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Alkylidenecyanamidium Salts. α-Bromination of Carbodiimides

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Carbodiimides (**15**) of type H – $\dot{C}$ – N = C = N – R react with *N*-bromosuccinimide (NBS) to afford unstable alkylidenecyanamidium bromides (**18**) which undergo von Braun elimination of R – Br giving the alkylidenecyanamides **19** if R is a tertiary alkyl group. Reaction of carbodiimides (**15**) of the type – $\dot{C}$H – $\dot{C}$H – N = C = N – R with *N*-bromosuccinimide results in bromination not only of the α but also of the β position, the latter occurring via De Kimpe halogenation[16] of **18**. Stable cyanamidium salts **18** could be obtained when compounds **19** were alkylated with *tert*-butyl chloride or 1-chloroadamantane and antimony pentachloride. The compound **18c** was also obtained from *N*-chlorobenzophenone imine, *tert*-butyl isocyanide, and antimony pentachloride. Alkylation of the *N*-cyanoguanidine **19r** with triethyloxonium tetrafluoroborate afforded the salt **18r**. Reactions of the alkylidenecyanamidium salts **18** with a sulfide (yielding a sulfonium salt and **19**), with amines (to give the alkylideneguanidinium salts **23**) and with alcohols (affording the alkylideneuronium salts **22**) are described. The structures of the new formal heterocumulenes are discussed.

Alkylidencyanamidiumsalze

α-Bromierung von Carbodiimiden

Carbodiimide (**15**) des Typs H – $\dot{C}$ – N = C = N – R reagieren mit *N*-Bromsuccinimid (NBS) zu den instabilen Alkylidencyanamidium-bromiden **18**, die, falls R eine tertiäre Alkylgruppe ist, unter von Braun-Eliminierung von R – Br zu den Alkylidencyanamiden **19** zerfallen. Bei Carbodiimiden (**15**) des Typs – $\dot{C}$H – $\dot{C}$H – N = C = N – R werden mit *N*-Bromsuccinimid die α- und die β-Wasserstoffatome durch Brom ersetzt, letztere durch De Kimpe-Halogenierung von **18**. Alkylierungen von Verbindungen **19** mit *tert*-Butylchlorid oder 1-Chloradamantan und Antimonpentachlorid ergeben isolierbare Alkylidencyanamidiumsalze **18**. Verbindung **18c** kann auch durch Umsetzen von *N*-Chlorbenzophenonimin mit *tert*-Butylisocyanid und Antimonpentachlorid erhalten werden. Alkylierung des *N*-Cyanguanidins **19r** mit Triethyloxonium-tetrafluoroborat ergibt das Salz **18r**. Es werden Reaktionen der Alkylidencyanamidiumsalze **18** mit einem Sulfid, wobei ein Sulfoniumsalz und **19** gebildet werden, mit Aminen zu den Alkylidenguanidiniumsalzen **23** und mit Alkoholen zu den Alkylidenuroniumsalzen **22** beschrieben. Die Konstitutionen der neuen formalen Heterokumulene werden diskutiert.

Bromination of olefins in the allylic position by *N*-bromosuccinimide (NBS) is an important synthetic method known as the Wohl-Ziegler reaction[1-4]. This reaction has been extended to certain heterosubstituted allylic systems.

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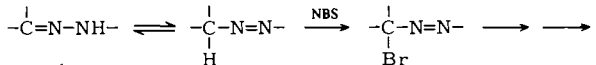
Hydrazones (**1**)[5,6] and oximes (**2**)[7,8] are reported to be oxidized by NBS under mild conditions. Possibly, the reactions proceed *via* the tautomeric azo or nitroso forms, resp. Bromides **4** are obtained from *O*-alkyloximes (**3**)[9].



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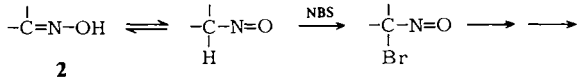

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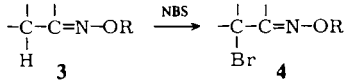
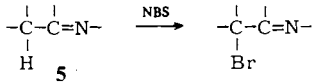


3 **4**



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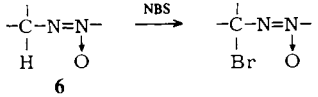

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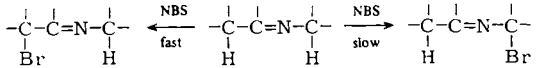
N-Substituted imines (**5**)[10-12] as well as azoxy compounds (**6**)[13] react to give the corresponding α-bromo compounds.

While the mechanism of the Wohl-Ziegler reaction has been generally accepted to be of the free radical type (Goldfinger mechanism[14,15]) little is known about the mechanism of the NBS brominations of heterosubstituted allylic systems. For the NBS bromination of **5** an ionic mechanism has been proposed[16]. There are two allylic positions in azomethines of the type **7**. The hydrogen atoms alpha to the imino carbon are usually much faster replaced than those alpha to the imino nitrogen. Thus, irradiating a solution of **9** in carbon tetrachloride at 50 °C in the presence of excess of NBS and a catalytic amount of trifluoroacetic acid afforded **8** but apparently



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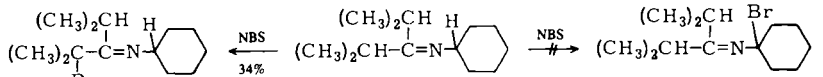
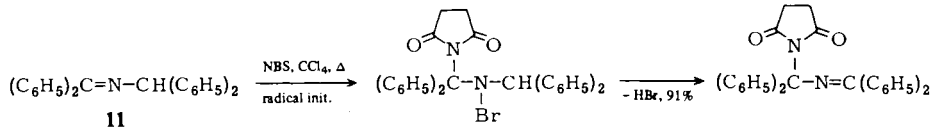


8 **9** **10**



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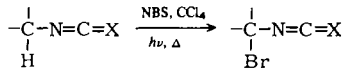
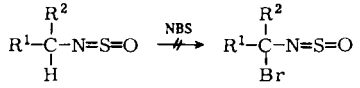
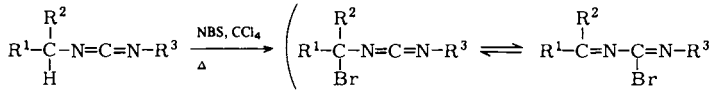


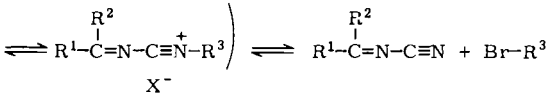
12: X = S
13: X = O



14a,b **a**: $R^1 = (CH_3)_2CH$, $R^2 = CO_2CH_3$
b: $R^1 = C_6H_5$, $R^2 = (CH_3)_3C$



15a-d **16** **17**



18a-r **19a-d, f-r**

15-19, 22, 23	R^1	R^2	R^3	R^4	R^5
a	$(CH_3)_3C$	$(CH_3)_3C$	$(CH_3)_3C$	$(CH_3)_3C$	H
b	$(CH_3)_3C$	C_6H_5	$(CH_3)_3C$	$(CH_3)_3C$	H
c	C_6H_5	C_6H_5	$(CH_3)_3C$	CH_3	–
d	α-$C_{10}H_7$	C_6H_5	$(CH_3)_3C$	$(CH_3)_3C$	H
e	$(CH_3)_2CH$	C_6H_5	$(CH_3)_3C$	–	–
f	$(CH_3)_2CBr$	C_6H_5	$(CH_3)_3C$	–	–
g	CH_3	CH_3	C_6H_5	–	–
h	C_6H_5	C_6H_5	C_6H_5	–	–
i	$(CH_3)_2CH$	CO_2CH_3	C_6H_5	–	–
j	CH_3	C_6H_5	$(CH_3)_3C$	–	–
k	*o*-C_6H_4–C_6H_4-*o*		$(CH_3)_3C$	–	–
l	$(CH_3)_3C$	$(CH_3)_3C$	1-adamantyl[a)]	$(CH_3)_3C$	H
m	$(CH_3)_3C$	C_6H_5	1-adamantyl	CH_3	–
n	C_6H_5	C_6H_5	1-adamantyl	CH_3	–
o	α-$C_{10}H_7$	C_6H_5	1-adamantyl	CH_3	–
p	CH_3	C_6H_5	1-adamantyl	$(CH_3)_3C$	H
q	CH_3S	CH_3S	$(CH_3)_3C$	$(CH_3)_3C$	H
r	$(CH_3)_2N$	$(CH_3)_2N$	C_2H_5	$(CH_3)_2CH$	$(CH_3)_2CH$

