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A New Synthesis of 2-Azaallenium Salts

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The α-chloro isocyanates **1** and the α-chloro isothiocyanate **2a** react with antimony pentachloride and ketones or aldehydes at low temperatures to give the 2-azaallenium hexachloroantimonates **5a – q** in high yields. The reaction proceeds via the 1-oxa-(or 1-thia)-3-azabutatrienium hexachloroantimonates **3**, **4**. The reaction is hindered by bulky substituents of both organic components and by electron withdrawing groups in the carbonyl compound. No stable 2-azaallenium salts **5** were obtained from carbonyl compounds with enolizable hydrogen atoms. Instead of reacting with the carbonyl group the α-chloro isocyanates **1** attack 4-benzoylpyridine at the nitrogen atom affording pyridinium salts (**19a**, **20g**). The products from the reaction of Michler's ketone with **1** must be regarded as monoaza monomethine cyanine dyes (**21**).

Eine neue Synthese von 2-Azaallenium-Salzen

Die α-Chlorisocyanate **1** und das α-Chlorisothiocyanat **2a** reagieren mit Antimonpentachlorid und Aldehyden oder Ketonen bei tiefen Temperaturen in hohen Ausbeuten zu den 2-Azaallenium-Salzen **5a – q**. Die Reaktion verläuft über 1-Oxa-(bzw. 1-Thia)-3-azabutatrienium-hexachloroantimonate **3**, **4**. Sterisch anspruchsvolle Substituenten in beiden organischen Komponenten und elektronenziehende Substituenten der Carbonylverbindung verhindern die Reaktion. Carbonylverbindungen mit enolisierbaren Wasserstoffatomen ergaben keine stabilen 2-Azaallenium-Salze **5**. Mit 4-Benzoylpyridin reagieren die α-Chlorisocyanate **1** nicht mit der Carbonylgruppe, sondern am Stickstoff. Man erhält die Pyridiniumsalze **19a**, **20g**. Aus Michlers Keton und **1** werden Monoazamonomethincyanin-Farbstoffe (**21**) gebildet.

Recently, we described preparations and *X*-ray structural analyses of the formal 3-azabutatrienium salts **3**, **4**$^{1,2)}$. We now found that the salts **3** and **4** react readily with ketones and aldehydes to give the 2-azaallenium hexachloroantimonates **5a – q** and CO_2 or COS, respectively.

The first 2-azaallenium salts **5** were prepared in 1969 by *Samuel* and *Wade*$^{3)}$ from ketiminomethyl chlorides **6** and Lewis acids MCl_n ($SbCl_5$, $AlCl_3$, BCl_3). Since (methyleneamino)methyl chlorides **6** are not generally accessible, the scope of this reaction is limited. The authors attributed a moderately strong IR absorption in the range 1820 – 1870 cm^{-1} to a skeletal stretching vibration of the linear $C = \overset{+}{N} = C$ unit of **5**.

Barton et al.$^{4)}$ obtained two 2-azaallenium salts **5** by hydride abstraction from (methyleneamino)methanes **7** with triphenylcarbenium tetrafluoroborate. By the same method compound **5a** (X = B_2F_7) was later prepared$^{5)}$. Again, the method seems not to be generally applicable. For instance, the hexachloroantimonate **5j** could not be obtained from the corresponding Schiff base **7** with trityl hexachloroantimonate.

A third access to 2-azaallenium salts **5** has recently been published by *Würthwein*$^{6)}$, who reacted iminals **8** with acetylium hexachloroantimonate.

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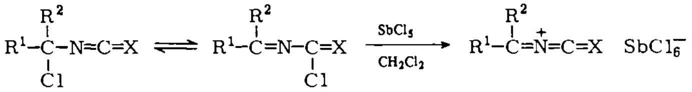
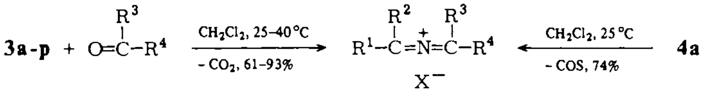


$$R^1-\underset{Cl}{\overset{R^2}{C}}-N=C=X \rightleftharpoons R^1-\overset{R^2}{C}=N-\underset{Cl}{C}=X \xrightarrow[CH_2Cl_2]{SbCl_5} R^1-\overset{R^2}{C}=\overset{+}{N}=C=X\ SbCl_6^-$$

1: X = O
2: X = S

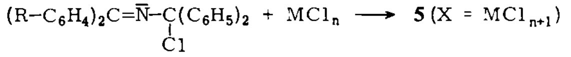
3: X = O
4: X = S



$$\mathbf{3a\text{-}p} + O=\overset{R^3}{C}-R^4 \xrightarrow[-CO_2,\ 61-93\%]{CH_2Cl_2,\ 25-40^\circ C} R^1-\overset{R^2}{C}=\overset{+}{N}=\overset{R^3}{C}-R^4\ X^- \xleftarrow[-COS,\ 74\%]{CH_2Cl_2,\ 25^\circ C} \mathbf{4a}$$

