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AMINO SUBSTITUTED 1-OXA-3-AZABUTATRIENIUM SALTS: PREPARATION, STRUCTURE AND REACTION WITH CARBONYL COMPOUNDS

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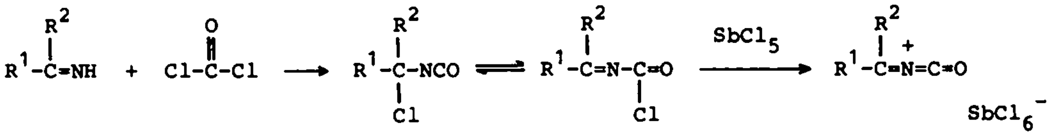
Abstract - N,N-Dimethylformamide (4a) and N,N-dimethylpivalamide (4b) react with carbonyl chloride isocyanate (5) in the presence of antimony pentachloride to afford the amino substituted 1-oxa-3-azabutatrienium hexachloroantimonates 6a,b. An X-ray diffraction analysis of 6a confirms the proposed structure. The heterocumulenes 6a,b react with aldehydes, ketones and tertiary carboxamides to give the amino substituted 2-azaallenium salts 13a-o in high yields.

We recently described [1] the preparation of 1-oxa-3-azabutatrienium salts 3, a new class of highly reactive heterocumulenes, from α-chloro isocyanates 2 [2] and Lewis acids, e.g. antimony pentachloride.



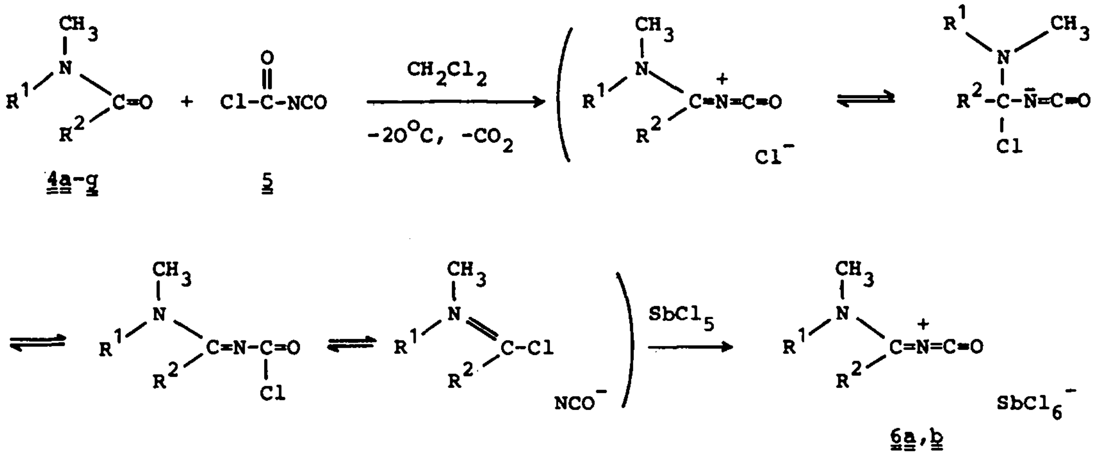
$$R^1-\overset{\overset{R^2}{|}}{C}=NH + Cl-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow R^1-\underset{\underset{Cl}{|}}{\overset{\overset{R^2}{|}}{C}}-NCO \rightleftharpoons R^1-\overset{\overset{R^2}{|}}{C}=N-\underset{\underset{Cl}{|}}{C}=O \xrightarrow{SbCl_5} R^1-\overset{\overset{R^2}{|}}{C}\overset{+}{=}N=C=O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

1 2 3

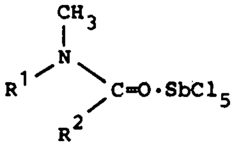
R^1, R^2 = aryl or alkyl

This reaction sequence requires imines 1 as starting materials, which are not widely accessible.

We have now found that the tertiary amides 4a,b react with commercially available carbonyl chloride isocyanate (5) [3] and antimony pentachloride to give the amino substituted 1-oxa-3-azabutatrienium hexachloroantimonates 6a,b. This transformation parallels the Vilsmeier-Arnold reaction of tertiary carboxamides with phosgene [4]. Thus, stirring a mixture of N,N-dimethylformamide (4a) and 5 in dichloromethane at -20°C gives an instable precipitate, which shows an isocyanate band in its IR spectrum (2200 cm^{-1} in CH_2Cl_2), but which might be a mixture of compounds according to its ^1H NMR spectrum. This precipitate can be transformed into a



4,**6**,**7**,**12**	R^1	R^2
a	CH_3	H
b	CH_3	$(CH_3)_3C$
c	CH_3	CH_3
d	$(CH_2)_3$	
e	CH_3	C_6H_5
f	CH_3	C_6H_5-CH=CH
g	CH_3	C_2H_5O



7b-**f**

homogeneous crystalline salt (**6a**) on addition of one equivalent of antimony pentachloride. Similarly, the hexachloroantimonate **6b** was obtained in 81% yield from N,N-dimethylpivalamide **4b**.

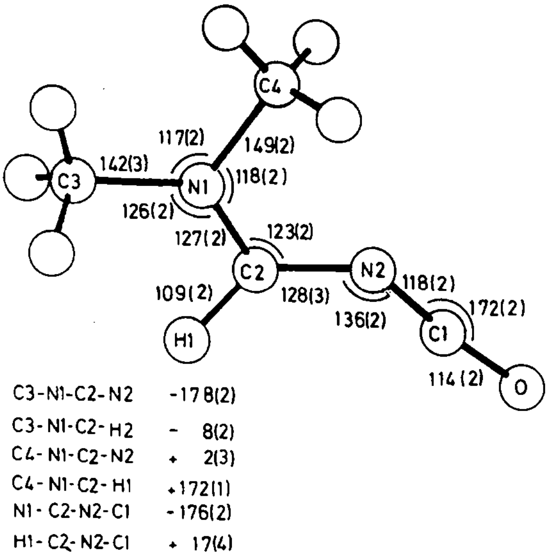
Attempts to react the tertiary amides **4c**-**f** or their antimony pentachloride complexes **7c**-**f** with carbonyl chloride isocyanate **5** under different conditions, led to mixtures of compounds. Apparently, only aliphatic carboxamides not bearing an α-hydrogen atom give **6** without side reactions. No reaction took place between **5** and the urethane **4g**.

