On the Reactions of α-Chlorocarbenium Ions with Ammonium Thiocyanate and Potassium Cyanate

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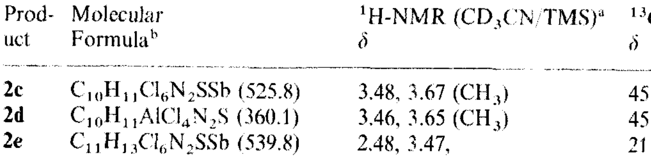
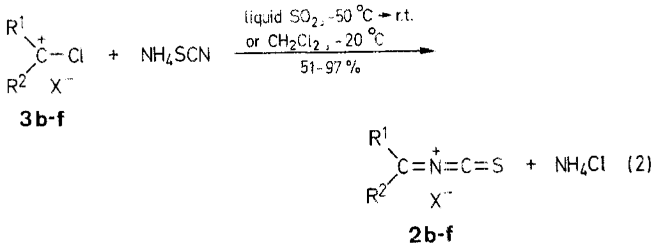
Preparations of 1-thia-3-azabutatrienium salts **2** from ammonium thiocyanate and α-chlorocarbenium salts **3** of the Vilsmeier-Arnold type, and of the geminal diisothiocyanates **6** are described. α-Chlorocarbenium salts react with potassium cyanate and ketones or tertiary carboxamides to give 2-azaallenium salts **9**. A mechanistically interesting reaction of α-chlorocarbenium cations with carbonyl compounds has been observed.

Reports on the reactive 1-thia-3-azabutatrienium salts **2** seem to be scarce.[1,2,3] The stable hexachloroantimonate **2a** was prepared by chloride abstraction from the α-chloro isothiocyanate **1**[2,4] with antimony pentachloride, while two other salts **2** were obtained by rather special methods.[1,3]



Since a synthesis of wider scope for compounds **2** seemed to be a prerequisite to the study of their chemical properties, we tried reactions of α-chlorocarbenium salts **3** with ammonium thiocyanate.



2–10[a]	R^1	R^2
b	$(CH_3)_2N$	H
c	$(CH_3)_2N$	C_6H_5
d	$(CH_3)_2N$	C_6H_5
e	$(CH_3)_2N$	$4\text{-}CH_3C_6H_4$
f	$(CH_3)_2N$	$(CH_3)_2N$
g	C_6H_5	C_6H_5
h	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$
i	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$
j	C_6H_5	C_6H_5
k	C_6H_5	Cl
l	$(CH_3)_2N$	H
m	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$
n	$CH_3(C_6H_5)N$	H

2–10[a]	R^3	R^4
b	$(CH_3)_2N$	H
c		
d		
e		
f		
g	C_6H_5	C_6H_5
h	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$
i	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$
j	C_6H_5	$4\text{-}CH_3OC_6H_4$
k	C_6H_5	C_6H_5
l	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$
m	$CH_3(C_6H_5)N$	H
n	$CH_3(C_6H_5)N$	H