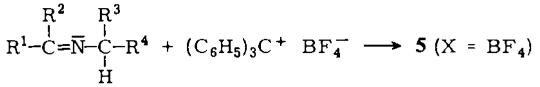
5a-q (X = $SbCl_6$)

	R^1	R^2	R^3	R^4
a	C_6H_5	C_6H_5	C_6H_5	C_6H_5
b	C_6H_5	C_6H_5	C_6H_5	H
c	C_6H_5	C_6H_5	C_6H_5	$C_6H_4CH_3$-(2)
d	C_6H_5	C_6H_5	$C(CH_3)_3$	H
e	C_6H_5	C_6H_5	$C_6H_4N(CH_3)_2$-(4)	$C_6H_4N(CH_3)_2$-(4)
f	C_6H_5	C_6H_4Br-(4)	2-C_6H_4–C_6H_4-2'	
g	2-C_6H_4–C_6H_4-2'		C_6H_5	$C_6H_4CH_3$-(2)
h	2-C_6H_4–C_6H_4-2'		C_6H_5	$C_6H_4CH_3$-(4)
i	2-C_6H_4–C_6H_4-2'		C_6H_5	1-$C_{10}H_7$
j	2-C_6H_4–C_6H_4-2'		2-C_6H_4–C_6H_4-2'	
k	2-C_6H_4–C_6H_4-2'		C_6H_5	H
l	2-C_6H_4–C_6H_4-2'		C_6H_5	$C_6H_4OCH_3$-(4)
m	2-C_6H_4–C_6H_4-2'		$C_6H_4OCH_3$-(4)	$C_6H_4OCH_3$-(4)
n	2-C_6H_4–C_6H_4-2'		$C_6H_4N(CH_3)_2$-(4)	$C_6H_4N(CH_3)_2$-(4)
o	1-$C_{10}H_7$	C_6H_5	$C_6H_4OCH_3$-(4)	$C_6H_4OCH_3$-(4)
p	1-$C_{10}H_7$	C_6H_5	$C_6H_4N(CH_3)_2$-(4)	$C_6H_4N(CH_3)_2$-(4)
q	C_6H_5	C_6H_5	$C_6H_4OCH_3$-(4)	$C_6H_4OCH_3$-(4)



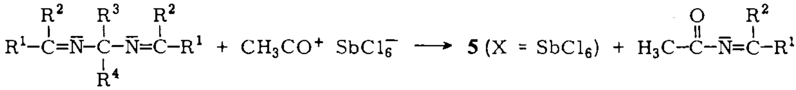
$$(R-C_6H_4)_2C=\bar{N}-\underset{Cl}{C}(C_6H_5)_2 + MCl_n \longrightarrow \mathbf{5}\ (X = MCl_{n+1})$$

6 (R = H, 4-CH_3)



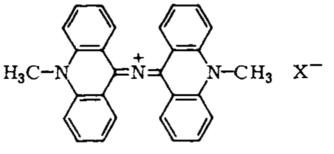
$$R^1-\overset{R^2}{C}=\bar{N}-\underset{H}{\overset{R^3}{C}}-R^4 + (C_6H_5)_3C^+\ BF_4^- \longrightarrow \mathbf{5}\ (X = BF_4)$$

7 (R^1, R^4 = H, R^2, R^3 = $C_6H_3OCH_3$-(4)-[$OCH_2C_6H_3Cl_2$-(2,6)]-(4) or
R^1, R^2 = R^3, R^4 = 2-C_6H_4–C_6H_4-2')



$$R^1-\overset{R^2}{C}=\bar{N}-\underset{R^4}{\overset{R^3}{C}}-\bar{N}=\overset{R^2}{C}-R^1 + CH_3CO^+\ SbCl_6^- \longrightarrow \mathbf{5}\ (X = SbCl_6) + H_3C-\overset{O}{\overset{\|}{C}}-\bar{N}=\overset{R^2}{C}-R^1$$

8 (R^1, R^2, R^3, R^4 = C_6H_5 or R^1, R^2, R^3 = C_6H_5, R^4 = H or
R^1, R^3 = C_6H_5, R^2, R^4 = H)



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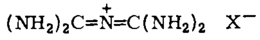
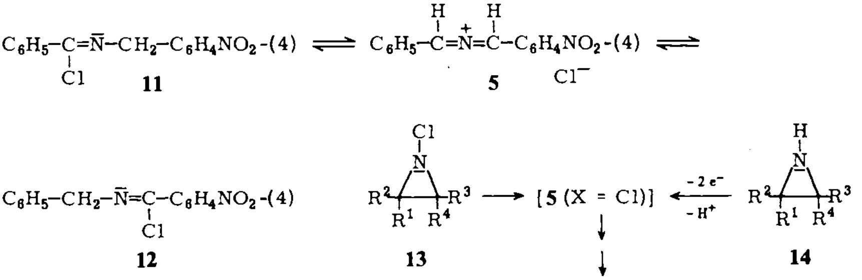


$(NH_2)_2C{=}\overset{+}{N}{=}C(NH_2)_2\ X^-$

10



$C_6H_5{-}\underset{Cl}{C}{=}\bar{N}{-}CH_2{-}C_6H_4NO_2\text{-}(4) \rightleftharpoons C_6H_5{-}\overset{H}{C}{=}\overset{+}{N}{=}\overset{H}{C}{-}C_6H_4NO_2\text{-}(4)\ Cl^- \rightleftharpoons$

11 **5**

$C_6H_5{-}CH_2{-}\bar{N}{=}\underset{Cl}{C}{-}C_6H_4NO_2\text{-}(4)$

12

$\mathbf{13} \longrightarrow [\mathbf{5}\ (X = Cl)] \xleftarrow[-H^+]{-2e^-} \mathbf{14}$

13 **14**

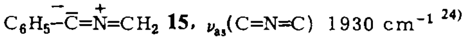
It should be mentioned that certain cyanine dyes, e. g. **9**[7], can formally be regarded as 2-azaallenium salts.