Strong IR absorptions (CH_2Cl_2) observed at 2240 and 1680 cm^{-1} for compound **6a**, and at 2260 and 1620 cm^{-1} for compound **6b** can be assigned to C=N=C=O and C=N functional groups. The NMR spectra of **6a**,**b** show nonequivalent NCH_3 groups indicating hindered rotation around the $(CH_3)_2N$-C bonds. To confirm the proposed structure **6** an X-ray diffraction analysis was carried out for **6a**.

X-Ray Diffraction Analysis of **6a**

6a, $[C_4H_7N_2O]^+[SbCl_6]^-$, monoclinic, space group $P2_1/c$ (No. 14 $^{5)}$), $Z = 4$, $a = 712.8(2)$, $b = 1196.8(4)$, $c = 1576.5(7)$ pm, $\beta = 95.85(3)^\circ$, $V = 1338 \cdot 10^6$ pm^3, $d_{calc} = 2.15$ gcm^{-3}, $\mu_{Mo-K_\alpha} = 32.4$ cm^{-1}, $T = 293$ K, ω-scan, $\Delta\omega = 1.0^\circ$, $2.3 < \dot{\omega} < 29.3^\circ min^{-1}$, $2^\circ < 2\Theta < 43^\circ$, 938 independent significant reflections ($I \geq 2\ (I)$). The cell constants and the reflections were measured on a Syntex-P3 diffractiometer with a graphite monochromator, $\lambda_{Mo-K_\alpha} = 71.069$ pm. The structure was solved using the program SHEL-XTL [6] by direct methods. The methyl hydrogen atoms were fixed on calculated geometrically ideal positions. The anisotropic refinement led to agreement factors $R_1 = 0.048$ and $R_2 = 0.052$.

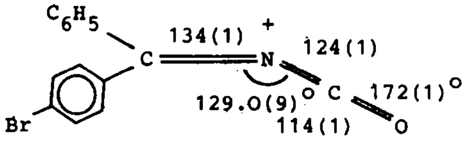
A list of atomic coordinates with LS-computed standard deviations is given in Table 1. Fig. 1 shows a molecular plot with selected bond lengths, bond angles and torsional angles for the cation of 6a.



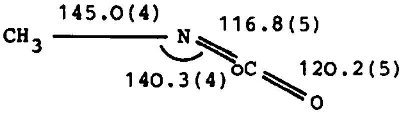
C3-N1-C2-N2	-178(2)
C3-N1-C2-H2	- 8(2)
C4-N1-C2-N2	+ 2(3)
C4-N1-C2-H1	+172(1)
N1-C2-N2-C1	-176(2)
H1-C2-N2-C1	+ 17(4)

Figure 1. Molecular Plot with Selected Bond Lengths [pm], Bond Angles and Torsional Angles [°] for the Cation of 6a.

The crystals of 6a consist of discrete $[C_4H_7N_2O]^+$ cations and $SbCl_6^-$ anions. The observed geometrical parameters may be compared with those of 8 (X-ray diffraction) [1,7], 9 (electron diffraction) [8], 10 (microwave spectroscopy) [9] and 11 (electron diffraction) [10] (bond distances in pm).



8 $SbCl_6^-$



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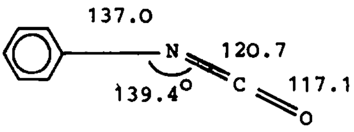

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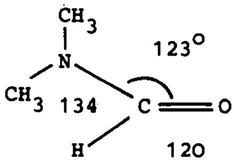
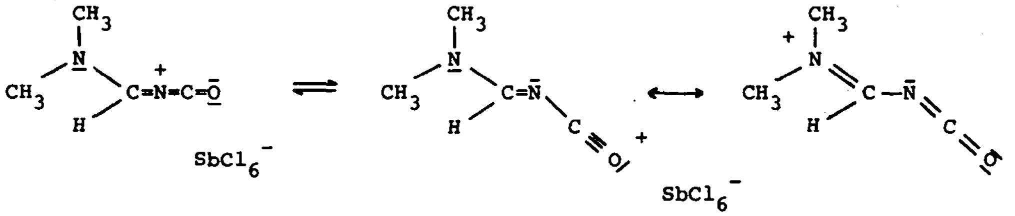


11

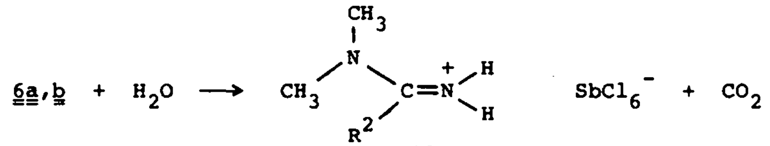
The cumulenic unit C2-N2-C1-O in 6a is not linear. The C2-N2-C1 bond angle (136(2)°) is larger than the corresponding angle in 8. In both molecules the NCO unit is slightly bent (172(2)°). This is, apparently, an inherent property of the molecules and not a consequence of crystal packing forces[11,12]. All heavy atoms of 6a are lying almost in one plane indicating charge delocalization over the whole molecule. To our knowledge X-ray structural data for simple isocyanates, which could be compared with those for 6a, have not been reported in the literature [13]. Noteworthy is the short N2-C2 distance (128(3) pm) in 6a as compared to 8 (134(1) pm). The C2-N1 bond length (127(2) pm) in 6a is numerically smaller than the corresponding distance (134(4) pm) in dimethylformamide (11), but comparable to that in the antimony pentachloride complex of dimethylformamide [14] (129(1) pm). These data, together with the short C1-O bond (114(2) pm), suggest important contributions of the canonical forms 6a' and 6a''. Typical acylium salts have C—O bond lengths of 111 pm [15].



6a 6a' 6a''

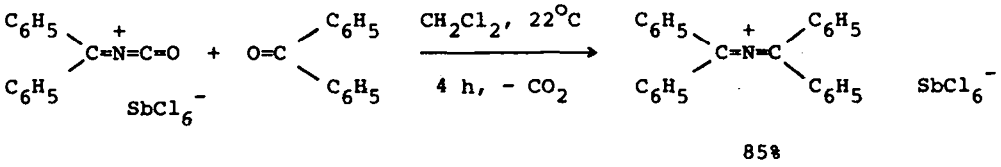
Some Reactions of Compounds 6

The butatrienium salts 6a,b are hydrolyzed with water to the amidinium salts 12a,b [1].