[a)] 1-adamantyl = 

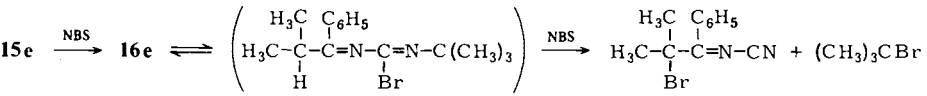
no **10**[12]. If there is no allylic hydrogen vicinal to the imino carbon as in **11**, addition of NBS to the C = N double bond seems to be preferred to allylic substitution alpha to the nitrogen atom [17]. To explain these results the type of the mechanism (ionic or free-radical), the different energies of the SOMO's of a 1-aza and a 2-aza allylic radical, and polar effects[18] will have to be considered.

Considering the above literature reports it was rather surprising that under typical Wohl-Ziegler conditions isothiocyanates (**12**)[19] and isocyanates (**13**)[20] are brominated in alpha position to the nitrogen in high yields. In this paper experiments are reported to extend the NBS bromination to sulfinylamines (**14**) and carbodiimides (**15**).

After heating or irradiating suspensions of the sulfinylamines **14a, b** and excess of NBS in carbon tetrachloride for more than twenty hours mainly starting materials were recovered. In the ^{1}H NMR spectra of the reaction mixture no signals for alpha brominated products were observed. Apparently, the Wohl-Ziegler reaction can not be applied to sulfinylamines (**14**).

Heating the carbodiimide **15a** for three and a half hours with excess of NBS in carbon tetrachloride afforded the alkylidenecyanamide **19a** in 70% yield. In the reaction mixture *tert*-butyl bromide was identified by ^{1}H NMR (CH_3 δ = 1.77 in CCl_4). Similarly, the carbodiimides **15b – d** react to give the corresponding alkylidenecyanamides (**19b – d**) in good yields. The reactions proceed sluggishly if solutions of **15** in carbon tetrachloride are irradiated instead of being heated in the presence of NBS. A plausible reaction mechanism would be a free-radical bromination of the carbodiimide **15** in analogy to a Goldfinger mechanism[14,15]. Although α-chlorocarbodiimides are known to be stable[21,22], the corresponding α-bromo compounds **16** seem to be involved in bromotropic equilibria with **17** and/or **18**. These intermediates are cleaved to **19** and the alkyl bromide R^3 – Br. This ionic von Braun elimination[23] is accelerated by heat and is favoured by a stable leaving carbenium ion $^+R^3$, e.g. R^3 = *tert*-alkyl.

Treating the carbodiimide **15e** with three equivalents of NBS in boiling carbon tetrachloride afforded the alkylidenecyanamide **19f** (88%). The formation of **19f** provides another argument for an intermediate **17** (or **18**). Compound **17e** contains an allylic system of the type $-\overset{|}{C}H-\overset{|}{C}=N-$ which is readily halogenated as is known from the work of *De Kimpe* et al.[16]. Following the reaction of **15g**[24] with a large excess of NBS by ^{1}H NMR (CCl_4) one observes the gradual disappearance of the signals of all hydrogens in beta position to nitrogen. Attempts to isolate stable products proved unsuccessful. Thus, due to *De Kimpe* bromination of intermediates **17/18**, carbodiimides with more than one beta hydrogen do not give synthetically useful reactions with NBS.



Carbodiimides **15g – i** with R^3 = phenyl, a bad leaving group in the von Braun elimination, reacted sluggishly with NBS in boiling carbon tetrachloride with or without irradiation. Apparently, either the reaction **15** → **16** must be reversible or some of the products poison this reaction. During the reaction of **15h** with NBS the carbodiimide stretching vibration at 2120 cm^{-1} disappeared within 20 hours and a new strong band at 2260 cm^{-1} gradually increased. The

product decomposed when attempts were made to isolate it. Since authentic alkylidenecyanamidium salts show strong $C\equiv\overset{+}{N}$ bands at 2260 cm^{-1} (see below), we believe that the product is the bromide **18h**.

In summary, the results indicate that carbodiimides of the type **15** undergo Wohl-Ziegler bromination. The reaction is synthetically useful affording alkylidenecyanamides which are not easily obtained by other methods[25,26] if there is only a single hydrogen in alpha position and no hydrogen in beta position to one of the carbodiimide nitrogens and a tertiary alkyl substituent (R^3) at the other nitrogen. That an α-hydrogen is indeed required for the reaction with NBS was demonstrated by the fact that di-*tert*-butylcarbodiimide failed to react with either NBS or with bromine in boiling carbon tetrachloride.

No example of a cyanamidium salt (**18**) seems to be reported in the literature. Since we were not able to isolate the bromides **18g–i** we tried to prepare such compounds with the less nucleophilic counterion $SbCl_6^-$ [27,28]. Alkylation of **19b** with *tert*-butyl chloride and antimony pentachloride in dichloromethane afforded the hexachloroantimonate **18b** (X = $SbCl_6$) in almost quantitative yield. Similarly, the salts **18a, c, d, f, j–q** (X = $SbCl_6$) were prepared. No reaction occurred between **19** and secondary or primary alkyl chlorides such as 2-chloropropane or benzyl chloride with antimony pentachloride. Apparently, here the equilibria of the complexed alkylidenecyanamide and the carbenium ions lie far to the left. In the case of **19r** the complex with antimony pentachloride (**20**) (of unknown structure) is so stable that it does not react even with *tert*-butyl chloride. A stable alkylidenecyanamidium salt (**18r**, X = BF_4) could however be obtained by alkylation of **19r** with triethyloxonium tetrafluoroborate. Finally, the salt **18c** (X = $SbCl_6$) was obtained in moderate yield from *tert*-butyl isocyanide, *N*-chlorobenzophenone imine, and antimony pentachloride, a reaction which could not be applied to other isonitriles[29].

$$\mathbf{19a\text{-}d,\ f,\ j\text{-}q} + Cl\text{–}R^3 + SbCl_5 \xrightarrow[-30\,^\circ C]{CH_2Cl_2} \mathbf{18a\text{-}d,\ f,\ j\text{-}q}\ (X = SbCl_6)$$

$$R^1\text{–}\overset{R^2}{\overset{|}{C}}\text{=N–CN}\cdot SbCl_5 + Cl\text{–}R^3 \rightleftharpoons R^1\text{–}\overset{R^2}{\overset{|}{C}}\text{=N–CN} + {}^+R^3\,SbCl_6^- \rightleftharpoons \mathbf{18}$$

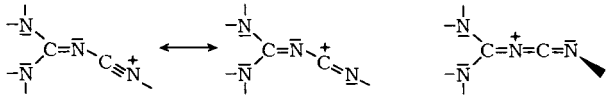
$$C_6H_5\text{–}\overset{C_6H_5}{\overset{|}{C}}\text{=N–Cl} + CN\text{–}C(CH_3)_3 + SbCl_5 \longrightarrow \mathbf{18c}\ (X = SbCl_6)\quad (44\%)$$

$$\mathbf{19r} + (C_2H_5)_3O^+BF_4^- \xrightarrow{ClCH_2CH_2Cl} \mathbf{18r}\ (X = BF_4)\quad (68\%)$$

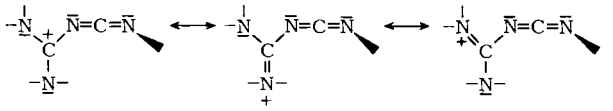
$$\mathbf{19r} + SbCl_5 \longrightarrow \begin{matrix}(CH_3)_2N\\ \diagdown\\ \quad C\text{=N–CN}\cdot SbCl_5\\ \diagup\\ (CH_3)_2N\end{matrix}\quad \mathbf{20}$$

The alkylidenecyanamidium salts **18** are moisture sensitive crystalline substances which are moderately stable in the solid state but decompose in solution above 0°C.