Heterosubstituted formal 2-azaallenium salts are known since 1879, when *Rathke*[8] described the preparation of the monoprotonated biguanide **10**. Since that time many oxa-, aza-, and chlorosubstituted 2-azaallenium salts **5** have been prepared[9].

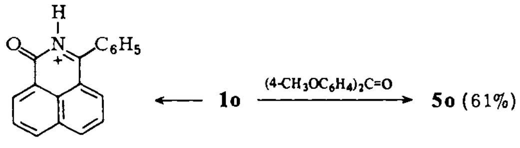
Occasionally, 2-azaallenium cations have been postulated as reactive intermediates. *Huisgen* et al.[10] observed an interconversion of the *N*-methylimidoyl chlorides **11** and **12** in the presence of triethylamine. This tautomerization is thought to take place – inter alia – via an intermediate **5**.

2-Azaallenium salts are obviously involved in the solvolysis of *N*-chloroaziridines **13**[11–13] and in the anionic oxidation of aziridines[14] **14**.

Substitution of halogen in *N*-(halogenomethyl)imines (e. g. **6**) by nucleophiles has been postulated to proceed by an S_N1 mechanism via 2-azaallenium salts **5**[15,16]. Intermediates **5** are formed by hydride abstraction from imines **7** with NO^+ [17] or by the cleavage of iminals[18]. The rearrangement of *N,N*-difluorobenzylamines is thought to take place via an intermediate **5**[19]. σ-Complex intermediates formed in the course of the electrophilic substitution of *N*-alkylideneanilines can be regarded as 2-azaallenium salts **5**[20,21]. An early proposal of an intermediate **5** was made by *Magat* et al.[22] who studied acid-catalyzed reactions of nitriles with formaldehyde. The IR spectrum of a zwitterionic cyclic 2-azaallenium compound has been reported by *Chapman* and *Sheridan*[23]. Finally, nitrile ylides, e. g. **15**[24], may be regarded as 2-azaallenium compounds.



$C_6H_5{-}\overset{-}{C}{=}\overset{+}{N}{=}CH_2$ **15**, $\nu_{as}(C{=}N{=}C)$ 1930 cm^{-1} [24]



16

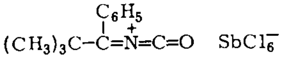
Stirring an equimolecular mixture of the α-chloro isocyanate **1a**[25,26], benzophenone, and antimony pentachloride in dry dichloromethane for 6 hours between –78 and

+ 23 °C afforded the known[3,6)] tetraphenyl-2-azaallenium hexachloroantimonate (**5a**) in 85% yield. Under similar conditions the reaction of the corresponding α-chloro isothiocyanate **2a** with benzophenone sluggishly gives **5a** in an impure state. But with the more electron rich 4,4′-dimethoxybenzophenone **2a** reacts smoothly to give **5q** (74%). In the IR spectrum of the reaction mixture a strong absorption at 2020 cm^{-1} can be attributed to COS. The enhanced reactivity of the isocyanates **3** as compared to the isothiocyanates **4** towards nucleophiles has already been observed[1)] in the reaction with carboxylic acids.

The 1-naphthyl cumulene **3o** has been shown[1)] to react in an intramolecular electrophilic substitution to give **16**. In the presence of benzophenone a mixture of compounds was obtained. But with 4,4′-dimethoxybenzophenone or with Michler's ketone the intermolecular formation of the 2-azaallenium salts **5o, p** is faster.

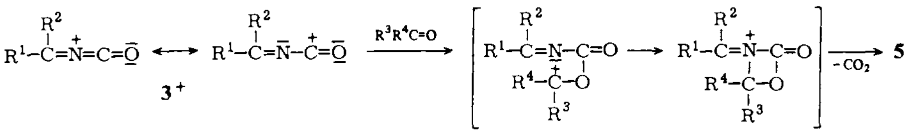
Reactions of isocyanates with carbonyl compounds have first been described by *Staudinger* et al.[27,28)], who heated phenyl isocyanate with 4-(dimethylamino)benzaldehyde for 14 hours at 190 °C to obtain *N*-[4-(dimethylamino)benzylidene]aniline.

The scope of the new reaction is critically limited by steric factors. While **3a** reacts smoothly with benzophenone, no 2-azaallenium salt **5** was obtained with 1-naphthyl phenyl ketone. On the other hand, the fluorene derivative **3g** and 1-naphthyl phenyl ketone gave **5i** without problems. The reaction of **3a** with 2-methylbenzophenone required prolonged heating to go to completion. The *tert*-butyl-substituted cumulene **3r** reacts neither with aldehydes nor with ketones.



