cooling to -50°C and slow addition of ether (100 ml) afforded an oily precipitate. The supernatant liquid was decanted and evaporated under reduced pressure leaving back a mixture of 4-methoxybenzophenone and dimethylformamide (^{1}H NMR, IR). The oily precipitate was dissolved in acetonitrile (5 ml). Slow addition of ether (50 ml) gave a yellow precipitate of 9p 2) (2.36 g, 51%, including work-up of the mother liquor). The mother liquor of this crystallization was evaporated under reduced pressure leaving back an oil, which crystallized from acetonitrile (3 ml)/ether (10 ml) at -20°C giving yellow prisms of 9n (1.26 g, 20%), which were recrystallized from dichloromethane (2 ml)/ether (2 ml); m.p.110-113°C (dec). (Found: C, 33.81; H, 3.15; N, 4.64. Calc for $[C_{17}H_{19}N_2O]SbCl_6$ (MW = 601.8): C, 33.93; H, 3.18, N, 4.66%).

1-(Dimethylamino)-3,3-bis(4-methoxyphenyl)-2-azaallenium Hexachloroantimonate (9o) 2): From 2j (X=Cl) (2.97 g, 10 mmol) and dimethylformamide (0.73 g, 10 mmol) as described for 9n. After stirring for 3 h at +23°C the reaction mixture was evaporated under reduced pressure and the oily residue was crystallized from chloroform (50 ml) at -20°C affording orange prisms (4.74 g, 75%); m.p. 156-158°C (dec) (ref. 2): 154-155°C).

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