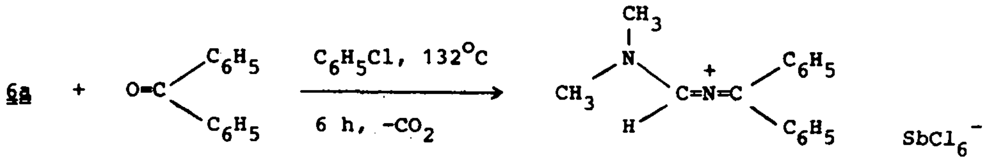
12a,b

Isocyanates with electron withdrawing substituents are known to react with carbonyl groups with elimination of carbon dioxide to give azomethines [16,17]. The reaction of 1-oxa-3-azabutatrienium salts, 3, with aldehydes, ketones [18] and tertiary carboxamides [19] has been used for a general synthesis of 2-azaallenium salts, e.g.

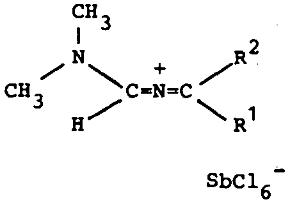


Due to the effective resonance stabilization of 6a the reaction of this compound with benzophenone requires stronger reaction conditions. Aldehydes, ketones and tertiary carboxamides, especially those with electron rich carbonyl groups, react similarly to give the 2-azaallenium salts 13a-k.

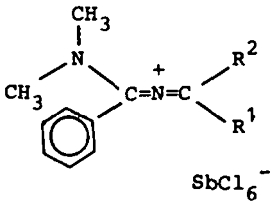
No reaction was observed between 6a and benzoquinone or anthraquinone. From



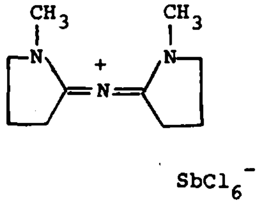
13a, 90%



13a-**k**



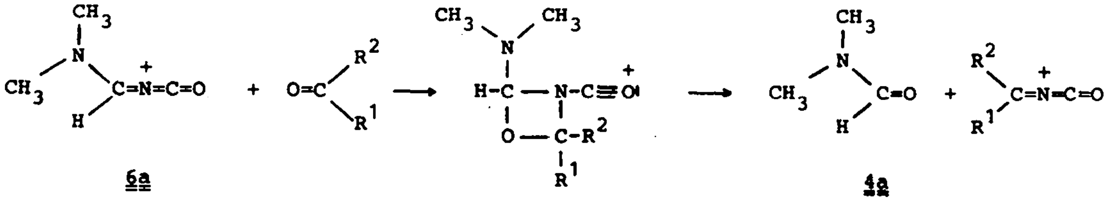
13l-**n**



13o

13	R^1	R^2
a	C_6H_5	C_6H_5
b	$2\text{-}C_6H_4\text{-}C_6H_4\text{-}2'$	
c	$C_6H_4OCH_3\text{-}(4)$	$C_6H_4OCH_3\text{-}(4)$
d	C_6H_5	$CH{=}CHC_6H_5$
e	$(CH)_6$	
f	C_6H_5	H
g	$CH{=}CHC_6H_5$	H
h	$C_6H_2(OCH_3)_3\text{-}(2,4,6)$	H
i	$(CH_3)_2N$	H
j	$(CH_3)_2N$	CH_3
k	$(CH_2)_3NCH_3$	
l	$(CH)_6$	
m	$C_6H_4OCH_3\text{-}(4)$	$C_6H_4OCH_3\text{-}(4)$
n	$(CH_3)_2N$	C_6H_5

the reaction of **6a** with tribromoacetaldehyde in boiling chlorobenzene Gold's salt **13i** [20) was isolated as the sole product in 82% yield. When **6a** and N,N-dimethylbenzamide, **4e**, or N,N-dimethylpivalamide, **4b**, were refluxed in chlorobenzene, mixtures of compounds were obtained containing, again, Gold's salt, **13i**, according to the NMR spectra. The formation of **13i** is not yet understood. In boiling chlorobenzene compound **13i** does not react with N,N-dimethylbenzamide, **4e**. No **13i** was formed when **6a** and N,N-dimethylbenzamide, **4e**, were refluxed in 1,2-dichloroethane (b.p. 83°C) instead of chlorobenzene (b.p. 132°C). An explanation for the formation of **13i** could be the attack of a carbonyl oxygen on the carbon α to the isocyanate group of the ambident electrophile **6a**.

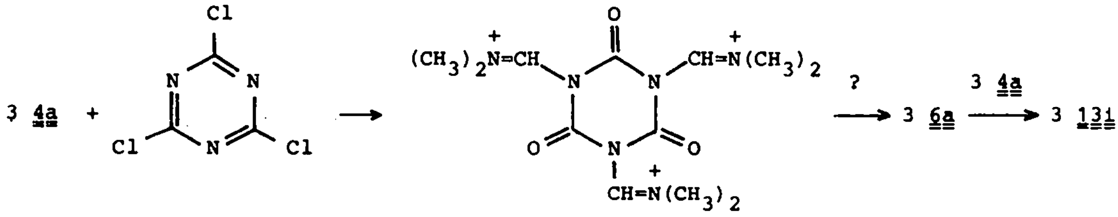


Dimethylformamide, **4a**, and excess of **6a** would then react to give **13i**.

No reactions were observed between the sterically hindered butatrienium salt **6b** and either tertiary carboxamides or aldehydes and ketones.

As mentioned above, the tertiary amides 4c-g did not give butatrienium salts 6 with carbonyl chloride isocyanate, 5. Assuming that the cumulenium salts 6 might nevertheless be formed as intermediates, which could be trapped by reactive carbonyl compounds, the amides 4c-f were treated with 5 in the presence of antimony pentachloride and one equivalent of a carbonyl compound. In this way the 2-azaallenium salts 13l-o could be prepared. In other cases only mixtures of compounds were obtained.

Gold [20)] prepared 13i (chloride) by the reaction of dimethylformamide, 4a, with cyanuric chloride. The reaction was thought to proceed via 14.



14

In contrast to the proposed [20)] intramolecular transformation of 14 to 13i it seems conceivable that 14 decomposes to three molecules of 6a (chloride), which react with excess dimethylformamide to give 13i.

It has been found recently [21)] that carbonyl chloride isocyanate, 5, reacts under forcing conditions with two equivalents of an aldehyde or ketone to give symmetrically substituted 2-azaallenium salts without heterosubstituents.

It should be mentioned that amino substituted 2-azaallenium salts have been obtained by diverse methods [22-37)]. Recently, Gold's salt has found interesting synthetic applications [38-41)].

EXPERIMENTAL SECTION

IR spectra: Perkin-Elmer IR 299, solutions in CH_2Cl_2. ^1H and ^{13}C NMR spectra: Bruker WM-250 spectrometer; solutions in CD_3CN, δ-scale, internal reference tetramethylsilane. The melting points are uncorrected. All experiments were carried out with exclusion of moisture in absolute solvents. The antimony pentachloride was distilled befor use.