$(CH_3)_3C-\overset{\overset{C_6H_5}{|}}{C}=\overset{+}{N}=C=O \quad SbCl_6^-$

3r

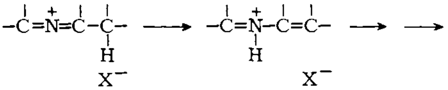


Especially clean reactions are obtained with electron rich ketones like Michler's ketone. Carbonyl compounds with electron withdrawing groups do not react, e. g. hexachloroacetone, trichloroacetaldehyde, or tribromoacetaldehyde.

These results suggest a Wittig-type mechanism[27,28)] for the reaction of **3**, **4** with carbonyl compounds. The reaction starts with a nucleophilic attack of the carbonyl oxygen on the acylium carbon of **3**, followed by ring closure to an oxazetidinium salt. Ring opening in the opposite direction gives the 2-azaallenium salt **5** and CO_2.

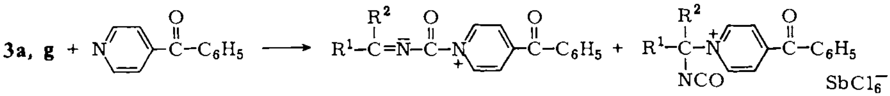
Aliphatic substituted carbonyl compounds without an α-hydrogen, e. g. pivalaldehyde, react normal, but ketones like acetophenone or acetone give black tars, which do not show a $C=\overset{+}{N}=C$ absorption above 1800 cm^{-1}. According to *Würthwein* et al.[29)], 2-azaallenium salts **17** with a hydrogen atom in allylic position to the nitrogen rearrange to the thermodynamically more stable 2-azabutadienium salts **18**, which tend to polymerize.

With 4-benzoylpyridine compounds **3a, g** react with the more nucleophilic nitrogen atom instead of the carbonyl oxygen affording the pyridinium salts **19a** and **20a, g**. The reaction product of **3a** shows only a weak NCO band at 2250 cm^{-1} (CH_2Cl_2) and two carbonyl resonances but no signal for an sp^3 hybridized carbon in the ^{13}C NMR spectrum indicating the presence of mainly **19a** contaminated with only traces of **20a**. Contrary to this, **3g** afforded pure **20g** (IR: NCO 2250 cm^{-1} (vs)) showing only one ^{13}C carbonyl resonance and a signal for an sp^2 carbon.



$-\overset{|}{C}=\overset{+}{N}=\overset{|}{C}-\underset{H}{\overset{|}{C}}-\ X^- \longrightarrow -\overset{|}{C}=\underset{H}{\overset{+}{N}}-\overset{|}{C}=\overset{|}{C}-\ X^- \longrightarrow \longrightarrow$

17 **18**

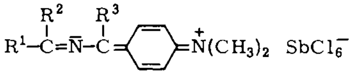


3a, g **19a** **20a, g**

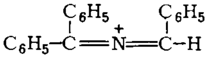
	R^1	R^2
a	C_6H_5	C_6H_5
g	$2\text{-}C_6H_4\text{-}C_6H_4\text{-}2'$	

Most of the 2-azaallenium salts **5** are stable, well crystallizing substances showing moderate sensitivity against moisture or nucleophiles. 2-Azaallenium salts with electron releasing substituents like **5p** can even be recrystallized from methanol. Less stable are the hydrogen-substituted salts **5b, d**, and **k** which decompose in acetonitrile solution at room temperature. Especially the aliphatic substituted compound **5d** is quickly hydrolyzed with traces of water and proved to be thermally instable. The compound could not be obtained completely pure.

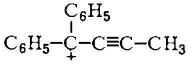
Contrary to allenes, the substituents have pronounced influence on the asymmetric C = N = C stretching vibration of the compounds **5**. For instance, the alkyl-substituted salt **5d** shows a strong IR absorption at 1912 cm^{-1}, while for **5g** ν_{CNC} is observed at 1830 cm^{-1}. No cumulene bands were found for the salts derived from Michler's ketone (**5e, n, p**). While **5n** has a broad signal of moderate intensity at 1690 cm^{-1} (in CH_2Cl_2), the salts **5e** and **p** show only bands at 1590 with shoulders at 1600 cm^{-1} indicating that these molecules must not be regarded as 2-azaallenium salts but rather as cyanine dyes **21**[7]. While the "true" 2-azaallenium salt **5a** is nearly colourless (λ_{max} = 293 nm (CH_2Cl_2)) the bis(dimethylamino)-substituted salt **5e** is deep green (λ_{max} = 542 nm).