The stability of the salts **18** is increased if R^1, R^2 are heterosubstituents (**18q, r**). The question of the charge distribution in **18** is interesting. The positive charge in **18r**, for instance, can be delocalized over six atoms. According to an X-ray structural analysis of **18d** (X = $SbCl_6$) and dynamic NMR measurements on **18c** (X = $SbCl_6$)[27] these compounds are bent alkylidenecyanamidium salts (**A**) in solution as well as in the solid state. Since all compounds **18** show a $C\equiv\overset{+}{N}$ stretching band at about 2160 cm^{-1} and very broad ^{13}C signals for $C\equiv\overset{+}{N}$ around δ = 102 ppm, they can probably all be regarded as alkylidenecyanamides (**A**). On the other hand, the thermal stability of the hexachloroantimonates **18** parallels the ability of the substituents R^1, R^2 to stabilize a carbenium ion, e.g. the stability increases in the order **18a** < **18c** < **18q** (X = $SbCl_6$) indicating that the carbodiimide form **C** is also of some importance. The cumulene **B** probably represents an energy maximum[27].

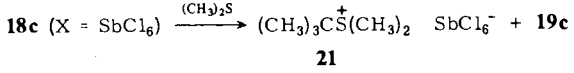


18r (cation) **A** **B**



C

The alkylidenecyanamidium salts **18** are moderately strong electrophiles. Compound **18c** (X = $SbCl_6$) reacts with dimethyl sulfide to give the sulfonium salt **21** and **19c**. This demonstrates that the formation of **18** from **19** and a carbenium ion is reversible. Alcohols and amines add to the nitrilium carbon of compounds **18** affording the alkylideneuronium salts **22** and the alkylideneguanidinium salts **23**, respectively.



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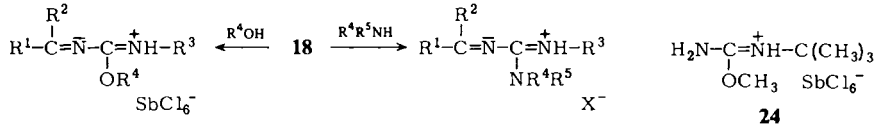
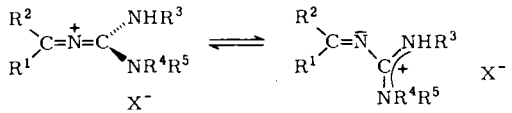


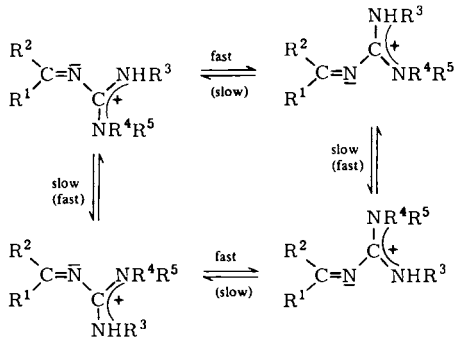
22c, m, n, o **23a, b, d, l, q, r** **24**



23A **23B**

In other cases mixtures of products were obtained. Further work is required to find out whether sometimes attack of the nucleophile on both carbons of the C=N–C≡N moiety of **18** occurs. The reaction mixture of **18c** (X = $SbCl_6$) and methanol always contained the uronium salt **24** (besides **22c**). It is not clear whether **24** is formed *via* hydrolysis of **22c** or *via* primary attack of the alcohol on the methylene carbon of **18c** (X = $SbCl_6$).

The structures of the alkylideneguanidinium salts **23** remain to be elucidated. These compounds could either be 2-azaallenium salts (**23A**) with linear or bent[30] $C=\overset{+}{N}=C$ units and substituents in perpendicular planes or planar imino substituted amidinium salts (**23B**) where the lone pair of electrons of the imino nitrogen is not involved in conjugation. 2-Azaallenium salts show $C=\overset{+}{N}=C$ stretching vibrations at about 1900 cm^{-1} [30], while compounds **23** show C=N bands between 1550 and 1690 cm^{-1}. In the ^1H and ^{13}C NMR spectra of **23b, d** (X = $SbCl_6$) with $R^1 \neq R^2$ the two $NHC(CH_3)_3$ groups are nonequivalent while for **23a, q** these groups are equivalent. For an allene **23A** the *N-tert*-butyl groups should be equivalent regardless of whether R^1 and R^2 are equal or not. The IR and NMR spectra are in accord with a pseudocumulenic[31] structure **23B** with either fast configurational inversion at the imino nitrogen and slow rotation around the imino N–C single bond or vice versa.



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Experimental Part

IR spectra: Perkin-Elmer IR 299 spectrometer. – ^1H NMR spectra: Jeol JNM-MH-100 and Bruker WM-250 instruments. – ^{13}C NMR spectra: Bruker WM-250 spectrometer. δ-Scale, internal reference tetramethylsilane. – The melting points are uncorrected.

Methyl 3-methyl-2-(sulfinylamino)butyrate (**14a**): To a stirred suspension of valine methyl ester hydrochloride (50.3 g, 300 mmol) and dry pyridine (71.2 g, 900 mmol) in dry benzene (400 ml) was added dropwise at –5 °C thionyl chloride (35.7 g, 300 mmol). The reaction mixture was stirred for 20 min at 22 °C and than boiled under reflux for 15 min. After cooling and filtration the solvent was evaporated under reduced pressure. The oily residue was twice distilled affording an unstable yellow oil (38.0 g, 72%) which was NMR spectroscopically pure; b. p. 55–60 °C/10^{-1}

Torr. – ^{1}H NMR (CCl_4): CH_3 δ = 0.94 (d, J = 7 Hz), 0.97 (d, J = 7 Hz), 3.73, CH 2.32 (m), 5.01 (d, J = 5 Hz). – ^{13}C NMR ($CDCl_3$, 251 K): CH_3 δ = 17.0, 19.3, 65.3, CH 31.7, 52.6, CO 168.7.

(2,2-Dimethyl-1-phenylpropyl)sulfinylamine (**14b**): To a stirred solution of 2,2-dimethyl-1-phenylpropanamine[32] (22.9 g, 140 mmol) and dry pyridine (16.6 g, 210 mmol) in dry benzene (220 ml) was added dropwise at –5 °C thionyl chloride (21.4 g, 180 mmol). The solution was refluxed for 12 h, filtrated and evaporated under reduced pressure. Distillation of the residue afforded a colourless oil (20.1 g, 69%); b.p. 70–72 °C/10^{-1} Torr. – ^{1}H NMR (CCl_4): CH_3 δ = 0.93, CH 5.51. – ^{13}C NMR ($CDCl_3$, 273 K): CH_3 δ = 26.3, C 36.1, CH 70.8.

$C_{11}H_{15}NOS$ (209.3) Calc. C 63.12 H 7.22 N 6.69 Found C 63.01 H 7.20 N 6.49

1-tert-Butyl-3-(1-tert-butyl-2,2-dimethylpropyl)thiourea: A mixture of 2,2,4,4-tetramethyl-3-pentanamine[33,34] (5.73 g, 40 mmol) and *tert*-butyl isothiocyanate (4.60 g, 40 mmol) in ether (100 ml) was refluxed for 1 h. The solvent was evaporated. Crystallization from CH_2Cl_2 (20 ml)/pentane (30 ml) afforded colourless crystals (8.38 g, 81%); m.p. 128–129 °C.

