Tetrahedron Vol. 41, No. 3, pp. 527 to 536, 1985
Printed in Great Britain.

0040–4020/85 $3.00 + .00

THE REACTION OF 2-AZAALLENIUM SALTS WITH CARBODIIMIDES AND TERT-BUTYL ISOCYANIDE

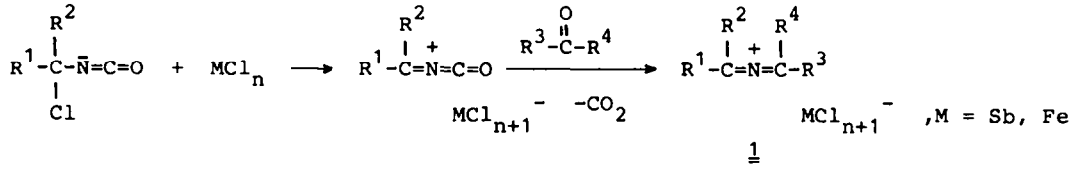
MAHMOUD AL-TALIB, IBRAHIM JIBRIL, JOHANNES C.JOCHIMS *, and GOTTFRIED HUTTNER

Chemistry Department, Yarmouk University, Irbid, Jordan,
and Fakultät für Chemie der Universität Konstanz,
Postfach 5560, D-7750 Konstanz

(*Received in Germany* 17 *October* 1984)

Abstract - 2-Azaallenium salts 1 react with diisopropyl carbodiimide to afford the formal dihydro-1,3-diazetium salts 5. The structure of 5c has been confirmed by an X-ray diffraction analysis. With the carbodiimide 2e the tetraphenyl-2-azaallenium salt 1a reacts to give the guanidinium compound 6. The diazetium salts 5 react with further carbodiimide to afford the formal 2-azaallenium salts 11. With tert-butyl isocyanide the 2-azaallenium salts 1 undergo an Ugi reaction to yield the nitriles 14.

Although 2-azaallenium salts 1 have been known since 1969 [1-4] a synthesis with broader scope has been published only recently [5]:

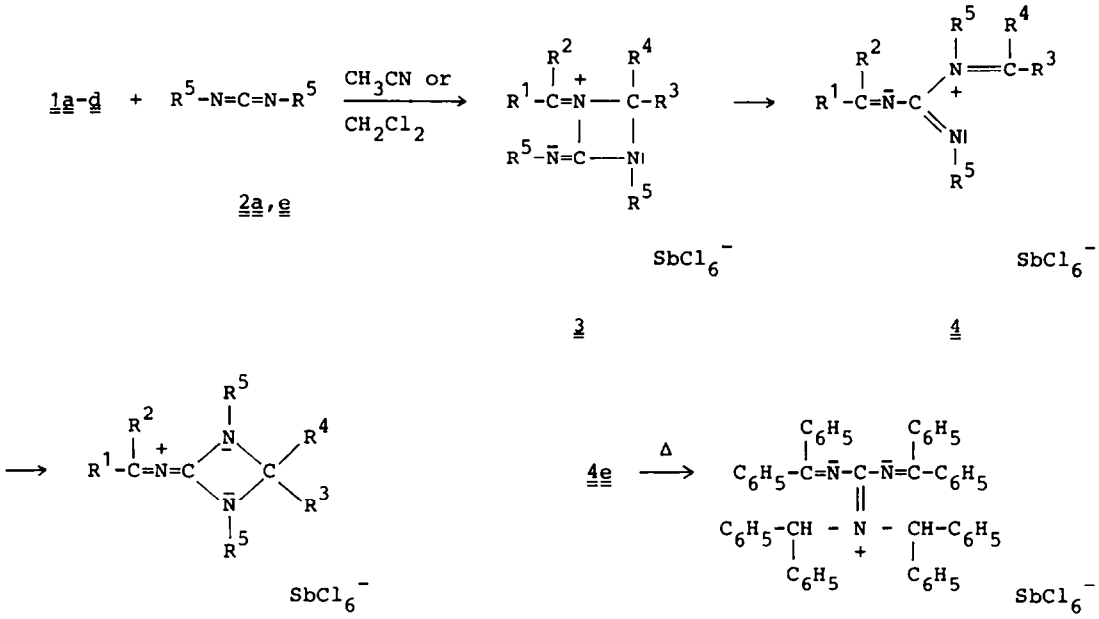


With the exception of reactions with simple nucleophiles like water, alcohols or amines [4-6], the chemistry of 2-azaallenium salts is virtually unexplored, mainly due to the limited access to these compounds. Recently, certain heterosubstituted formal 2-azaallenium salts, e.g. Gold's salt [7] $(CH_3)_2\overset{+}{N}CH{=}N{=}CHN(CH_3)_2\ Cl^-$, have found interesting synthetic applications [8-15].