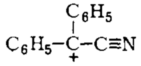
21



$C_6H_5-\overset{C_6H_5}{\overset{|}{C}}=\overset{+}{N}=\overset{C_6H_5}{\overset{|}{C}}-H$



$C_6H_5-\underset{+}{\overset{C_6H_5}{\overset{|}{C}}}-C\equiv C-CH_3$



$C_6H_5-\underset{+}{\overset{C_6H_5}{\overset{|}{C}}}-C\equiv N$

δ = 157.7 143.0 195.7 165.1 168.8

5b$^+$ **22** **23**

In the ^{13}C NMR spectra the signals for the 2-azaallenium carbons are found in the range $\delta = 143 - 166$ indicating that these carbons carry less positive charge than those in the related cations **22** and **23**[30].

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Experimental Part

IR spectra: Perkin-Elmer IR 299 spectrometer, dichloromethane. – UV spectra: Cary 118 spectrometer, dichloromethane. – ^1H NMR spectra: Jeol JNM-MH-100 and Bruker WM-250 instruments. – ^{13}C NMR spectra: Bruker WM-250 spectrometer. δ-Scale, internal reference TMS. – Melting points: uncorrected.

Tetraphenyl-2-azaallenium Hexachloroantimonate (**5a**)[3,6]: To **1a**[25] (1.22 g, 5.00 mmol) and benzophenone (0.92 g, 5.05 mmol) in absol. dichloromethane (20 ml) was added dropwise under stirring at −78 °C a solution of antimony pentachloride (1.50 g, 5.00 mmol, freshly distilled) in absol. dichloromethane (10 ml). The reaction mixture was warmed to +23 °C within 2 h and stirred for additional 4 h at this temperature. The product was precipitated by dropwise addition of absol. pentane (50 ml). Recrystallization from absol. dichloromethane (10 ml)/pentane (40 ml) afforded a pale red powder (2.89 g, 85%); m. p. 185 – 189 °C (dec.) (lit.[3] 158 – 162 °C (dec.)). – IR: CNC 1860 (shoulder 1845, 1830) cm^{-1}. – ^{13}C NMR (CD_2Cl_2): C=N $\delta = 157.4$, *i*-C 127.5, *o*-C 131.9, *m*-C 130.9, *p*-C 136.6. – UV: $\lambda_{max} = 293$ (shoulder 303) nm (log $\varepsilon = 4.62$).

Triphenyl-2-azaallenium Hexachloroantimonate (**5b**)[6]: From benzaldehyde (0.54 g, 5.08 mmol, free of benzoic acid) as described for **5a**. The product was not recrystallized. Yield 2.66 g (88%) of a nearly colourless powder; m. p. 144 – 147 °C (dec.). – IR: CNC 1885 cm^{-1}. – ^1H NMR (CD_2Cl_2, 243 K): CH $\delta = 9.64$. – ^{13}C NMR (CD_2Cl_2, 243 K): C=N $\delta = 157.7$, HC=N 143.0, 3-phenyl: *i*-C 124.1, *p*-C 138.5, *o*-C 132.5, *m*-C 131.1, 1-phenyl: *i*-C 126.3, *p*-C 136.8, *o*-C 132.3, *m*-C 130.5. – UV: $\lambda_{max} = 294$ (log $\varepsilon = 4.40$), 260 nm (4.21).

$[C_{20}H_{16}N]SbCl_6$ (604.8) Calcd. C 39.72 H 2.67 N 2.32 Found C 39.61 H 2.81 N 2.26

(2-Methylphenyl)triphenyl-2-azaallenium Hexachloroantimonate (**5c**): From 2-methylbenzophenone (0.99 g, 5.05 mmol) as described for **5a**. The reaction mixture was refluxed in dichloromethane for 8 h until the yellow precipitate of **3a** was completely dissolved. After evaporation of the solvent the brown residue was dissolved in dry dichloromethane (10 ml). Slow addition of dry pentane (40 ml) afforded an oil, which solidified after a short time of stirring. Yield 3.09 g (89%) of a brownish powder, which was recrystallized from dichloromethane (3 ml)/pentane at −25 °C; m. p. 168 – 172 °C. – IR: 1870 cm^{-1}. – ^1H NMR (CD_2Cl_2): CH_3 $\delta = 2.18$. – ^{13}C NMR (CD_2Cl_2): CH_3 $\delta = 21.0$, C=N 156.1, 155.8, 14 aromatic C.

$[C_{27}H_{22}N]SbCl_6$ (694.9) Calcd. C 46.66 H 3.19 N 2.02 Found C 46.82 H 3.19 N 1.97

3-tert-Butyl-1,1-diphenyl-2-azaalenium Hexachloroantimonate (**5d**): From pivalaldehyde (0.43 g, 5.03 mmol) as described for **5a**. Yield 2.45 g (84%) of an instable yellow-orange powder; decomposition without melting above 80 °C. – IR: 1912 cm^{-1}. – ^1H NMR (CD_3CN, 263 K): CH_3 $\delta = 1.40$, NCH 8.83. – ^{13}C NMR (CD_2Cl_2, 263 K): HCN $\delta = 153.2$ (?), C=N 155.8, CH_3 26.3, C 41.1, *p*-C 136.5, *o*-C 132.4, *m*-C 130.8, *i*-C 126.9.