$C_{14}H_{30}N_2S$ (258.5) Calc. C 65.05 H 11.70 N 10.84 Found C 64.87 H 11.99 N 10.97

1-tert-Butyl-3-(1-tert-butyl-2,2-dimethylpropyl)carbodiimide (**15a**): A suspension of 1-*tert*-butyl-3-(1-*tert*-butyl-2,2-dimethylpropyl)thiourea (7.77 g, 30 mmol) and of dry activated yellow mercury oxide[35] (16.2 g, 75 mmol) in carbon disulfide (150 ml) was shaken for 12 h at 22 °C. Filtration and distillation afforded a colourless oil (5.36 g, 80%); b.p. 47–48 °C/10^{-1} Torr. – IR (film): 2130 cm^{-1}. – ^{1}H NMR (CCl_4): CH_3 δ = 1.04 (18H), 1.25, CH 2.84. – ^{13}C NMR ($CDCl_3$): CH_3 δ = 29.7 (6 C), 31.9, CH 76.8, C 37.9, 54.7, NCN 137.3.

$C_{14}H_{28}N_2$ (224.4) Calc. C 74.94 H 12.58 N 12.49 Found C 75.19 H 12.40 N 12.56

1-tert-Butyl-3-(2,2-dimethyl-1-phenylpropyl)carbodiimide (**15b**): 1-*tert*-Butyl-3-(2,2-dimethyl-1-phenylpropyl)thiourea (114.0 g, 82%) was prepared in the usual way from 2,2-dimethyl-1-phenylpropanamine (81.7 g, 500 mmol) and *tert*-butyl isothiocyanate (57.6 g, 500 mmol) in ether (100 ml). The thiourea was used without purification for the preparation of **15b** as described for **15a**. Yield 79.25 g (79%) of a colourless oil; b.p. 90–91 °C/10^{-1} Torr. – IR (film): 2130 cm^{-1}. – ^{1}H NMR ($CDCl_3$): CH_3 δ = 0.91, 1.15, CH 4.20. – ^{13}C NMR ($CDCl_3$): CH_3 δ = 26.7, 31.4, CH 72.2, C 35.9, 55.1, NCN 138.9.

$C_{16}H_{24}N_2$ (244.4) Calc. C 78.63 H 9.90 N 11.47 Found C 78.54 H 9.91 N 11.57

1-tert-Butyl-3-(diphenylmethyl)carbodiimide (**15c**): From 1-*tert*-butyl-3-(diphenylmethyl)-thiourea[36] (59.7 g, 200 mmol) and yellow mercury oxide (100.0 g, 460 mmol) in carbon disulfide (800 ml) as described for **15a**. Yield 51.8 g (98%) of a colourless oil; b.p. 112–115 °C/10^{-1} Torr. – IR (film): NCN 2120 cm^{-1}. – ^{1}H NMR (CCl_4): CH_3 δ = 1.00, CH 5.57. – ^{13}C NMR ($CDCl_3$, 263 K): CH_3 δ = 30.9, CH 64.4, C 55.5, NCN 140.6, aryl C 127.1, 127.2, 128.3, 142.2.

$C_{18}H_{20}N_2$ (264.4) Calc. C 81.78 H 7.63 N 10.60 Found C 81.57 H 7.53 N 10.39

1-tert-Butyl-3-(2-methyl-1-phenylpropyl)carbodiimide (**15e**): 1-*tert*-Butyl-3-(2-methyl-1-phenylpropyl)thiourea was prepared from 2-methyl-1-phenylpropanamine (15.0 g, 100 mmol) and *tert*-butyl isothiocyanate (11.6 g, 100 mmol) in ether (100 ml). Recrystallization from dichloromethane/pentane afforded colourless prisms (20.5 g, 78%); m.p. 114–115 °C. The carbodiimide **15e** was prepared from the thiourea (20.5 g, 70 mmol) and yellow mercury oxide (37.9 g, 175 mmol) in CS_2 (250 ml) as described for **15a**. Yield 11.8 g (73%) of a colourless oil; b.p. 73–74 °C/10^{-1} Torr. – IR (film): NCN 2120 cm^{-1}. – ^{1}H NMR (CCl_4): CH_3 δ = 0.77 (d, J = 7 Hz), 0.95 (d, J = 7 Hz), 1.07, CH 1.93 (m), 4.00 (d, J = 7 Hz).

$C_{15}H_{22}N_2$ (230.4) Calc. C 78.21 H 9.63 N 12.16 Found C 78.23 H 9.56 N 12.11

1-(Diphenylmethyl)-3-phenylthiourea: Refluxing diphenylmethanamine (36.6 g, 200 mmol) and phenyl isothiocyanate (27.0 g, 200 mmol) for 1 h in ether (80 ml) afforded after work-up a colourless powder (63.2 g, 99%) which was recrystallized from dichloromethane/pentane; m. p. 178 – 179 °C.

$C_{20}H_{18}N_2S$ (318.4) Calc. C 75.44 H 5.69 N 8.80 Found C 75.32 H 5.61 N 8.69

1-(Diphenylmethyl)-3-phenylcarbodiimide (**15h**): From 1-(diphenylmethyl)-3-phenylthiourea (31.8 g, 100 mmol) and yellow mercury oxide (54.0 g, 250 mmol) in CS_2 (400 ml) as described for **15a**. The crude product was treated with active charcoal in ether. Crystallization from ether (5 ml)/pentane (15 ml) at – 25 °C and work-up of the mother liquors afforded colourless needles (22.3 g, 79%); m. p. 34 – 36 °C. – IR (KBr): NCN 2130 cm^{-1}. – ^1H NMR (CCl_4): CH δ = 5.80. – ^{13}C NMR ($CDCl_3$): CH δ = 65.3, NCN 137.5.

$C_{20}H_{16}N_2$ (284.4) Calc. C 84.47 H 5.67 N 9.85 Found C 84.37 H 5.64 N 9.85

Methyl 3-methyl-2-(3-phenylureido)butyrate: To methyl 2-isocyanato-3-methylbutyrate[37] (62.8 g, 400 mmol) in dry ether (300 ml) was added dropwise at – 40 °C a solution of aniline (37.3 g, 400 mmol) in dry ether (80 ml). The mixture was stirred for 2 h at 22 °C and then evaporated to dryness. The residue was crystallized from dichloromethane (400 ml)/petroleum ether (200 ml) affording a colourless powder (92.6 g, 93%); m. p. 98 – 101 °C. – ^1H NMR ([D_6]DMSO): δ = 0.88 (d, J = 7 Hz), 0.91 (d, J = 7 Hz), 3.67, CH 2.04 (m), 4.20 (q, J = 6 Hz, 9 Hz), NH 6.52 (d, J = 9 Hz), 8.58.

$C_{13}H_{18}N_2O_3$ (250.3) Calc. C 62.38 H 7.25 N 11.20 Found C 62.67 H 7.29 N 11.25

Methyl 3-methyl-2-[(phenylcarbonimidoyl)amino]butyrate (**15i**): A solution of methyl 3-methyl-2-(3-phenylureido)butyrate (50.1 g, 200 mmol), dry triethylamine (20.2 g, 200 mmol) and triphenylphosphane (68.2 g, 260 mmol) in dry carbon tetrachloride (31.5 g, 205 mmol) was refluxed for 7 h. Triphenylphosphane (68.2 g, 260 mmol) was added and the mixture refluxed for another 7 h. The solvent was evaporated under reduced pressure and the residue extracted with eight portions (150 ml) of petroleum ether. The combined extracts were evaporated under reduced pressure. Distillation of the residue afforded a colourless oil (29.4 g, 63%); b. p. 124 – 125 °C/10^{-1} Torr. – IR (film): NCN 2140 cm^{-1}. – ^1H NMR (CCl_4): CH_3 δ = 0.97 (d, J = 7 Hz), 1.04 (d, J = 7 Hz), 3.73, CH 2.20 (m), 3.90 (d, J = 5 Hz). – ^{13}C NMR ($CDCl_3$): CH_3 δ = 17.5, 19.6, 52.6, CH 32.5, 65.6, NCN 136.8, CO 171.6, aryl C 124.2, 125.0, 129.5, 140.2.