<u>4-(Dimethylamino)-1-oxa-3-azabutatrienium Hexachloroantimonate</u> (6a): To carbonyl chloride isocyanate, 5, (5.27 g, 50 mmol) in dichloromethane (30 ml) was added dropwise at -20°C a solution of 4a (3.66 g, 50 mmol) in dichloromethane (5 ml). After stirring for 30 min at -20°C a solution of antimony pentachloride (14.95 g, 50 mmol) in dichloromethane (5 ml) was added dropwise. After stirring for another 30 min at -20°C the product was precipitated by slow addition of ether (40 ml). Yield 19.55 g (90%) of a colourless moisture sensitive powder; m.p. 200-203°C (dec). Addition of dichloromethane to a saturated solution of 6a in acetonitrile at -20°C afforded large colourless prisms. For this very hygroscopic product no satisfactory elemental analysis was obtained. IR: 2240, 1680 cm^{-1}. ^1H NMR(263 K): CH_3

δ = 3.39(d, J = 1.2 Hz), 3.54(d, J = 1.1 Hz), CH 8.49. ^{13}C NMR(263 K): CH_3 δ = 41.2, 45.4, C=O 132.7(t, J = 4 Hz), C=N 157.8. (Found: C, 10.02; H, 1.50; N, 6.32. Calc for $[C_4H_7N_2O]SbCl_6$ (MW = 433.6): C, 11.08; H, 1.63; N, 6.46%).

4-tert-Butyl-4-(dimethylamino)-1-oxa-3-azabutatrienium Hexachloroantimonate (**6b**): Analogous to **6a** from **4b** (2.58 g, 20 mmol). Yield 7.95 g (81%) of a colourless, moisture sensitive powder; dec. above 247°C. Recrystallization from acetonitrile/dichloromethane at -20°C afforded prisms which, according to the NMR spectra, contained impurities resulting from partial hydrolysis. IR: 2060, 1615 cm^{-1}. ^{1}H NMR (263 K): CH_3 δ = 1.52, 3.53, 3.65. ^{13}C NMR(263 K): CH_3 δ = 28.0, 43.9, 45.2, C 48.6, C=O 127.9, C=N 174.1. (Found: C, 19.18; H, 3.01; N, 5.63. Calc for $[C_8H_{15}N_2O]SbCl_6$ (MW = 489.7): C, 19.62; H, 3.09; N, 5.72%).

Antimony Pentachloride - N,N-Dimethyl-(2,2-dimethylpropane)amide (**7b**): To **4b** (1.29 g, 10 mmol) in dichloromethane (5 ml) at -5°C a solution of antimony pentachloride (2.99 g, 10 mmol) in dichloromethane (5 ml) was added dropwise. After 30 min at -5°C the product was precipitated by slow addition of ether (20 ml) affording a pale yellow powder (4.15 g, 97%); m.p. 143-145°C (dec). IR: 1660, 1570 cm^{-1}. ^{1}H NMR (263 K): CH_3 δ = 1.53, 3.48, 3.55. ^{13}C NMR)263 K): CH_3 δ = 28.2, 41.9, 43.1, C 46.5, C=O 182.8. (Found: C, 19.80; H, 3.57; N, 3.12. Calc for $C_7H_{15}NO\cdot SbCl_5$ (MW = 428.2): C, 19.63; H, 3.53; N, 3.27%).

Antimony Pentachloride - N,N-Dimethylacetamide (**7c**): Analogous to **7b** from **4c** (0.87 g, 10 mmol). Yield 3.25 g (84%) of a colourless powder; m.p. 158-160°C. IR: 1600 cm^{-1}. ^{1}H NMR(263 K): CH_3 δ = 2.65, 3.29, 3.36. ^{13}C NMR(263 K): CH_3 δ = 21.2, 40.4, 41.3, C=O 175.0. (Found: C, 12.54; H, 2.09; N, 3.60. Calc for $C_4H_9NO\cdot SbCl_5$ (MW = 386.1): C, 12.44; H, 2.35; N, 3.63%).

Antimony Pentachloride - N-Methylpyrrolidone (**7d**): Analogous to **7b** from **4d** (0.99 g, 10 mmol). Yield 3.58 g (90%) of a colourless powder; m.p. 136-138°C. IR: 1620 cm^{-1}. ^{1}H NMR(263 K): CH_3 δ = 3.16, CH_2 2.22 (quint., J = 7.6 Hz), 3.26 (t, J = 7.6 Hz), 3.75 (t, J = 7.6 Hz). ^{13}C NMR(263 K): CH_2, CH_3 δ = 18.5, 32.8, 33.4, 53.4, C=O 178.4. (Found: C, 15.15; H, 2.22; N, 3.48. Calc for $C_5H_9NO\cdot SbCl_5$ (MW = 398.2): C, 15.08; H, 2.28; N, 3.52%).

Antimony Pentachloride - N,N-Dimethylbenzamide (**7e**): Analogous to **7b** from **4e** (1.49 g, 10 mmol). Yield 4.21 g (94%) of yellow prisms (from acetonitrile/dichloromethane); m.p. 145-148°C. IR: 1665, 1590 cm^{-1}. ^{1}H NMR(263 K): CH_3 δ = 3.31, 3.61. ^{13}C NMR(263 K): CH_3 δ = 41.2, 43.5, C=O 173.5. (Found: C, 23.86; H, 2.45; N, 3.09. Calc for $C_9H_{11}NO\cdot SbCl_5$ (MW = 448.2): C, 21.12; H, 2.47; N, 3.13%).

Antimony Pentachloride - N,N-Dimethylcinnamamide (**7f**): Analogous to **7b** from **4f** (1.75 g, 10 mmol). Yield 4.55 g (96%) of an orange powder; m.p. 172-174°C. IR: 1620, 1570 cm^{-1}. ^{1}H NMR(300 K): CH_3 δ = 3.50, 3.57, CH 7.11 (d, J = 15.8 Hz), 7.99 (d, J = 15.8 Hz). ^{13}C NMR(300 K): CH_3 δ = 41.8, 42.4, CH 115.1, 152.6, phenyl 129.8, 130.0, 132.7, 134.7, C=O 170.5. (Found: C, 28.13; H, 2.97; N, 3.10. Calc for $C_{11}H_{13}NO\cdot SbCl_5$ (MW = 474.2): C, 27.86; H, 2.76; N, 2.96%).