a $X = SbCl_6$ in all cases except for **d**, where $X = AlCl_4$

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

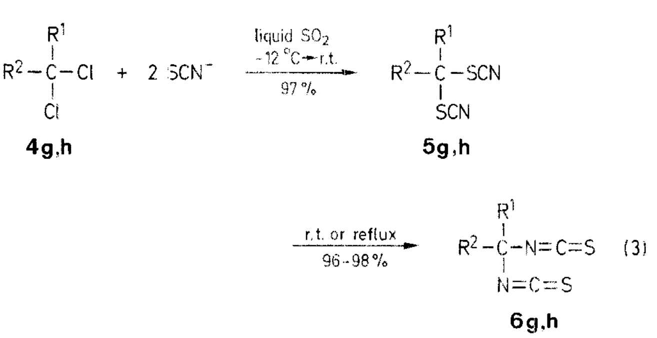
Product	Molecular Formula[b]	^{1}H-NMR (CD_3CN/TMS)[a] δ	^{13}C-NMR (CD_3CN/TMS)[a] δ	IR (CH_2Cl_2) ν (cm^{-1})
2c	$C_{10}H_{11}Cl_6N_2SSb$ (525.8)	3.48, 3.67 (CH_3)	45.4, 45.5 (CH_3); 154.9, 164.8 (C=N)	1920, 1640
2d	$C_{10}H_{11}AlCl_4N_2S$ (360.1)	3.46, 3.65 (CH_3)	45.3, 45.4 (CH_3); 155.0, 164.7 (C=N)	1920, 1630
2e	$C_{11}H_{13}Cl_6N_2SSb$ (539.8)	2.48, 3.47, 3.63 (CH_3)	21.9, 45.5 (CH_3); 154.6, 164.6 (C=N); 127.4, 129.2, 130.6, 131.1 (Ph)	1920, 1620
2f	$C_6H_{12}Cl_6N_3SSb$ (492.7)	3.18 (CH_3)	42.8 (CH_3); 151.5, 147.0 (C=N)	1990, 1640
3e	$C_{10}H_{13}Cl_7NSb$ (517.1)	2.48, 3.74, 3.87 (CH_3)	21.9, 49.2, 50.2 (CH_3); 175.0 (C=N); 128.5, 130.1, 131.0, 148.1 (Ph)	1620, 1600
5h[c]	$C_{15}H_8Cl_2N_2S_2$ (351.3)	7.46 (Ph)	74.9 (C); 108.3 (SCN); 129.2, 129.5, 135.6, 136.8 (Ph)	2140, 1585
6g	$C_{15}H_{10}N_2S_2$ (282.4)		84.9 (C); 146.1 (NCS); 126.0, 129.8, 130.4, 141.7 (Ph)	1975
6h[c]	$C_{15}H_8Cl_2N_2S_2$ (351.3)	7.36 (Ph)	82.3 (C); 146.3 (NCS); 126.6, 128.3, 135.2, 138.9 (Ph)	1980
9m	$C_{23}H_{23}Cl_6N_2O_2Sb$ (693.9)	3.92 (NCH_3), 3.95 (OCH_3), 836 (=CH)	39.9 (NCH_3); 56.9 (OCH_3); 163.1 (HC=N); 186.8 (C=N)	1680
9n	$C_{16}H_{18}Cl_6N_3Sb$ (586.7)	3.77 (CH_3), 8.74 (CH)	38.2 (CH_3); 167.9 (C=N); 123.6, 130.0, 130.9, 143.0 (Ph)	1600, 1550

[a] Bruker WM-250-spectrometer; ^{1}H-NMR at 303 K, 250 MHz; ^{13}C-NMR at 263 K.

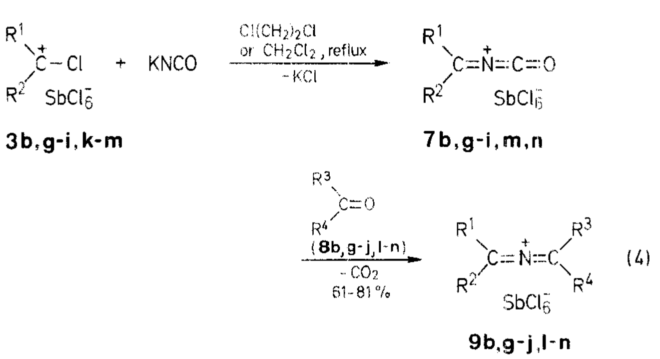
[b] Satisfactory microanalyses obtained: C ±0.30, H ±0.30, N ±0.30; except for **2d**, which was very hygroscopic.

[c] NMR spectra in $CDCl_3$.