$C_{13}H_{16}N_2O_2$ (232.3) Calc. C 67.22 H 6.94 N 12.06 Found C 67.01 H 6.82 N 12.21

3-tert-Butyl-1-(2,2-dimethyl-1-phenylpropylidene)cyanamidium hexachloroantimonate (**18b**): To a stirred solution of antimony pentachloride (8.97 g, 30 mmol) in dry dichloromethane (30 ml) at – 70 °C was added dropwise a solution of **19b** (5.59 g, 30 mmol) in dry dichloromethane (15 ml). After warming up to – 40 °C a solution of *tert*-butyl chloride (3.06 g, 33 mmol) in dry dichloromethane (10 ml) was added. Stirring at – 40 °C was continued for 90 min. Then, 130 ml of dry ether were added slowly at – 40 °C. The precipitate was quickly filtered off with exclusion of moisture. Dissolving the residue in dry dichloromethane (20 ml) at – 40 °C and precipitating by addition of dry ether (90 ml) afforded a pale violet powder (13.52 g, 78%); m. p. 88 – 91 °C (dec.). The compound is very moisture sensitive and slowly decomposes in solution above 0 °C. – IR (CH_2Cl_2): $C\equiv\overset{+}{N}$ 2260 cm^{-1} (shoulder 2300, 2220). – ^1H NMR (CH_2Cl_2): CH_3 δ = 1.50, 1.54. – ^{13}C NMR (CD_2Cl_2, 273 K): CH_3 δ = 28.6, 29.3, C 46.3, 65.3, C=N 228.6, aromatic C 125.9, 129.8, 134.1, 137.6.

$[C_{16}H_{23}N_2]SbCl_6$ (577.8) Calc. C 33.26 H 4.01 N 4.85 Found C 32.60 H 3.82 N 4.59

3-tert-Butyl-1-(diphenylmethylene)cyanamidium hexachloroantimonate (**18c**)[27]: To a stirred solution of *tert*-butyl isocyanide (0.83 g, 10 mmol) and *N*-chlorodiphenylmethanimine (3.24 g,

15 mmol) in dry dichloromethane (10 mmol) was added dropwise at −70°C a solution of antimony pentachloride (2.99 g, 10 mmol) in dry dichloromethane (5 ml). After stirring for 2 h at −40°C followed by addition of dry carbon tetrachloride (5 ml) an almost colourless powder was filtered off (2.63 g, 44%), the IR-, ^{13}C- and ^{1}H NMR spectra of which were identical with those reported[27].

1-(2-Bromo-2-methyl-1-phenylpropylidene)-3-tert-butylcyanamidium hexachloroantimonate (**18f**): As described for **18b** from antimony pentachloride (0.60 g, 2.00 mmol), **19f** (0.50 g, 2.00 mmol) and *tert*-butyl chloride (0.21 g, 2.20 mmol) in dry dichloromethane (10 ml). Precipitation with dry pentane (10 ml) at −40°C afforded a yellow powder (1.04 g, 81%) which decomposed at temperatures above 0°C. – IR (CH_2Cl_2): C≡N̂ 2280, 2320, 2200 cm^{-1}. – ^{1}H NMR (CD_2Cl_2, 263 K): CH_3 δ = 1.61, 2.16. – ^{13}C NMR (CD_2Cl_2, 263 K): CH_3 δ = 29.4 (3 C), 31.3 (2 C), C 60.1, 66.2, C≡N 101.9 (br.), C=N 213.3, aromatic C 128.8, 130.3, 135.3, 136.2.

$[C_{15}H_{20}BrN_2]SbCl_6$ (642.7) Calc. C 28.03 H 3.14 N 4.36 Found C 27.95 H 3.18 N 4.39

3-tert-Butyl-1-(1-phenylethylidene)cyanamidium hexachloroantimonate (**18j**): As described for **18b** from antimony pentachloride (2.99 g, 10 mmol), **19j**[25] (1.44 g, 10 mmol) and *tert*-butyl chloride (1.02 g, 11 mmol) in dry dichloromethane (30 ml). Precipitating at −30°C with dry pentane (90 ml) afforded a pale yellow powder (5.30 g, 99%) which was recrystallized from dry dichloromethane/cyclohexane at −30°C; m. p. 108–111°C (dec.). – IR (CH_2Cl_2): C≡N̂ 2260, 2310 cm^{-1}. – ^{1}H NMR (CD_2Cl_2): CH_3 δ = 1.80, 3.25. – ^{13}C NMR (CD_2Cl_2, 263 K): CH_3 δ = 29.5 (1 C), 30.1 (3 C), C 65.2, C=N 206.0, aromatic C 130.2, 132.4, 133.8, 140.7.

$[C_{13}H_{17}N_2]SbCl_6$ (535.8) Calc. C 29.14 H 3.20 N 5.23 Found C 29.22 H 3.13 N 5.31

3-tert-Butyl-1-(9-fluorenylidene)cyanamidium hexachloroantimonate (**18k**): As described for **18b** from antimony pentachloride (2.99 g, 10 mmol), **19k**[25,38] (2.04 g, 10 mmol) and *tert*-butyl chloride (1.02 g, 11 mmol) in dry dichloromethane (30 ml). Precipitating with pentane (75 ml) at −30°C (5.54 g, 93%) and recrystallization from dry dichloromethane afforded black-violet needles; m. p. 109–111°C (dec.). In the solid state the compound is stable at room temperature. Due to low solubility and fast decomposition in solution NMR spectra of **18k** could not be obtained. – IR (CH_2Cl_2): C≡N̂ 2270 cm^{-1}.

$[C_{18}H_{17}N_2]SbCl_6$ (595.8) Calc. C 36.28 H 2.88 N 4.70 Found C 36.21 H 2.80 N 4.72

1-(1-tert-Butyl-2,2-dimethylpropylidene)-3-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)cyanamidium hexachloroantimonate (**18l**): As described for **18b** from antimony pentachloride (2.99 g, 10 mmol), **19l** (1.66 g, 10 mmol) and 1-chloroadamantane (1.71 g, 10 mmol) in dry dichloromethane (45 ml). The reaction mixture was stirred for 2 h at −10°C. Precipitating with dry pentane (100 ml) afforded a white powder (5.28 g, 10 mmol) which was recrystallized from dichloromethane at −20°C; m. p. 160–164°C (dec.). – IR (CH_2Cl_2): C≡N̂ 2250, C=N 1660 cm^{-1}. – ^{1}H NMR (CH_2Cl_2): CH_3 δ = 1.51.

$[C_{20}H_{33}N_2]SbCl_6$ (636.0) Calc. C 37.77 H 5.23 N 4.41 Found C 37.68 H 5.17 N 4.40

1-(2,2-Dimethyl-1-phenylpropylidene)-3-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)cyanamidium hexachloroantimonate (**18m**): As described for **18l** from antimony pentachloride (5.98 g, 20 mmol), **19b** (3.73 g, 20 mmol) and 1-chloroadamantane (3.42 g, 20 mmol) in dry dichloromethane (45 ml). Precipitation with pentane (100 ml) afforded a colourless powder (12.07 g, 92%) which could not be recrystallized without decomposition; m. p. 146–149°C (dec.). – IR (CH_2Cl_2): C≡N̂ 2260 cm^{-1} (shoulder 2320). – ^{1}H NMR (CD_2Cl_2): CH_3 δ = 1.50.

$[C_{22}H_{29}N_2]SbCl_6$ (656.0) Calc. C 40.28 H 4.46 N 4.27 Found C 39.80 H 4.69 N 4.29

1-(Diphenylmethylene)-3-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)cyanamidium hexachloroantimonate (**18n**): As described for **18b** from antimony pentachloride (2.99 g, 10 mmol), **19c** (2.06 g, 10 mmol)

and 1-chloroadamantane (1.71 g, 10 mmol) in dry dichloromethane (30 ml). Precipitation with pentane (50 ml) at −40°C (5.95 g, 88%) and recrystallization from dichloromethane/ether afforded pale yellow leaflets; m.p. 187–190°C (dec.). – IR (CH_2Cl_2): C≡N̂ 2270 cm^{-1}. – ^{13}C NMR (CD_2Cl_2, 243 K): CH_2, CH δ = 29.1, 35.0, 42.2, C 63.6, C=N 201.0, NCN 103.2 (br.), aryl C 130.1, 133.2, 134.9, 138.5.