N,N-Dimethylformamidinium Hexachloroantimonate (**12a**): To **6a** (2.17 g, 5 mmol) in acetonitrile (10 ml) a solution of water (0.18 g, 10 mmol) in acetonitrile (5 ml) was added dropwise. After 30 min the evolution of CO_2 had ceased and the solvent was evaporated under reduced pressure. The residue crystallized from acetonitrile (5 ml)/ether(15 ml) giving yellow needles (1.35 g, 66%); m.p. 243-245°C. IR: 1710, 1610 cm^{-1}. ^{1}H NMR(300 K): CH_3 δ = 2.99, 3.22, CH 7.61 (q, J = 7 Hz and 15 Hz), NH 7.08 (broad). ^{13}C NMR(300 K): CH_3 δ = 36.7, 44.2, C=N 156.3. (Found: C, 8.99; H, 1.99; N, 6.74. Calc for $C_3H_8N_2\cdot HSbCl_6$ (MW = 407.6): C, 8.84; H, 2.23; N, 6.88%).

N,N-Dimethyl-(2,2-dimethylpropane)amidinium Hexachloroantimonate (**12b**): Analogous to **12a** from **6b** (2.45 g, 5 mmol). Yield (without recrystallization) 1.95 g (84%) of a pale yellow powder; m.p. 251-253°C (dec). IR: 1640, 1590 cm^{-1}. ^{1}H NMR(300 K):

CH_3 δ = 1.40, 3.06, 3.35. ^{13}C NMR(300 K): CH_3, C δ = 28.0, 38.1, 42.8, 43.2, C=N 173.8. (Found: C, 18.43; H, 3.68; N, 6.32. Calc for $C_7H_{16}N_2\cdot HSbCl_6$ (MW = 463.7): C, 18.13; H, 3.70; N, 6.04%).

3-(Dimethylamino)-1,1-diphenyl-2-azaallenium Hexachloroantimonate (13a) [19]: A mixture of benzophenone (1.82 g, 10 mmol) and 6a (4.34 g, 10 mmol) in chlorobenzene (20 ml) was boiled under reflux for 6 h. After cooling the product was precipitated by slow addition of ether(25 ml)/pentane(25 ml). Recrystallization from dichloromethane (20 ml)/pentane (10 ml) afforded yellow prisms (3.77 g, 66%); m.p. 176-178°C (lit [19]: 171-175°C).

[(Dimethylamino)methylene]-9-fluorenylideneammonium Hexachloroantimonate (13b)[19]: From 9-fluorenone (1.80 g, 10 mmol) as described for 13a. The reaction mixture was boiled for 3 h under reflux. Recrystallization from acetonitrile (10 ml)/ pentane (5 ml) afforded brick-red leaflets (3.82 g, 67%); m.p. 174-176°C (lit [19]: 169-172°C).

3-(Dimethylamino)-1,1-bis(4-methoxyphenyl)-2-azaallenium Hexachloroantimonate (13c): To 5 (1.06 g, 10 mmol) in chlorobenzene (10 ml) a solution of 4a (0.73 g, 10 mmol) in chlorobenzene (5 ml) was added dropwise. After 30 min the reaction mixture was cooled to -20°C. A solution of antimony pentachloride (2.99 g, 10 mmol) in chlorobenzene (5 ml) was added dropwise, followed by a solution of 4,4'-dimethoxybenzophenone (2.42 g, 10 mmol) in chlorobenzene (10 ml). The reaction mixture was boiled under reflux for 2 h. After cooling the product was precipitated by slow addition of ether (25 ml)/pentane (25 ml). Recrystallization from dichloromethane (5 ml)/ acetonitrile (4 ml) afforded orange prisms (4.42 g, 70%); m.p. 154-155°C. IR: 1635, 1590 cm^{-1}. ^{1}H NMR(300 K): CH_3 δ = 3.47, 3.50 (d, J = 1.0 Hz), 3.94 (6 H), CH 8.10, phenyl 7.13 (d, J = 9 Hz), 7.66 (d, J = 9 Hz). ^{13}C NMR(300 K): NCH_3 δ = 39.1, 44.7, OCH_3 56.8, C=N 163.9, 185.4, p-C 166.1, o-C 135.8, i-C 128.8, m-C 115.5. (Found: C, 33.93; H, 3.45; N, 4.41. Calc for $[C_{18}H_{21}N_2O_2]SbCl_6$ (MW = 631.8): C, 34.21; H, 3.35; N, 4.44%).

3-(Dimethylamino)-1-phenyl-1-styryl-2-azaallenium Hexachloroantimonate (13d): To 6a (4.34 g, 10 mmol) in dichloromethane (20 ml), a solution of chalcone (2.08 g, 10 mmol) in dichloromethane (10 ml) was added dropwise at -10°C. After stirring for 2 h at +22°C the product was precipitated by dropwise addition of ether (25 ml)/ pentane (25 ml). Recrystallization from acetonitrile (8 ml)/ether (20 ml) afforded orange prisms (4.07 g, 68%, after work-up of the mother liquor); m.p. 162-164°C (dec). IR:1640, 1590, 1570, 1500 cm^{-1}. ^{1}H NMR(303 K): CH_3 δ = 3.47 (d, J = 0.9 Hz), 3.52, CH 8.53, 7.88 (d, J = 7.0 Hz). ^{13}C NMR (303 K): CH_3 δ = 39.3, 45.1, HC=N 163.5, C=N 182.0, HC= 153.0, 125.0(?). (Found:C, 36.20; H, 3.33; N, 4.35. Calc for $[C_{18}H_{19}N_2]SbCl_6$ (MW = 597.8): C, 36.16; H, 3.20; N, 4.69%).

1-(2,4,6-Cycloheptatrienylidene)-3,3-dimethylformamidinium Hexachloroantimonate (13e): Analogous to 13d from tropone (1.06 g, 10 mmol). Recrystallization from acetonitrile (7 ml)/ether (7 ml) afforded orange prisms (3.67 g, 74%); m.p. 181-183°C. IR: 1640, 1610 cm^{-1}. ^{1}H NMR(300 K): CH_3 δ = 3.30, 3.40, NCH 8.33. ^{13}C NMR(300 K): CH_3 δ = 37.5, 43.6, C=N 160.4, 175.7, CH 141.5, 142.7, 145.6. (Found: C, 23.97; H, 2.73; N, 5.46. Calc for $[C_{10}H_{13}N_2]SbCl_6$ (MW = 495.7): C, 24.23; H, 2.64; N, 5.65%).