Treating the Vilsmeier-Arnold reagent **3b** with one equivalent of ammonium thiocyanate in liquid sulfur dioxide resulted in the formation of the hexachloroantimonate **2b** in 83 % yield. Compounds **2c–f** were similarly prepared. These cumulenes all show strong and broad IR absorptions for N=C=S between 1910 and 1990 cm^{-1} (Table). Interestingly, the bis(dimethylamino)-substituted salt **2f** is stable in its monomeric form, while the 1-oxa analogue of **2f** can only be obtained as a dimer. Stable diarylchlorocarbenium salts have been described by Volz and coworkers.[5,6] It turned out that reactions of diarylchlorocarbenium hexachloroantimonates **3g, h** with thiocyanate under different conditions afforded only mixtures. On the other hand, when the dichloromethane **4h** was treated with two equivalents of ammonium thiocyanate in liquid sulfur dioxide the dithiocyanate **5h** was obtained almost quantitatively. With one equivalent of thiocyanate mixtures of compounds containing **5h** were obtained. In boiling 1,2-dichloroethane the dithiocyanate **5h** rearranged smoothly to the geminal diisothiocyanate **6h**. Under similar conditions the dichlorodiphenylmethane **4g** gave the geminal diisothiocyanante **6g** directly. Apparently, the intermediary dithiocyanate **5g** rearranges too fast to permit its isolation. Thus, while cumulenes **2** can not be obtained by reaction of diarylchlorocarbenium salts or dichlorodiarylmethanes with thiocyanate ions, the preparations of **6g, h** themselves may be of interest since only few geminal diisothiocyanates seem to be known in the literature.[7]

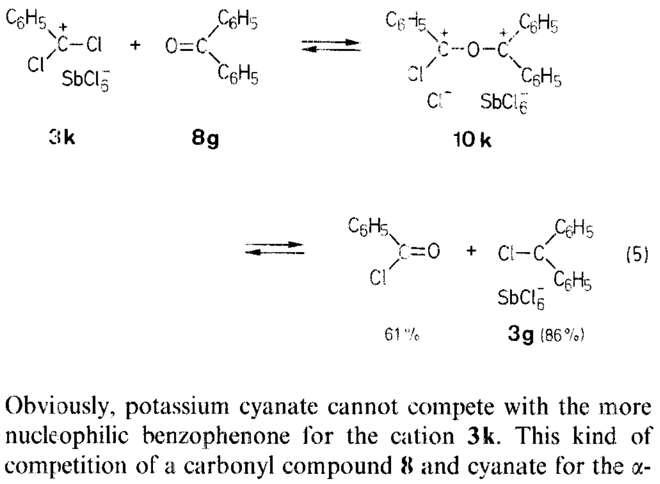


The question then arose, whether in the reactions described so far the thiocyanate ion could be replaced by cyanate. Kantlehner et al.[8] described the reaction of the Vilsmeier-Arnold reagent **3b** (X=Cl) with potassium cyanate in the presence of *N,N*-dimethylformamide to obtain **9b** in 86 % yield. It was now found that, probably due to low solubility, the reaction of potassium cyanate with the diarylchlorocarbenium salts **3g–i** in liquid sulfur dioxide is slow, but in boiling dichloromethane (b.p. 40 °C) or 1,2-dichloroethane (b.p. 83 °C) the characteristic[2] IR absorption at 2220 cm^{-1} for C=N=C=O soon developed, indicating the formation of 1-oxa-3-aza-butatrienium salts **7**. Since cumulenes **7** are thermally unstable in solution, we were not able to isolate pure compounds. Therefore, the reactions were repeated in the presence of ketones **8**, which are known[9] to react with **7** to give 2-azaallenium salts **9**. Compounds **9g–j** were indeed isolated in high yields. Unfortunately, only thermally stable 2-azaallenium salts **9** can be prepared by this inexpensive method.



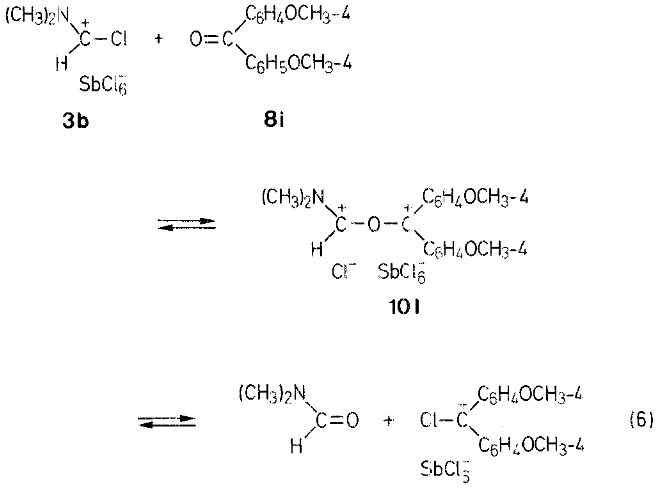
1-Oxa-3-azubutatrienium salts **7** have recently been synthesized by diverse methods.[2,10–12]