$[C_{18}H_{20}N]SbCl_6$ (584.8) Calcd. C 36.97 H 3.45 N 2.40 Found C 36.43 H 3.11 N 2.44

1,1-Bis(4-dimethylamino)-3,3-diphenyl-2-azaallenium Hexachloroantimonate (**5e**): From 4,4'-bis(dimethylamino)benzophenone (1.35 g, 5.03 mmol) as described for **5a**. The reaction mixture was evaporated under reduced pressure. The residue was dissolved in dichloromethane (20 ml)/methanol (20 ml). Slow addition of pentane afforded green crystals (2.99 g, 78%); dec. above 140°C. – IR: 1590 cm^{-1}. – ^{1}H NMR (CD_3CN): CH_3 δ = 3.16. – ^{13}C NMR (CD_3CN): CH_3 δ = 40.9, C=N 165.1, 156.8, 1-aryl 175.0, 137.0, 117.0, 114.1, 3-aryl 135.4, 133.3, 130.7, 129.8. – UV: λ_{max} = 542 (log ε = 4.69), 423 (4.52), 284 (4.43), 263 nm (4.47).

$[C_{30}H_{30}N_2]SbCl_6$ (767.0) Calcd. C 46.97 H 3.94 N 5.48 Found C 46.73 H 3.98 N 5.52

1,1-(Biphenyl-2,2'-diyl)-3-(4-bromophenyl)-3-phenyl-2-azaallenium Hexachloroantimonate (**5f**): From **1f**$^{25)}$ (1.61 g, 5.00 mmol) and 9-fluorenone (0.91 g, 5.05 mmol) as described for **5a**. The reaction mixture was boiled under reflux for 5 h. Recrystallization from dichloromethane (10 ml)/pentane (15 ml) afforded yellow needles (2.84 g, 75%); m. p. 170–175°C (dec.). – IR: 1880, 1600, 1580 cm^{-1}. – ^{13}C NMR (CD_2Cl_2, 263 K): C=N δ = 161.3, 150.6.

$[C_{26}H_{17}BrN]SbCl_6$ (757.8) Calcd. C 41.21 H 2.26 N 1.85 Found C 41.30 H 2.24 N 1.85

1,1-(Biphenyl-2,2'-diyl)-3-(2-methylphenyl)-3-phenyl-2-azaallenium Hexachloroantimonate (**5g**): From 2-methylbenzophenone (0.99 g, 5.05 mmol) and **1g**$^{31)}$ (1.21 g, 5.00 mmol) as described for **5a**. The reaction mixture was stirred for 10 h at 23°C. With absol. pentane (70 ml) a dark green powder (2.98 g, 86%) was precipitated, which crystallized from acetone/pentane in orange plates; m. p. 193–195°C. – IR: 1880, 1600 cm^{-1}. – ^{1}H NMR (CD_2Cl_2, 263 K): CH_3 δ = 2.51. – ^{13}C NMR (CD_2Cl_2, 263 K): CH_3 δ = 21.7, C=N 160.9, 148.7.

$[C_{27}H_{20}N]SbCl_6$ (692.9) Calcd. C 46.80 H 2.91 N 2.02 Found C 46.75 H 2.77 N 2.05

1,1-(Biphenyl-2,2'-diyl)-3-(4-methylphenyl)-3-phenyl-2-azaallenium Hexachloroantimonate (**5h**): From 4-methylbenzophenone (0.99 g, 5.05 mmol) as described for **5g**. The product was precipitated from the reaction mixture by slow addition of absol. ether (80 ml) affording an orange powder (3.12 g, 90%), which was recrystallized from dichloromethane/ether; m. p. 158–160°C (dec.). – IR: 1880, 1600 cm^{-1}. – ^{1}H NMR (CD_2Cl_2): CH_3 δ = 2.56. – ^{13}C NMR (CD_2Cl_2): CH_3 δ = 22.4, C=N 163.8, 151.1.

$[C_{27}H_{20}N]SbCl_6$ (692.9) Calcd. C 46.80 H 2.91 N 2.02 Found C 46.89 H 2.95 N 1.95

1,1-(Biphenyl-2,2'-diyl)-3-(1-naphthyl)-3-phenyl-2-azaallenium Hexachloroantimonate (**5i**): From-1-benzoylnaphthalene (1.17 g, 5.04 mmol) as described for **5g**. Yield 3.28 g (90%) of a green powder, which was recrystallized from dichloromethane/acetonitrile affording orange needles; m. p. 255–265°C (dec.). – IR: 1880, 1600 cm^{-1}. – ^{13}C NMR (CD_2Cl_2, 263 K): C=N δ = 161.1, 149.3.

$[C_{30}H_{20}N]SbCl_6$ (728.9) Calcd. C 49.43 H 2.77 N 1.92 Found C 49.29 H 2.80 N 2.28

1,1:3,3-Bis(biphenyl-2,2'-diyl)-2-azaallenium Hexachloroantimonate (**5j**): From 9-fluorenone (0.91 g, 5.05 mmol) as described for **5g**. Yield 2.88 g (85%) of a dark green powder, which was recrystallized from hot acetonitrile affording brown crystals; m. p. 255–258°C (dec.). – IR: 1900 (shoulder 1825), 1600 cm^{-1}. – ^{13}C NMR (CH_2Cl_2/CD_3CN 2:1, 263 K): C=N δ = 165.8, 144.6 (2,2'?), 139.2 (4,4'?), 130.6 (6,6'?), 129.7 (1,1'?), 129.0 (5,5'?), 123.7 (3,3'?). – UV: λ_{max} = 342 (log ε = 4.48), 283 (4.51), 264 (5.10), 257 nm (4.99).