1-(Dimethylamino)-3-phenyl-2-azaallenium Hexachloroantimonate (13f): Analogous to 13d from benzaldehyde (0.53 g, 5 mmol). After stirring for 20 h at + 22°C the product was filtered off and recrystallized from dichloromethane (5 ml)/acetonitrile (5 ml) affording nearly colourless leaflets (1.69 g, 68%); m.p. 216-218°C (dec). IR: 1550, 1580 cm^{-1}. ^{1}H NMR(300 K): CH_3 δ = 3.64, CH 8.72, 9.08. ^{13}C NMR(300 K): CH_3 δ = 40.3, 45.8, C=N 169.8, 183.6, phenyl 130.6, 133.5, 134.4, 138.4. (Found: C, 23.93; H, 2.75; N, 5.63. Calc for $[C_{10}H_{13}N_2]SbCl_6$ (MW = 495.7): C, 24.23; H, 2.64; N, 5.65%).

1-(Dimethylamino)-3-styryl-2-azaallenium Hexachloroantimonate (13g): Analogous to 13d from cinnamaldehyde (1.32 g, 10 mmol). After stirring for 1 h at -10°C the product was precipitated by slow addition of ether (50 ml). Recrystallization from acetonitrile (9 ml)/ether (6 ml) afforded, after work-up of the mother liquor, 3.50 g (67%) of yellow-orange prisms; m.p. 163-164°C (dec). IR: 1590, 1540 cm^{-1}. ^1H NMR (300 K): CH_3 δ = 3.53, 3.56, NCH 8.55, 8.79 (d, J = 9.4 Hz), CH 7.29 (q, J = 9.5 and 15.6 Hz), 7.99 (d, J = 15.6 Hz). ^{13}C NMR(300 K): CH_3 δ = 39.8, 45.5, C=N 169.8, 184.7, =C 127.4, 161.4, phenyl 130.3, 130.9, 134.1, 135.1. (Found: C, 27.91; H, 3.07; N, 5.21. Calc for $[C_{12}H_{15}N_2]SbCl_6$ (MW = 521.7): C, 27.62; H, 2.90; N, 5.37%).

1-(Dimethylamino)-3-(2,4,6-trimethoxyphenyl)-2-azaallenium Hexachloroantimonate (13h): Analogous to 13g from 2,4,6-trimethoxybenzaldehyde (1.96 g, 10 mmol). Recrystallization from hot acetonitrile (30 ml) afforded red-brown needles (4.16 g, 71%); m.p. 158-160°C (dec). IR: 1600, 1550, 1530 cm^{-1}. ^1H NMR(300 K): CH_3 δ = 3.45, 3.48, 3.96 (6 H), 3.98, NCHN 8.40, NCHC 9.20, phenyl 6.25. ^{13}C NMR(300 K): NCH_3 δ = 39.0, 44.3, OCH_3 57.5, 57.6 (2 C), m-C 92.6, i-C 107.8, C=N,o,p-C 167.5, 171.2, 172.9, 175.0. (Found: C, 26.69; H, 3.43; N, 4.71. Calc for $[C_{13}H_{19}N_2O_3]SbCl_6$ (MW = 585.8): C, 26.65; H, 3.27; N, 4.78%).

1,3-Bis(dimethylamino)-2-azaallenium Hexachloroantimonate (13i): a) To 5 (1.06 g, 10 mmol) in dichloromethane (10 ml) a solution of antimony pentachloride (2.99 g, 10 mmol) in dichloromethane (5 ml) was added dropwise at 0°C, followed by a solution of 4a (1.46 g, 20 mmol) in dichloromethane (5 ml). After 30 min at +22°C the product was precipitated by dropwise addition of pentane (30 ml). Recrystallization from boiling methanol (20 ml) afforded yellow prisms (3.33 g, 72%); m.p. 133-135°C. IR: 1600 cm^{-1}. ^1H NMR(263 K): CH_3 δ = 3.21, 3.26, CH 8.15. ^{13}C NMR(263 K): CH_3 δ = 36.8, 43.0, C=N 166.5. (Found: C, 15.57; H, 2.88; N, 8.83. Calc for $[C_6H_{14}N_3]SbCl_6$ (MW = 462.7): C, 15.58; H, 3.05; N, 9.08%).

b) A solution of 6a (2.17 g, 5 mmol) and tribromoacetaldehyde (1.40 g, 5 mmol) in chlorobenzene (25 ml) was boiled under reflux for 27 h. Addition of ether (25 ml)/pentane (25 ml) to the cold solution afforded 13i (0.95 g, 82%), according to the IR and NMR spectra. Repeating the experiment in the absence of tribromoacetaldehyde gave the same product, while the isocyanate 6a was isolated unchanged from boiling 1,2-dichloroethane.

1,3-Bis(dimethylamino)-1-methyl-2-azaallenium Hexachloroantimonate (13j): To 6a (8.67 g, 20 mmol) in dichloromethane (30 ml) a solution of 4c (1.74 g, 20 mmol) was added dropwise with stirring. After 30 min at +22°C the product was precipitated by slow addition of ether (25 ml)/pentane (25 ml). Recrystallization from acetonitrile (8 ml)/ether (30 ml) at -20°C afforded a yellow powder (4.67 g, 49%); m.p. 136-139°C. IR: 1650, 1580 cm^{-1}. ^1H NMR(263 K): CH_3 δ = 2.32, 3.17, 3.26, 3.27, 3.30, CH 8.20. ^{13}C NMR(263 K): CH_3 δ = 16.3, 36.4, 40.1, 41.2, 42.6, C=N 161.5, 172.4. (Found: C, 17.76; H, 3.46; N, 8.95. Calc for $[C_7H_{16}N_3]SbCl_6$ (MW = 476.7): C, 17,64; H, 3.38; N, 8.82%).

1,1-Dimethyl-3-(1-methyl-2-pyrrolidinylidene)formamidinium Hexachloroantimonate (13k): Analogous to 13j from 4d (0.99g, 10 mmol). The product was precipitated at -20°C by slow addition of ether (50 ml). Recrystallization from acetonitrile (6 ml)/ether (20 ml) afforded yellow plates (3.23 g, 66%); m.p. 138-140°C (dec). IR: 1600, 1660 cm^{-1}. ^1H NMR(300 K): CH_3 δ = 3.16, 3.20, 3.25, CH_2 2.17 (quint., J = 7.6 Hz), 2.93 (t, J = 7.6 Hz), 3.74 (t, J = 7.6, Hz), CH 8.10. ^{13}C NMR(300 K): CH_3, CH_2 δ = 19.1, 30.2, 33.2, 36.4, 42.7, 55.0, C=N 164.2, 176.6. (Found: C, 19.54; H, 3.36; N, 8.43. Calc for $[C_8H_{16}N_3]SbCl_6$ (MW = 488.7): C, 19.66; H, 3.30; N, 8.60%).