An interesting exchange of oxygen was observed for the reaction of the dichlorocarbenium ion **3k** with benzophenone. In the presence or absence of potassium cyanate only benzoyl chloride and **3g** were obtained. This reaction may be explained by an attack of benzophenone on the carbenium ion **3k** according to the following scheme:



Obviously, potassium cyanate cannot compete with the more nucleophilic benzophenone for the cation **3k**. This kind of competition of a carbonyl compound **8** and cyanate for the α-chlorocarbenium cation **3** also has to be taken into account in the following reactions.

For instance, the Vilsmeier-Arnold reagent **3b** reacts with potassium cyanate in the presence of 4,4′-dimethoxybenzophenone **8i** to give a mixture of Gold's salt[13] **9b** and the expected compound **9l** in the ratio 2:1, together with an unidentified product. The formation of **9b** must be explained as arising from a reaction sequence (eq. 6) *via* the dication ether **10l**.[12] The dimethylformamide **8b** formed then enters the sequence depicted in eq. 4 to give Gold's salt **9b** with still unreacted **3b** *via* **7b**.



Exchange reactions according to eq. 6 have first been described by Fritz et al.[14] For the exchange reaction (eq. 6) between the Vilsmeier-Arnold reagent **3b** and *N,N*-dimethylformamide, a barrier to activation $\Delta G^{\neq}$ of about 67 kJmol^{-1} was measured.[15] Generally, if the sequences represented by eqs. 4 and 6 are simultaneously operative, two carbonyl compounds **8** (R^1R^2CO and R^3R^4CO) can react with two butatrienium cations **7** (R^1R^2CNCO and R^3R^4CNCO) to give three different 2-azaallenium ions **9** ($R^1R^2CNCR^1R^2$, $R^1R^2CNCR^3R^4$, and $R^3R^4CNCR^3R^4$). In the experiment described above the combination $R^3R^4CNCR^3R^4$ was not observed.

It has been reported[16] that cumulenes **7** react with tertiary carboxamides leading to aza substituted 2-azaallenium salts. When **3i** was treated with *N*-methylformanilide **8m** in the presence of potassium cyanate a mixture of **9m** and the symmetric salt **9n**[17] in the ratio 4:1 was obtained.

This result again indicates that the reaction sequences represented by eqs. 4 and 6 are both operative, but that this time the combination $R^1R^2CNCR^1R^2$ **(9i)** was not formed.

The chemistry of dication ethers of type **10** has recently been investigated.[18-20]

Only absolute solvents dried by standard methods and distilled antimony pentachloride are used in the following procedures. All experiments are carried out with exclusion of moisture.

4-(Dimethylamino)-1-thia-3-azabutatrienium Hexachloroantimonate (2b):[3]
A solution of ammonium thiocyanate (3.81 g, 50 mmol) in liquid sulfur dioxide (50 mL) is added dropwise within 2 h to a solution of **3b**[21] (21.35 g, 50 mmol) in liquid sulfur dioxide (80 mL) at −50 °C. A voluminous colorless precipitate dissolves slowly when the reaction mixture is warmed to +23 °C. After slow (about 6 h) evaporation of the solvent the residue is suspended in acetonitrile (100 mL). Filtration of ammonium chloride and evaporation of the solvent affords a yellow powder; yield: 18.69 g (83 %); m.p. 122–124 °C; Lit.[3] m.p. 122–124 °C).