$[C_{26}H_{16}N]SbCl_6$ (676.9) Calcd. C 46.13 H 2.38 N 2.07 Found C 45.91 H 2.28 N 2.15

1,1-(Biphenyl-2,2'-diyl)-3-phenyl-2-azaallenium Hexachloroantimonate (**5k**): From benzaldehyde (0.54 g, 5.08 mmol) as described for **5g**. Addition of absol. pentane (30 ml) to the orange suspension yielded an orange powder (2.65 g, 88%); m. p. 189–190°C (dec.). – IR: 1905, 1700, 1590 cm^{-1}. – ^{1}H NMR (CD_3CN/CD_2Cl_2 2:1, 263 K): NCH δ = 9.56. – ^{13}C NMR (CD_3CN/CD_2Cl_2, 2:1, 263 K): C=N δ = 148.0, 145.6 (?), 125.2 (*ipso*?), 133.5 (*o*?), 131.1 (*m*?), 138.6 (*p*?), 129.6 (1,1'?), 144.4 (2,2'?), 123.7 (3,3'?), 138.8 (4,4'?'), 129.0 (5,5'?), 130.7 (6,6'?).

$[C_{20}H_{14}N]SbCl_6$ (602.8) Calcd. C 39.85 H 2.34 N 2.32 Found C 40.04 H 2.41 N 2.52

1,1-(Biphenyl-2,2'-diyl)-3-(4-methoxyphenyl)-3-phenyl-2-azaallenium Hexachloroantimonate (**5l**): From 4-methoxybenzophenone (1.07 g, 5.05 mmol) as described for **5g**. Yield 3.03 g (93%) of an orange powder; m.p. 165 – 168 °C (dec.). – IR: 1870 (shoulder 1810), 1590 cm^{-1}. – ^1H NMR (CD_2Cl_2): CH_3 δ = 4.01. – ^{13}C NMR (CD_2Cl_2): C=N δ = 165.5, 151.9, CH_3 65.9, CO 168.5. – UV: λ_{max} = 346 (log ε = 4.46), 280 (4.43), 262 (4.82), 256 nm (4.75).

$[C_{27}H_{20}NO]SbCl_6$ (708.9) Calcd. C 45.74 H 2.84 N 1.98 Found C 45.69 H 2.54 N 1.99

1,1-(Biphenyl-2,2'-diyl)-3,3-bis(4-methoxyphenyl)-2-azaallenium Hexachloroantimonate (**5m**): From 4,4'-dimethoxybenzophenone (1.22 g, 5.04 mmol) as described for **5g**. The reaction mixture was stirred for 10 h at 23 °C. Precipitation with pentane (70 ml) yielded an orange-yellow powder (3.18 g, 86%); m.p. 190 – 192 °C (dec.). – IR: 1860, 1790 (broad), 1590 cm^{-1}. – ^1H NMR (CD_2Cl_2): CH_3 δ = 3.99. – ^{13}C NMR (CD_2Cl_2): C=N δ = 168.7, 152.9, CO 168.0, CH_3 56.9. – UV: λ_{max} = 372 (log ε = 4.49), 349 (4.53), 262 (4.83), 256 nm (4.77).

$[C_{28}H_{22}NO_2]SbCl_6$ (738.9) Calcd. C 45.51 H 3.00 N 1.90 Found C 45.16 H 3.05 N 1.81

1,1-(Biphenyl-2,2'-diyl)-3,3-bis[4-(dimethylamino)phenyl]-2-azaallenium Hexachloroantimonate (**5n**): From 4,4'-bis(dimethylamino)benzophenone (1.35 g, 5.03 mmol) as described for **5m**. The reaction mixture was evaporated under reduced pressure. Addition of pentane (20 ml) to a solution of the residue in dichloromethane (20 ml)/methanol (20 ml) afforded brown-violet crystals (3.33 g, 87%); dec. above 155 °C. – IR: 1690, 1590 cm^{-1}. – ^1H NMR ([D_6]acetone): CH_3 δ = 3.30. – ^{13}C NMR ([D_6]acetone): C=N δ = 159.9, 157.3, 1-aryl 177.3, 137.4, 115.7, 114.1, 3-aryl 144.4, 135.5, 132.8, 130.0, 126.8, 122.4. – UV: λ_{max} = 556 (log ε = 4.87), 425 (4.54), 304 (4.30), 297 (4.32), 261 (4.87), 254 nm (4.80).