1-(2,4,6-Cycloheptatrienylidene)-3,3-dimethylbenzamidinium Hexachloroantimonate (**13l**): A solution of **4e** (1.49 g, 10 mmol) in dichloromethane (5 ml) was added dropwise to a solution of **5** (1.05 g, 10 mmol) in dichloromethane (15 ml). To the white reaction mixture antimony pentachloride (2.99 g, 10 mmol) in dichloromethane (5 ml) was added dropwise. After stirring for 12 h at +22°C the product was precipitated by slow addition of ether (25 ml)/pentane (40 ml). Recrystallization from acetonitrile (10 ml)/ether (20 ml) afforded dark yellow prisms (3.15 g, 55%); m.p. 157-159°C. IR: 1580 cm^{-1}. ^{1}H NMR(300 K): CH_3 δ = 3.32, 3.35. ^{13}C NMR(300 K): CH_3 δ = 41.1, 43.3, C=N 170.0, 155.8, 7 signals for C=. (Found: C, 33.60; H, 2.80; N, 4.69. Calc for $[C_{16}H_{17}N_2]SbCl_6$ (MW = 571.8): C, 33.61; H, 3.00; N, 4.90%).

1-(Dimethylamino)-3,3-bis(4-methoxyphenyl)-1-phenyl-2-azaallenium Hexachloroantimonate (**13m**): To **5** (1.06 g, 10 mmol) in 1,2-dichloroethane (10 ml) a solution of **4e** (1.49 g, 10 mmol) in 1,2-dichloroethane (10 ml) was added dropwise. When the exothermic reaction with evolution of CO_2 and formation of a colourless precipitate was finished, the reaction mixture was cooled to -30°C. A solution of antimony pentachloride (2.99 g, 10 mmol) in 1,2-dichloroethane (5 ml) was added dropwise, followed by a solution of 4,4'-dimethoxybenzophenone (2.42 g, 10 mmol) in 1,2-dichloroethane (10 ml). The reaction mixture was boiled under reflux for 18 h. After cooling the product was precipitated by slow addition of ether(15 ml)/pentane (30 ml). Recrystallization from boiling methanol (30 ml) afforded dark yellow prisms (5.45 g, 77%); m.p. 165-167°C. IR: 1600, 1570 (shoulder), 1540 (shoulder), 1500 (shoulder) cm^{-1}. ^{1}H NMR(300 K): CH_3 δ = 3.40, 3.54, 3.88 (6 H). ^{13}C NMR(300 K): CH_3 δ = 42.0, 44.2, 56.6 (2 C), C=N 172.9, 177.5. (Found: C, 40.81; H, 3.85; N, 3.95. Calc for $[C_{24}H_{25}N_2O_2]SbCl_6$ (MW = 707.9): C, 40.72; H, 3.56; N, 3.96%).

1,3-Bis(dimethylamino)-1,3-diphenyl-2-azaallenium Hexachloroantimonate (**13n**): A mixture of **4e** (2.98 g, 20 mmol), antimony pentachloride (2.99 g, 10 mmol) and **5** (1.06 g, 10 mmol) in chlorobenzene (20 ml) was boiled under reflux for 2 h. From the cold solution the product was precipitated by slow addition of ether (25 ml). Yield 5.35 g (87%) of a pale yellow powder; m.p. 207-209°C. IR: 1540, 1600 cm^{-1}. ^{1}H NMR(263 K): CH_3 δ = 3.05, 3.42, o-H 6.80 (d, J = 7.9 Hz), m-H 7.15 (t, J = 7.9 Hz), p-H 7.32 (t, J = 7.6 Hz). ^{13}C NMR(263 K): CH_3 δ = 40.0, 42.4, phenyl 128.3, 129.1, 131.4, 133.8, C=N 170.4. (Found: C, 35.42; H, 3.56; N, 6.86. Calc for $[C_{18}H_{22}N_3]SbCl_6$ (MW = 614.9): C, 35.16; H, 3.61; N, 6.84%).

Bis(1-methyl-2-pyrrolidinylidene)ammonium Hexachloroantimonate (**13o**): Analogous to **13n** from **4d** (1.98 g, 20 mmol). The reaction mixture was boiled for 1 h. Yield after recrystallization from boiling methanol (100 ml) 2.83 g (55%) of yellow needles; m.p.178-180°C (dec). IR: 1575 cm^{-1}. ^{1}H NMR(300 K): CH_3 δ = 3.12, CH_2 2.14 (quint., J = 7.6 Hz), 2.89 (t, J = 7.6 Hz), 3.68 (t, J = 7.6 Hz). ^{13}C NMR (300 K): CH_3, CH_2 δ = 19.6, 32.8, 33.3, 54.0, C=N 173.6. (Found: C, 23.48; H, 3.56; N, 8.03. Calc for $[C_{10}H_{18}N_3]SbCl_6$ (MW = 514.8): C, 23.33; H, 3.53; N, 8.17%).

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Table 1. Fractional Atomic Coordinates and Temperature Parameters for **6a** a)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Sb	0.2838(2)	0.2458(1)	0.41162(7)	C3	0.737(3)	0.133(2)	0.167(1)
Cl1	0.2530(8)	0.3072(5)	0.2694(3)	C4	0.832(3)	0.309(2)	0.100(1)
Cl2	0.3214(8)	0.1872(5)	0.5535(3)	O	0.756(2)	0.561(1)	0.3379(9)
Cl3	0.4951(7)	0.1069(4)	0.3782(3)	C1	0.766(3)	0.484(2)	0.296(1)
Cl4	0.0288(8)	0.1245(5)	0.3816(4)	C2	0.744(3)	0.308(2)	0.241(1)
Cl5	0.5373(8)	0.3698(4)	0.4381(3)	H1 b)	0.67760	0.25210	0.28360
Cl6	0.0767(8)	0.3856(4)	0.4456(3)	N2	0.769(2)	0.414(1)	0.243(1)
N1	0.767(2)	0.250(1)	0.1750(8)				