4-(Dimethylamino)-4-phenyl-1-thia-3-azabutatrienium Hexachloroantimonate (2c):
Compound **3c**[12] (5.03 g, 10 mmol) is reacted in liquid sulfur dioxide (50 mL) as described for **2b**. After evaporation of the solvent the residue is stirred in CH_2Cl_2 (70 mL). Filtration and evaporation of solvent gives a yellow powder, which is recrystallized from CH_2Cl_2/CCl_4 (6:5, 110 mL) at −20 °C; yield: 4.10 g (78 %); m.p. 137–140 °C.

4-(Dimethylamino)-4-phenyl-1-thia-3-azabutatrienum Tetrachloroaluminate (2d):
Aluminum chloride (2.67 g, 20 mmol) is added to a solution of **3d** (X = Cl;[22,23] 4.08 g, 20 mmol) in CH_2Cl_2 (25 mL) at −20 °C. After stirring for 2 h at −20 °C, during which time the suspended aluminum chloride dissolves, the solvent is removed under reduced pressure leaving a brown oil, which is added to a solution of ammonium thiocyanate (1.53 g, 20 mmol) in liquid sulfur dioxide (20 mL) at −60 °C. After 1 h at −20 °C and slow (7 h) evaporation of the solvent the residue is suspended in CH_2Cl_2/acetonitrile (1:1, 80 mL). Filtration and evaporation of solvent gives a hygroscopic, pale yellow solid; yield: 5.98 g (83 %); m.p. 80–81 °C.

4-(Dimethylamino)-4-(4-methylphenyl)-1-thia-3-azabutatrienium Hexachloroantimonate (2e):
Compound **3e** (5.17 g, 10 mmol) is reacted in liquid sulfur dioxide (60 mL) as described for **2c**, but without recrystallization, to give **2e** as a yellow, moisture sensitive powder; yield: 5.23 g (97 %).

4,4-Bis(dimethylamino)-1-thia-3-azabutatrienium Hexachloroantimonate (2f):
A solution of **3f** (X = Cl;[12] 3.42 g, 20 mmol) in CH_2Cl_2 (20 mL) is added dropwise to a solution of ammonium thiocyanate (1.55 g, 20.4 mmol) in liquid sulfur dioxide (70 mL) at −20 °C. The mixture is stirred for 120 h at −20 °C. After filtration of ammonium chloride, the solution is again cooled to −20 °C and antimony pentachloride (5.98 g, 20 mmol) is added. After stirring for 15 min and warming to +23 °C, the mixture is concentrated under reduced pressure to a volume of 5 mL. The precipitate is filtered to give a yellow powder; yield: 5.05 g (51 %); m.p.: dec above 189 °C.

From the mother liquor further **2f** is isolated, which is contaminated mainly with **3f**.

Chloro(dimethylamino)(4-methylphenyl)methenium Hexachloroantimonate (3e):
At −30 °C a solution of *N,N*-dimethyl-4-methylbenzamide (16.32 g, 10 mmol) in CH_2Cl_2 (100 mL) is added dropwise to liquid phosgene (60 mL). *Caution:* working with phosgene is extremely hazardous and requires special precautionary measures.[24] After stirring for 17 h at −30 °C excess phosgene and CH_2Cl_2 are removed under reduced pressure. The residue is dissolved in CH_2Cl_2 (100 mL). At 0 °C antimony pentachloride (29.90 g, 10 mmol) is added dropwise. The colorless precipitate is isolated and washed with a small portion of CH_2Cl_2; yield: 42.92 g (83 %); m.p. 145–147 °C.

Bis(4-chlorophenyl)methyl Dithiocyanate (5h):
A solution of **4h**[25] (3.06 g, 10 mmol) and ammonium thiocyanate (1.52 g, 20 mmol) in liquid sulfur dioxide (50 mL) is stirred for 1 h at −12 °C. The mixture is slowly warmed to +23 °C. When the sulfur dioxide is completely evaporated, the residue is stirred for 5 min in CH_2Cl_2 (150 mL). Filtration and evaporation of the solvent under reduced pressure affords a colorless powder; yield: 3.41 g (97 %; m.p. 144–146 °C.