$[C_{24}H_{25}N_2]SbCl_6$ (675.9) Calc. C 42.64 H 3.73 N 4.15 Found C 42.51 H 3.69 N 4.14

1-(α-Naphthylphenylmethylene)-3-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)cyanamidium hexachloroantimonate (**18o**): As described for **18b** from antimony pentachloride (2.99 g, 10 mmol), **19d** (2.56 g, 10 mmol) and 1-chloroadamantane (1.71 g, 10 mmol) in dry dichloromethane (40 ml). Precipitating with dry ether (120 ml) at −40°C afforded an orange powder which was recrystallized from dichloromethane/ether; m.p. 153–155°C (dec.). – IR (CH_2Cl_2): C≡N̂ 2260 cm^{-1}. – ^{13}C NMR (CD_2Cl_2, 253 K): CH_2, CH δ = 28.9, 34.8, 42.0, C 63.4, C≡N̂ 103.3 (br.), C=N 201.7.

$[C_{28}H_{27}N_2]SbCl_6 \cdot 1/4\ CH_2Cl_2$ (747.2) Calc. C 45.41 H 3.71 N 3.75
Found C 45.38 H 3.68 N 3.73

1-(1-Phenylethylidene)-3-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)cyanamidium hexachloroantimonate (**18p**): As described for **18b** from antimony pentachloride (2.99 g, 10 mmol), **19j** (1.44 g, 10 mmol) and 1-chloroadamantane (1.71 g, 10 mmol) in dry dichloromethane (20 ml). Precipitation at 22°C with pentane (30 ml) afforded a pale yellow powder (5.10 g, 83%) which was recrystallized from dichloromethane at −20°C; m.p. 138–141°C (dec.). – IR (CH_2Cl_2): C≡N̂ 2260 cm^{-1}. – ^{13}C NMR (CD_2Cl_2): CH_3, CH_2, CH δ = 29.2, 29.7, 35.3, 43.0, C 65.4, C=N 206.3, aryl C 130.3, 132.5, 134.2, 140.7.

$[C_{19}H_{23}N_2]SbCl_6$ (613.9) Calc. C 37.17 H 3.78 N 4.57 Found C 37.07 H 3.64 N 4.58

1-[Bis(methylthio)methylene]-3-tert-butylcyanamidium hexachloroantimonate (**18q**): As described for **18b** from **19q**[39] (1.46 g, 10 mmol), antimony pentachloride (2.99 g, 10 mmol) and *tert*-butyl chloride (0.93 g, 10 mmol) in dry dichloromethane (30 ml). After stirring for 2 h at 0°C the product was precipitated by addition of dry pentane (40 ml). The oily product soon crystallized affording a yellow powder (4.84 g, 90%) which crystallized from dichloromethane in form of large prisms; m.p. 104–107°C (dec.). – IR (CH_2Cl_2): C≡N̂ 2240 cm^{-1} (shoulder 2310). – ^1H NMR (CD_2Cl_2, 240 K): CH_3 δ = 1.70, 2.93. – ^{13}C NMR (CD_2Cl_2, 240 K): CH_3 δ = 19.2, 30.1, C 63.5, C=N 211.6, C≡N 101.5 (br.).

$[C_8H_{15}N_2S_2]SbCl_6$ (537.8) Calc. C 17.87 H 2.81 N 5.21 Found C 17.96 H 2.67 N 5.19

1-[Bis(dimethylamino)methylene]-3-ethylcyanamidium tetrafluoroborate (**18r**): To a stirred solution of **19r**[40] (28.04 g, 200 mmol) in dry 1,2-dichloroethane (70 ml) was added dropwise at −30°C a solution of triethyloxonium tetrafluoroborate (38.00 g, 200 mmol) in dry 1,2-dichloroethane (100 ml). Stirring was continued for 1 h at +22°C. After addition of dry pentane (200 ml) the mixture was kept for 12 h at −20°C and then filtrated. The filtrate was concentrated under reduced pressure to a volume of 150 ml and diluted with dry ether (100 ml). During 12 h at −20°C colourless hygroscopic crystals formed (34.82 g, 68%) which were recrystallized from 1,2-dichloroethane/ether; m.p. 83–85°C. – IR (CH_2Cl_2): C≡N̂ 2260 cm^{-1}. – ^1H NMR (CD_2Cl_2): CH_3 δ = 1.41 (t, J = 7 Hz), 3.12, CH_2 3.82 (q, J = 7 Hz). – ^{13}C NMR (CD_2Cl_2): CH_3 δ = 15.4, 41.5, CH_2 41.1, C≡N 111.8 (br.), C=N 161.7.

$[C_8H_{17}N_4]BF_4$ (256.1) Calc. C 37.52 H 6.69 N 21.89 Found C 37.36 H 6.82 N 21.74

(1-tert-Butyl-2,2-dimethylpropylidene)cyanamide (**19a**): A suspension of **15a** (11.22 g, 50 mmol) and NBS (19.58 g, 110 mmol) was refluxed in dry carbon tetrachloride (90 ml) for 210 min. After filtration the solution was concentrated to a volume of 50 ml and kept at 5°C for 24 h. Filtration from a small amount of succinimide and evaporation of the solvent at reduced pressure gave an

oil which crystallized from ether (1 ml)/pentane (3 ml) affording a pale yellow powder (5.82 g, 70%); m. p. 64 – 66 °C. – IR (CH_2Cl_2): C≡N 2180, C=N 1600 cm^{-1}. – ^1H NMR (CCl_4): CH_3 δ = 1.41. – ^{13}C NMR ($CDCl_3$): CH_3 δ = 29.3, C 45.4, C≡N 112.7, C=N 212.4.

$C_{10}H_{18}N_2$ (166.3) Calc. C 72.24 H 10.91 N 16.85
Found C 72.01 H 11.08 N 16.94 mole peak 166 (MS)

(2,2-Dimethyl-1-phenylpropylidene)cyanamide (**19b**)[26]: A suspension of **15b** (14.66 g, 60 mmol) and NBS (12.46 g, 70 mmol) was refluxed in dry carbon tetrachloride (200 ml) for 3 h. After filtration and concentration to a volume of 50 ml cyclohexane (25 ml) was added. At – 25 °C residual succinimide crystallized which was removed by filtration. Evaporation of the solvent under reduced pressure and distillation of the residue afforded a colourless oil (6.30 g, 56%); b. p. 85 – 90 °C/10^{-1} Torr. The IR and ^1H NMR spectra were identical with the spectra of an authentic sample[26].

(Diphenylmethylene)cyanamide (**19c**)[25]: As described for **19b** from **15c** (39.66 g, 150 mmol) and NBS (60.52 g, 340 mmol) in dry carbon tetrachloride (250 ml). The NBS was added in two portions. The solid product was recrystallized from ether (35 ml)/hexane (25 ml) at + 5 °C affording yellow prisms (17.1 g, 55%); m. p. 78 – 79 °C (lit.[25] m. p. 81 – 83 °C).

(α-Naphthylphenylmethylene)cyanamide (**19d**): As described for **19b** from **15d**[41] (18.80 g, 60 mmol) and NBS (17.8 g, 100 mmol, in two portions) in dry carbon tetrachloride (600 ml) within 4 h. After filtration the reaction mixture was concentrated to a volume of 300 ml. At 5 °C residual succinimide crystallized which was removed by filtration. The filtrate was evaporated under reduced pressure. The residue was dissolved in dichloromethane (100 ml)/ether (75 ml). The solution was concentrated under reduced pressure until crystallization commenced. At – 25 °C pale yellow prisms (10.50 g, 68%) formed; m. p. 108 – 109 °C. – IR (KBr): C≡N 2180 cm^{-1}. – ^{13}C NMR ($CDCl_3$): C≡N δ = 114.4, C=N 190.9.