atom	U11	U22	U33	U23	U13	U12
Sb	0.0529(7)	0.0454(6)	0.0347(6)	-0.0027(6)	0.0028(4)	0.0046(8)
Cl1	0.079(4)	0.099(4)	0.036(3)	0.003(3)	-0.001(2)	0.008(3)
Cl2	0.085(4)	0.084(4)	0.047(3)	0.019(3)	0.013(3)	0.014(3)
Cl3	0.060(4)	0.060(3)	0.070(3)	-0.014(3)	0.010(3)	0.015(3)
Cl4	0.063(4)	0.079(4)	0.090(4)	-0.013(3)	-0.001(3)	-0.007(3)
Cl5	0.076(4)	0.062(3)	0.049(3)	0.001(2)	0.001(3)	-0.021(3)
Cl6	0.095(5)	0.059(3)	0.062(3)	0.004(3)	0.019(3)	0.025(3)
N1	0.051(9)	0.06(1)	0.050(9)	-0.005(9)	0.005(7)	0.03(1)
C3	0.11(2)	0.06(1)	0.08(2)	-0.01(1)	-0.01(1)	0.01(1)
C4	0.10(2)	0.11(2)	0.03(1)	-0.01(1)	0.02(1)	-0.05(1)
O	0.14(2)	0.052(8)	0.080(9)	-0.002(7)	0.03(1)	0.020(9)
C1	0.11(2)	0.05(1)	0.05(1)	0.01(1)	0.01(1)	0.01(1)
C2	0.06(1)	0.06(1)	0.04(1)	0.01(1)	0.011(9)	0.00(1)
N2	0.05(1)	0.06(1)	0.06(1)	-0.002(9)	0.012(8)	0.017(9)

a) The anisotropic thermal parameters are defined by the equation: $T = \exp(-2\pi^2 \cdot [U_{11}h^2a*^2 + U_{22}k^2b*^2 + U_{33}l^2c*^2 + 2U_{12}hka*b* + 2U_{13}hla*c* + 2U_{23}klb*c*])$.

b) U = 0.09000.

A complete computer print-out of refined coordinates, bond distances, structure factors etc is available from the Cambridge Crystallographic Data Centre respectively from the British Library, Lending Devision, on request.

REFERENCES

1 M.Al-Talib, I.Jibril, J.C.Jochims, and G.Huttner, Chem.Ber. 117, 3211 (1984).
2 V.I.Gorbatenko and L.I.Samarai, Synthesis 1980, 85.
3 H.Hagemann, Angew.Chem. 89, 789 (1977); Angew.Chem.,Int.Ed.Engl. 16, 743(1977).
4 C.Jutz, Iminium Salts in Organic Chemistry, in Advances in Organic Chemistry, Vol.9, p225, H.Böhme and H.G.Viehe Ed's, Wiley 1976.
5 International Tables for X-ray Crystallography, The Kynoch Press, Birmingham 1969.
6 SHEL-XTL system of programs of W.S.Sheldrick, Göttingen, revision 1979.
7 M.Al-Talib, I.Jibril, J.C.Jochims, and G.Huttner, Tetrahedron, in press.
8 D.W.W.Anderson, D.W.H.Rankin, and A.Robertson, J.Mol.Struct. 14, 385 (1972).
9 A.Bouchy and G.Roussy, C.R.Acad.Sci., Ser.C277, 143 (1973).
10 L.V.Vilkov, P.A.Akishin, and V.M.Presnyakova, Zh.Strukt.Khim. 3, 5 (1962).
11 C.Glidewell and C.Thomson, Chem.Phys.Lett. 86, 340 (1982).
12 D.Poppinger and L.Radom, J.Am.Chem.Soc. 100,3674 (1978).

13 R.B.Wilson, Y.-S.Chen, I.C.Paul, and D.Y.Curtin, J.Am.Chem.Soc. 105, 1672 (1983).

14 L.Brun and C.-I.Brändén, Acta Crystallogr. 20, 749 (1966).

15 G.A.Olah, A.Germain, and A.M.White, Carbonium Ions, Vol V, p. 2102, G.A.Olah and P. von R.Schleyer Ed's, Wiley 1976.

16 R.Graf, Angew.Chem. 80, 179 (1968); Angew. Chem., Int.Ed.Engl. 7, 172 (1968).

17 The chemistry of cyanates and their thio derivatives, S.Patai Ed., Wiley 1977.

18 M.Al-Talib and J.C.Jochims, Chem.Ber. 117, 3222 (1984).

19 M.Al-Talib, I.Jibril, G.Huttner, and J.C.Jochims, Chem.Ber., submitted for publication.

20 H.Gold, Angew.Chem. 72, 956 (1960).

21 E.-U.Würthwein, private communication.

22 B.Rathke, Ber.Dtsch.Chem.Ges. 11, 967 (1878); 12, 776 (1879).

23 E.Allenstein and P.Quis, Chem.Ber. 96, 2918 (1963).

24 E.Allenstein, Z.anorg.allgem.Chem. 322, 276 (1963).

25 C.Jutz and W.Müller, Angew.Chem. 78, 1059 (1966); Angew.Chem., Int.Ed. Engl. 5, 1042 (1966).

26 K.Bredereck and R.Richter, Chem.Ber. 99, 2454 (1966).

27 J.Liebscher and H.Hartmann, Z.Chem. 14, 358 (1974).

28 J.Liebscher and H.Hartmann, Z.Chem. 15, 16 (1975).

29 J.Liebscher and H.Hartmann, Tetrahedron Lett. 1975, 2977.

30 J.Liebscher and H.Hartmann, Coll. Czechoslov.Chem.Commun. 41, 1565 (1976).

31 J.Liebscher, E.Mitzner, A.Knoll, and H.Hartmann, Z.Chem. 23, 405 (1983).

32 Z.Csürös, R.Soos, A.Antus-Ercsenyi, I.Bitter, and J.Tamas, Acta Chim. Scient. Hung. 78, 419 (1973).

33 Z.Janousek and H.G.Viehe, Angew.Chem. 85, 90 (1973); Angew.Chem., Int.Ed.Engl. 12, 74 (1973).

34 R.Gompper and F.Towae, Synthesis 1975, 522.

35 R.Gompper and J.Schelble, Synthesis 1981, 647.

36 J.C.Jochims, R.Abu-El-Halawa, I.Jibril, and G.Huttner, Chem.Ber. 117, 1900 (1984).

37 G.V.Boyd, P.F.Lindley, G.A.Nicolaou, J.Chem.Soc., Chem.Commun. 1984, 1105.

38 J.T.Gupton, C.Colon, C.R.Harrison, M.J.Lizzi, and D.E.Polk, J.Org.Chem. 45, 4522 (1980).

39 J.T.Gupton and D.E.Polk, Synthet.Commun. 11, 571 (1981).

40 J.T.Gupton, S.S.Andrew, and C.Colon, Synthet.Commun. 12, 35 (1982).

41 J.T.Gupton, M.J.Lizzi, and D.E.Polk, Synthet.Commun. 12, 939 (1982).