Diphenylmethyl Diisothiocyanate (6g):
A solution of **4g** (4.74 g, 20 mmol) and ammonium thiocyanate (3.05 g, 40 mmol) in liquid sulfur dioxide (100 mL) is stirred for 6 h at −12 °C. After warming to +23 °C and evaporation of sulfur dioxide, the residue is stirred in CH_2Cl_2 (120 mL) for 1 h. The suspension is filtered, and the solvent is removed under reduced pressure leaving a brownish oil, which could not be distilled without decomposition; yield: 5.42 g (96 %).

Bis(4-chlorophenyl)methyl Diisothiocyanate (6h):
A solution of **5h** (3.51 g, 10 mmol) in 1,2-dichloroethane (50 mL) is refluxed for 24 h. Evaporation of the solvent under reduced pressure affords a brown oil, which decomposed on attempted distillation; yield: 3.44 g (98 %).

Reaction of 3g with Potassium Cyanate:
To a mixture of **4g** (1.19 g, 5 mmol) and potassium cyanate (0.41 g, 5 mmol) in CH_2Cl_2 (20 mL), a solution of antimony pentachloride (1.50 g, 5 mmol) in CH_2Cl_2 (10 mL) is added dropwise at −40 °C. After refluxing for 15 h, the reaction mixture showed a strong IR absorption at 2220 cm^{-1} (Lit.[2]: 2218 cm^{-1}), characteristic for **7g**, together with other strong bands between 1580 and 1860 cm^{-1}, which do not arise from **7g**. Evaporation of the solvent affords a mixture of compounds.

Tetraphenyl-2-azaallenium Hexachloroantimonate (9g):[9]
Antimony pentachloride (2.99 g, 10 mmol) in 1,2-dichloroethane (10 mL), is added dropwise at −40 °C to a mixture of **4g** (1.19 g, 5 mmol), **8g** (0.91 g, 5 mmol), and potassium cyanate (0.41 g, 5 mmol) in 1,2-dichloroethane (30 mL). After stirring for 15 min the mixture is refluxed for 2 h. Filtration and evaporation of the solvent gives, after washing with ether, a dark red-violet powder; yield: 2.76 g (81 %).

Recrystallization from acetonitrile/ether (1:12, 65 mL) at −50 °C affords a pure sample; m.p. 186–189 °C (Lit.[9] m.p. 185–189 °C (dec)).

Tetrakis(4-chlorophenyl)-2-azaallenium Hexachloroantimonate (9h):[12]
Compounds **4h** (1.53 g, 5 mmol) and **8h** (1.26 g, 5 mmol) are reacted as described for **9g**. After refluxing for 8 h and filtration, the reaction mixture is cooled to −20 °C. Dropwise addition of pentane (20 mL) results in the formation of a pale yellow powder; yield: 2.74 g (67 %; m.p.: dec above 222 °C (Lit.[12] m.p.: dec above 230 °C).

Tetrakis(4-methoxyphenyl)-2-azaallenium Hexachloroantimonate (9i):[12]
Compounds **4i**[26] (1.50 g, 5 mmol) and **8i** (1.21 g, 5 mmol) are reacted as described for **9g** (but 5 h reflux). The oily product solidifies to a yellow-brown powder on washing with ether; yield: 2.54 g (63 %).

Chromatography on silica gel (20 cm, ∅ 2 cm) with CH_2Cl_2 as eluent affords the pure compound; m.p. 191–194 °C (dec) (Lit.[12] m.p. 189–192 °C (dec)).

(4-Methoxyphenyl)triphenyl-2-azaallenium Hexachloroantimonate (9j):[12]
Compounds **4g** (2.37 g, 10 mmol) and **8j** (2.12 g, 10 mmol) are reacted as described for **9g**. The oily product is purified by chromatography on silica gel (30 cm, ∅ 4 cm) with CH_2Cl_2 as eluent affording a yellow powder; yield: 4.33 g (61 %); m.p. 145–147 °C (dec) (Lit.[12] m.p. 144–146 °C (dec)).