$C_{18}H_{12}N_2$ (256.3) Calc. C 84.35 H 4.72 N 10.93 Found C 84.48 H 4.60 N 10.92

(2-Bromo-2-methyl-1-phenylpropylidene)cyanamide (**19f**): As described for **19b** from **15e** (4.61 g, 20 mmol) and NBS (10.68 g, 60 mmol, in two portions) in dry carbon tetrachloride (100 ml) within 3 h. After filtration the solution was concentrated under reduced pressure to a volume of 15 ml. After addition of cyclohexane (30 ml) residual succinimide crystallized at – 25 °C and was removed by filtration. The solvent was evaporated under reduced pressure. The oily residue could not be distilled without decomposition. Drying for 6 h at 65 °C/10^{-1} Torr afforded a brownish oil (4.41 g, 88%). – IR (film): C≡N 2190 cm^{-1}. – ^1H NMR ($CDCl_3$, 263 K): CH_3 δ = 1.96. – ^{13}C NMR ($CDCl_3$, 263 K): CH_3 δ = 31.2, C 61.0, C≡N 112.8, C=N 197.1, aryl C 126.9, 128.5, 131.0, 134.4.

$C_{11}H_{11}BrN_2$ (251.1) Calc. C 52.61 H 4.42 Br 31.82
Found C 51.80 H 4.43 Br 31.94 mole peak 251, 253 (MS)

Antimony pentachloride – 2-cyanotetramethylguanidine (**20**): To a stirred solution of antimony pentachloride (1.79 g, 6 mmol) in dry dichloromethane (4 ml) was added dropwise at – 78 °C a solution of **19r**[40] (0.84 g, 6 mmol) in dry dichloromethane (5 ml). Stirring was continued for 2 h at 0 °C during which time a part of the product crystallized. Addition of pentane (15 ml) and filtration afforded a yellow powder (2.60 g, 99%) which was recrystallized from dichloromethane; m. p. 150 – 153 °C. – IR (CH_2Cl_2): C≡N 2130 cm^{-1}. – ^1H NMR (CD_3CN): CH_3 δ = 3.12.

$[C_6H_{12}N_4]SbCl_5$ (439.2) Calc. C 16.41 H 2.75 N 12.76 Found C 16.18 H 2.61 N 12.30

tert-Butyldimethylsulfonium hexachloroantimonate (**21**): A solution of **18c** (X = $SbCl_6$) (3.00 g, 5.0 mmol) and dimethyl sulfide (0.33 g, 5.2 mmol) in dry dichloromethane (8 ml) was stirred for 48 h at + 26 °C. Filtration and washing of the residue with dichloromethane afforded a nearly

colourless powder (1.10 g, 49%); m.p. 158–159°C (dec.). – ^{1}H NMR ([D$_6$]acetone): CH$_3$ δ = 1.70 (9H), 3.08 (6H). – ^{13}C NMR ([D$_6$]acetone): CH$_3$ δ = 21.0 (2 C), 25.1 (3 C), C 55.6.

[$C_6H_{15}S$]$SbCl_6$ (453.7) Calc. C 15.88 H 3.33 Found C 15.83 H 3.29

The filtrate of **21** was evaporated under reduced pressure. Chromatography of the remaining oil on silica gel (20 cm × 2.5 cm) with ether/benzene (3:1) as eluent afforded after recrystallization from ether/benzene at –20°C colourless prisms of **19c** (0.50 g, 48%); m.p. 77–79°C.

1-tert-Butyl-3-(diphenylmethylene)-2-methyluronium hexachloroantimonate (**22c**): A solution of **18c** (X = $SbCl_6$) (1.20 g, 2 mmol) and methanol (0.07 g, 2 mmol) in dry dichloromethane (10 ml) was stirred for 24 h at 22°C. Evaporation of the solvent and crystallization from ether (1 ml)/hexane (5 ml) afforded a grey moisture sensitive powder (0.96 g, 68%); m.p. 148–151°C (dec.). – ^{1}H NMR (CD_3CN): CH$_3$ δ = 1.18, 4.29. – ^{13}C NMR (CD_3CN): CH$_3$ δ = 28.2, 61.0, C 57.4, C=N 182.3, NCN 168.5, phenyl C 134.9, 134.5, 131.3, 130.0.

[$C_{19}H_{23}N_2O$]$SbCl_6$ (629.9) Calc. C 36.23 H 3.68 N 4.45 Found C 36.16 H 3.62 N 4.43

1-(2,2-Dimethyl-1-phenylpropylidene)-2-methyl-3-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)uronium hexachloroantimonate (**22m**): A solution of **18m** (X = $SbCl_6$) (1.31 g, 2 mmol) and dry methanol (0.07 g, 2 mmol) in dichloromethane (10 ml) was stirred for 60 h at 22°C. Precipitation of the product with pentane at –20°C and recrystallization from dichloromethane/pentane afforded colourless crystals (0.74 g, 54%); m.p. 146–150°C. – ^{1}H NMR (CD_2Cl_2): CH$_3$ δ = 1.41, 4.22, NH 6.31. – ^{13}C NMR (CD_2Cl_2): C=N δ = 199.1, NCN 167.9.

[$C_{23}H_{33}N_2O$]$SbCl_6$ (688.0) Calc. C 40.15 H 4.83 N 4.07 Found C 39.98 H 4.68 N 4.08

1-(Diphenylmethylene)-2-methyl-3-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)uronium hexachloroantimonate (**22n**): As described for **22c** from **18n** (X = $SbCl_6$) (0.68 g, 1 mmol) and methanol (0.03 g, 1 mmol) in dry dichloromethane (5 ml). The product (0.69 g, 97%) was precipitated with pentane and recrystallized from dichloromethane/ether/pentane affording yellow leaflets; m.p. 170–173°C. – ^{1}H NMR (CD_2Cl_2): OCH$_3$ δ = 4.33. – ^{13}C NMR (CD_2Cl_2): OCH$_3$ δ = 60.6, C=N 182.4, NCN 167.7.

[$C_{25}H_{29}N_2O$]$SbCl_6$ (708.0) Calc. C 42.41 H 4.13 N 3.96 Found C 42.13 H 4.00 N 3.88

2-Methyl-1-(α-naphthylphenylmethylene)-3-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)uronium hexachloroantimonate (**22o**): As described for **22c** from **18o** (X = $SbCl_6$) (1.49 g, 2 mmol) and methanol (0.06 g, 2 mmol) in dichloromethane (10 ml) during 60 h at 22°C. Recrystallization from chloroform (8 ml)/ether (3 ml) at –20°C afforded yellow prisms (0.94 g, 62%); m.p. 165–168°C. – ^{1}H NMR (CD_2Cl_2, 263 K): CH$_3$ δ = 4.36, NH 5.89. – ^{13}C NMR (CD_2Cl_2, 263 K): OCH$_3$ δ = 61.1, C=N 182.9, NCN 167.5.

[$C_{29}H_{31}N_2O$]$SbCl_6$ (758.0) Calc. C 45.95 H 4.12 N 3.70 Found C 45.82 H 3.95 N 3.71

N,N'-Di-tert-butyl-N''-(1-tert-butyl-2,2-dimethylpropylidene)guanidinium hexachloroantimonate (**23a**, X = $SbCl_6$): To a stirred solution of antimony pentachloride (1.50 g, 5 mmol) in dry dichloromethane (5 ml) was added dropwise at –70°C a solution of **19a** (0.83 g, 5 mmol) in dry dichloromethane (5 ml) and subsequently a solution of *tert*-butyl chloride (0.47 g, 5 mmol) in dry dichloromethane (2 ml). After 1 h at –70°C the mixture was warmed up to –30°C and the product was precipitated by slow addition of pentane affording a thermally labile moisture sensitive almost colourless powder of **18a** (X = $SbCl_6$) (2.29 g, 82%); m.p. 91–93°C (dec.). – IR (CH_2Cl_2): C≡N 2260 cm^{-1}. – ^{1}H NMR (CH_2Cl_2): CH$_3$ δ = 1.54 (18H), 1.76 (9H). – ^{13}C NMR (CD_2Cl_2, 263 K): CH$_3$ δ = 29.6 (3 C), 29.8 (6 C), C 50.4, 65.6, C=N 239.3, C≡N 102.0 (br.).