$[C_{30}H_{28}N_3]SbCl_6$ (765.0) Calcd. C 47.10 H 3.69 N 5.49 Found C 47.10 H 3.52 N 5.44

1,1-Bis(4-methoxyphenyl)-3-(1-naphthyl)-3-phenyl-2-azaallenium Hexachloroantimonate (**5o**): From **1o**[25)] (1.47 g, 5.00 mmol) and 4,4'-dimethoxybenzophenone (1.22 g, 5.04 mmol) as described for **5a**. Yield 2.41 g (61%) of yellow-green crystals; m.p. 180 – 183 °C (dec.). – IR: 1850 (shoulder 1830), 1580 cm^{-1}. – ^1H NMR (CD_2Cl_2): CH_3 δ = 3.98. – ^{13}C NMR (CD_2Cl_2): C=N δ = 159.3, 156.3, CH_3 56.7. – UV: λ_{max} = 355 (log ε = 4.53), 271 nm (4.39).

$[C_{32}H_{26}NO_2]SbCl_6$ (791.0) Calcd. C 48.59 H 3.31 N 1.77 Found C 48.88 H 3.18 N 1.80

1,1-Bis[4-(dimethylamino)phenyl]-3-(1-naphthyl)-3-phenyl-2-azaallenium Hexachloroantimonate (**5p**): From 4,4'-bis(dimethylamino)benzophenone (1.35 g, 5.03 mmol) as described for **5o**. The reaction mixture was evaporated under reduced pressure. To the violet solution of the residue in dichloromethane (10 ml)/methanol (20 ml) was added dropwise under stirring pentane (15 ml) precipitating green-brown crystals (2.90 g, 71%); m.p. 160 – 170 °C (dec.). – IR: 1590 cm^{-1}. – ^1H NMR ([D_6]acetone): CH_3 δ = 3.26. – ^{13}C NMR ([D_6]acetone): C=N δ = 165.3, 156.9, CH_3 40.7. – UV: λ_{max} = 546 (log ε = 4.68), 424 (4.51), 282 (4.43), 262 nm (4.44).

$[C_{34}H_{32}N_3]SbCl_6$ (817.1) Calcd. C 49.98 H 3.95 N 5.14 Found C 50.27 H 3.84 N 5.07

1,1-Bis(4-methoxyphenyl)-3,3-diphenyl-2-azaallenium Hexachloroantimonate (**5q**): From **2a**[32)] (1.30 g, 5.00 mmol) and 4,4'-dimethoxybenzophenone (1.22 g, 5.04 mmol) as described for **5a**. Recrystallization from dichloromethane (10 ml)/ether (15 ml) afforded pale yellow crystals (2.75 g, 74%); m.p. 202 – 205 °C (dec.). – IR: 1830 cm^{-1} (broad). – ^1H NMR ($CDCl_3$): CH_3 δ = 3.97. – ^{13}C NMR ($CDCl_3$): CH_3 δ = 56.4, CO 166.6, C=N 160.3, 157.3.

$[C_{28}H_{24}NO_2]SbCl_6$ (740.9) Calcd. C 45.39 H 3.27 N 1.89 Found C 45.78 H 3.17 N 1.99

4-Benzoyl-1-[(diphenylmethylene)carbamoyl]pyridinium Hexachloroantimonate (**19a**): From **1a** (1.22 g, 5.00 mmol) and 4-benzoylpyridine (0.93 g, 5.08 mmol) as described for **5a**. Yield 3.04 g (75%) of a pale yellow powder, which was recrystallized from dichloromethane (10 ml)/acetonitrile (2 ml)/pentane; m.p. 71 – 74 °C (dec.). – IR: NCO 2250 (w), CO 1760 (vs), 1720, 1670 (vs) cm^{-1}. – ^1H NMR (CD_3CN): 2-H δ = 9.65 (d, *J* = 6.7 Hz), 3-H 8.38 (d, *J* = 6.7 Hz), CH_2Cl_2 5.43. – ^{13}C NMR (CD_3CN): CO, CN, C-2,6, C-4 δ = 192.1, 186.8, 158.7, 143.2, 153.0, CH_2Cl_2 55.1, no other signals for sp^3 carbons.

$[C_{26}H_{19}N_2O_2]SbCl_6 \cdot CH_2Cl_2$ (810.8) Calcd. C 39.99 H 2.61 N 3.46
Found C 39.80 H 2.49 N 3.32

4-Benzoyl-1-(9-isocyanato-9-fluorenyl)pyridinium Hexachloroantimonate (**20g**): From **1g** (1.21 g, 5.00 mmol) and 4-benzoylpyridine (0.93 g, 5.08 mmol) as described for **5a**. Yield 3.36 g (83%) of an orange powder, which was recrystallized from dichloromethane/pentane; m.p. 101 – 104°C (dec.). – IR: NCO 2250 (vs), CO 1720, 1670, 1600 cm^{-1}. – ^1H-NMR (CD_3CN, 163 K): 2,6-H δ = 9.14 (d, *J* = 6.7 Hz), 3,5-H 8.17 (d, *J* = 6.7 Hz), CH_2Cl_2 5.46. – ^{13}C NMR (CD_3CN, 163 K): CO δ = 192.3, C-4 154.9, sp^3-C 89.6, CH_2Cl_2 55.4.

$[C_{26}H_{17}N_2O_2]SbCl_6 \cdot CH_2Cl_2$ (808.8) Calcd. C 40.09 H 2.37 N 3.46
Found C 40.25 H 2.23 N 3.67

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