Reaction of Trichlorophenylmethane with Antimony Pentachloride and Benzophenone:
A solution of antimony pentachloride (2.99 g, 10 mmol) in CH_2Cl_2 (10 mL) is added dropwise at −50°C to a solution of trichlorophenylmethane (1.96 g, 10 mmol) in CH_2Cl_2 (20 mL). An orange solid, assumed to be **3k**, precipitates. It dissolves again after dropwise addition of a solution of **8g** (1.82 g, 10 mmol) in CH_2Cl_2 (10 mL) at +23°C. After stirring for 24 h at +23°C, pentane (20 mL) is added to the reddish-brown reaction mixture, and a yellow powder is filtered off; yield: 4.63 g (86%).

The IR (1590, 1570, 1360 cm^{-1} in CH_2Cl_2) and the complicated ^1H-NMR spectra of this product are identical to those of authentic **3g**.[5]

The filtrate is evaporated under reduced pressure leaving a colorless oil, identified as pure benzoyl chloride (IR, NMR); yield: 0.86 g (61%).

The same products are obtained when the experiment is repeated in the presence of potassium cyanate (0.82 g, 10 mmol).

Reaction of 3b with Potassium Cyanate and 8i:
Oxalyl chloride (1.27 g, 10 mmol) in CH_2Cl_2 (10 mL) is added dropwise to a solution of **8b** (0.73 g, 10 mmol) in CH_2Cl_2 (20 mL) at 0°C. When the evolution of carbon dioxide has ceased (ca. 30 min), potassium cyanate (0.81 g, 10 mmol) and a solution of **8i** (2.47 g, 10 mmol) in CH_2Cl_2 (10 mL) are added. The mixture is cooled to −40°C, and a solution of antimony pentachloride (2.99 g, 10 mmol) in CH_2Cl_2 (10 mL) is added dropwise. Stirring for 3 h at +23°C, filtration and evaporation of the solvent affords an oil, which solidifies on stirring in pentane (50 mL) and then in ether (50 mL) to give an orange powder (3.51 g). According to the ^1H-NMR spectrum, this powder consists of a mixture of starting materials **8i** and **3b** plus **9b**[11] and **9l**[11] plus an unidentified compound in the ratio 2:2:2:1:2.

Reaction of 3i with Potassium Cyanate and 8m:
A mixture of **4i** (2.97 g, 10 mmol) and potassium cyanate (0.82 g, 10 mmol) in CH_2Cl_2 (40 mL) show no reaction after reflux for 30 h. After cooling the reaction mixture to −40°C, solutions first of **8m** (1.35 g, 10 mmol) in CH_2Cl_2 (10 mL) and then of antimony pentachloride (2.99 g, 10 mmol) in CH_2Cl_2 (10 mL) are added dropwise. The reaction mixture is stirred for 20 h at +23°C. Filtration of potassium chloride, evaporation of the solvent, and stirring of the oily residue in pentane (50 mL) and then in ether (50 mL) affords an orange-red powder (3.61 g), which according to the ^1H-NMR spectrum consists of a mixture of **9m** and **9n** in the ratio 4:1.

1,1-Bis(4-methoxyphenyl)-3-(*N*-methyl-*N*-phenylamino)-2-azaallenium Hexachloroantimonate (9m):
A solution of **8i** (1.21 g, 5 mmol) in CH_2Cl_2 (10 mL) is added dropwise to a solution of **7n**[12] (2.48 g, 5 mmol) in CH_2Cl_2 (40 mL). After stirring for 2 h at +23°C the solvent is evaporated. The residue is dissolved in CH_2Cl_2 (10 mL). Slow addition of ether (40 mL) at −40°C and recrystallization of the precipitate from $CHCl_3$ (20 mL) affords a yellow powder; yield: 2.50 g (72%); m.p. 153–156°C (dec).

1,3-Bis(N-methyl-N-phenylamino)-2-azaallenium Hexachloroantimonate (9n):
Compound **8m** (0.68 g, 5 mmol) is reacted as described for **9m**. The crude product is stirred in $CHCl_3$ (10 mL) giving a yellow powder; yield: 2.08 g (71%); m.p. 193–195°C (dec).

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