To a stirred solution of the crude **18a** (X = $SbCl_6$) (0.56 g, 1 mmol) in dry dichloromethane (5 ml) was added dropwise at –50°C a solution of *tert*-butylamine (0.08 g, 1 mmol) in dry dichloromethane (2 ml). Stirring at –50°C was continued for 1 h. Addition of pentane (10 ml)

and recrystallization from dichloromethane (5 ml)/ether (10 ml) afforded a colourless powder (0.44 g, 70%); m.p. 169–172°C. – IR (CH_2Cl_2): C=N 1690, 1580 cm^{-1}. – ^1H NMR ($CDCl_3$): CH_3 δ = 1.46, 1.54, NH 5.22. – ^{13}C NMR ($CDCl_3$): CH_3 δ = 29.9, 30.3, C 46.4, 55.6, C=N 157.0, NCN 195.3.

$[C_{18}H_{38}N_3]SbCl_6$ (631.0) Calc. C 34.26 H 6.07 N 6.66 Found C 34.18 H 6.14 N 6.67

N,N'-Di-tert-butyl-N''-(2,2-dimethyl-1-phenylpropylidene)guanidinium hexachloroantimonate (**23b**, X = $SbCl_6$): From **18b** (X = $SbCl_6$) (0.58 g, 1 mmol) and *tert*-butylamine (0.08 g, 1 mmol) as described for **23a** (X = $SbCl_6$). The crude product was recrystallized from dichloromethane (5 ml)/pentane (15 ml) at –30°C affording a colourless powder (0.49 g, 75%); m.p. 153–156°C. – IR (CH_2Cl_2): C=N 1610 cm^{-1}. – ^1H NMR (CD_2Cl_2, 263 K): CH_3 δ = 1.13 (br.), 1.37, 1.57 (br.), NH 5.06, 5.35. – ^{13}C NMR (CH_2Cl_2, 263 K): CH_3 δ = 27.5, 28.5 (br.), C 43.1, 57.3, C=N 193.8, HCN 160.4, phenyl C 125.9, 129.2, 130.6, 133.8.

$[C_{20}H_{34}N_3]SbCl_6$ (651.0) Calc. C 36.90 H 5.26 N 6.45 Found C 37.17 H 5.35 N 6.56

N,N'-Di-tert-butyl-N''-(α-naphthylphenylmethylene)guanidinium hexachloroantimonate (**23d**, X = $SbCl_6$): From **18d** (X = $SbCl_6$)[27] (0.65 g, 1 mmol) and *tert*-butylamine (0.08 g, 1 mmol) as described for **23a** (X = $SbCl_6$). The reaction mixture was stirred for 2 h at + 22°C and then concentrated to a volume of 3 ml. Precipitation with ether (15 ml) afforded a yellow powder (0.69 g, 95%) which was recrystallized from dichloromethane/ether; m.p. 185–187°C. – IR (CH_2Cl_2): C=N 1610 cm^{-1}. – ^1H NMR (CD_2Cl_2, 310 K): CH_3 δ = 0.77 (br.), 1.17 (br.), NH 4.86, 5.45. – ^{13}C NMR (CD_2Cl_2, 263 K): CH_3 δ = 28.0, 30.1, C 53.7, 57.5, C=N 160.0, NCN 179.4.

$[C_{26}H_{32}N_3]SbCl_6$ (721.0) Calc. C 43.31 H 4.47 N 5.83 Found C 43.04 H 4.50 N 5.78

N-tert-Butyl-N'-(1-tert-butyl-2,2-dimethylpropylidene)-N''-(tricyclo[3.3.1.1^{3,7}]dec-1-yl)-guanidinium hexachloroantimonate (**23l**, X = $SbCl_6$): From **18l** (X = $SbCl_6$) (0.64 g, 1 mmol) and *tert*-butylamine (0.08 g, 1 mmol) as described for **23d** (X = $SbCl_6$). Precipitation with pentane afforded a yellow powder (0.65 g, 91%) which was recrystallized from dichloromethane/ether/hexane; m.p. 186–189°C (dec.). – IR (CH_2Cl_2): C=N 1680, 1570 cm^{-1}. – ^1H NMR (CD_2Cl_2): CH_3 δ = 1.44 (18H), 1.52, NH 4.93, 5.00. – ^{13}C NMR (CD_2Cl_2): NCN δ = 156.9, C=N 195.5.

$[C_{24}H_{44}N_3]SbCl_6$ (709.1) Calc. C 40.65 H 6.25 N 5.93 Found C 40.62 H 6.39 N 5.94

N-[Bis(methylthio)methylene]-N',N''-di-tert-butylguanidinium hexachloroantimonate (**23q**, X = $SbCl_6$): From **18q** (X = $SbCl_6$) (0.54 g, 1 mmol) and *tert*-butylamine (0.08 g, 1 mmol) as described for **23d** (X = $SbCl_6$). Precipitation with pentane and recrystallization from dichloromethane (3 ml)/ether (4 ml) afforded yellow prisms (0.42 g, 69%); m.p. 141–144°C. – IR (CH_2Cl_2): C=N 1560, 1590 cm^{-1}. – ^1H NMR (CD_2Cl_2): CH_3 δ = 1.48 (18H), 2.68, NH 5.74 (2H). – ^{13}C NMR (CD_2Cl_2): CH_3 δ = 16.4, 29.6 (6 C), C 55.9, NCN 159.6, C=N 183.7.

$[C_{12}H_{26}N_3S_2]SbCl_6$ (611.0) Calc. C 23.59 H 4.29 N 6.88 Found C 23.72 H 4.24 N 6.85

N-[Bis(dimethylamino)methylene]-N'-ethyl-N'',N''-diisopropylguanidinium tetrafluoroborate (**23r**, X = BF_4): A solution of **18r** (5.12 g, 20 mmol) in dry dichloromethane (10 ml) was mixed with diisopropylamine (2.03 g, 20 mmol) in dry dichloromethane (10 ml) at –30°C. After stirring for 6 h at +22°C and addition of ether (20 ml) at –20°C colourless prisms (6.43 g, 90%) crystallized. The product was recrystallized from dichloromethane/ether; m.p. 136–137°C. – ^1H NMR ($CDCl_3$): CH_3 δ = 1.25 (t, J = 7 Hz), 1.32 (d, J = 7 Hz), 2.92, CH_2 4.12 (m), CH 2.98 (m), NH 5.70 (t, $J \approx 6$ Hz). – ^{13}C NMR ($CDCl_3$): CH_3 δ = 15.1, 20.7, 39.7, CH_2, CH 38.5, 47.9, C=N 157.9, 162.2.

$[C_{14}H_{32}N_5]BF_4$ (357.3) Calc. C 46.07 H 9.03 N 19.61 Found C 46.91 H 9.20 N 19.39

1-tert-Butyl-2-methyluronium hexachloroantimonate (**24**): A mixture of **18c** (X = $SbCl_6$)[27] (1.20 g, 2 mmol) and aqueous (13% water) methanol (0.19 g, 6 mmol) in dichloromethane (15 ml) was stirred for 4 h at 22 °C. The solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (7 ml) and precipitated with pentane (12 ml). Recrystallization from dichloromethane (7 ml)/hexane (10 ml) afforded a pale yellow powder (0.37 g, 40%); m.p. 147 – 151 °C. – IR (CH_2Cl_2): C=N 1660 cm^{-1}. – ^1H NMR (CD_3CN): CH_3 δ = 1.34, 4.03. – ^{13}C NMR (CD_3CN): CH_3 δ = 29.1, 59.4, C 55.3, NCN 161.7.

$[C_6H_{15}NO]SbCl_6$ (465.7) Calc. C 15.47 H 3.25 N 6.02 Found C 15.62 H 3.33 N 5.98

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