In this communication we would like to report on reactions of 2-azaallenium salts 1 with carbodiimides and with tert-butyl isocyanide.

Tetraphenyl-2-azaallenium hexachloroantimonate 1a [5] and diisopropylcarbodiimide 2a react in dry acetonitrile at room temperature to give a crystalline 1:1 adduct (71%), to which, according to NMR arguments, structure 5a must be assigned.

Similarly, compounds 5b-d were prepared.



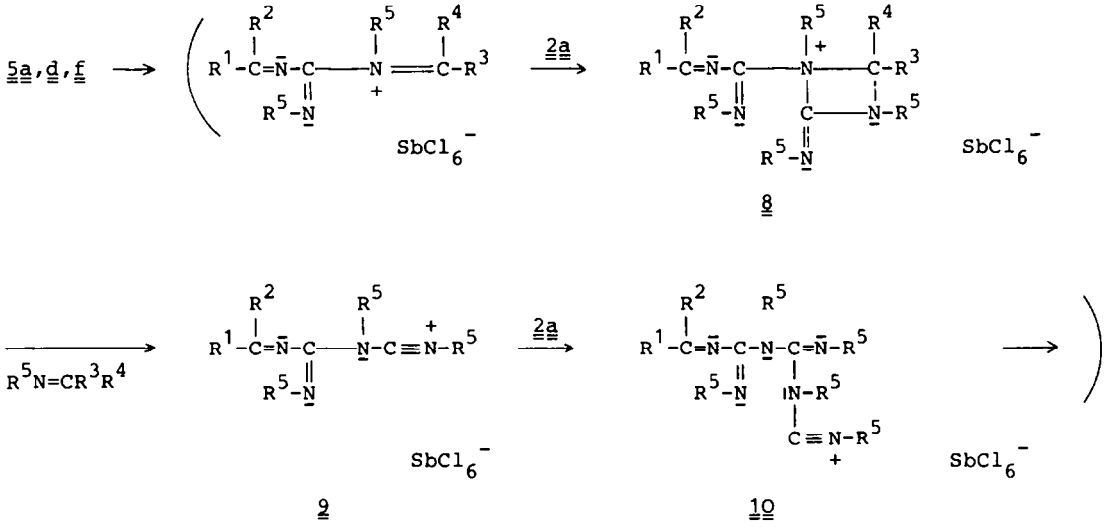
	R^1	R^2	R^3	R^4	R^5
a	C_6H_5	C_6H_5	C_6H_5	C_6H_5	$CH(CH_3)_2$
b	C_6H_5	C_6H_5	o-C_6H_4-C_6H_4-o'		$CH(CH_3)_2$
c	C_6H_5	$C_6H_4OCH_3$-(4)	o-C_6H_4-C_6H_4-o'		$CH(CH_3)_2$
d	C_6H_5	$C_6H_4CH_3$-(4)	o-C_6H_4-C_6H_4-o'		$CH(CH_3)_2$
e	C_6H_5	C_6H_5	C_6H_5	C_6H_5	$CH(C_6H_5)_2$
f	o-C_6H_4-C_6H_4-o'		o-C_6H_4-C_6H_4-o'		$CH(CH_3)_2$
g	$C_6H_4OCH_3$-(4)	$C_6H_4OCH_3$-(4)	o-C_6H_4-C_6H_4-o'		-
h	H	$N(CH_3)_2$	o-C_6H_4-C_6H_4-o'		-

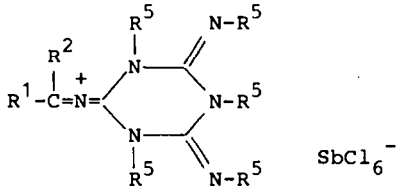
The ^1H and ^{13}C NMR spectra of 5a show equivalent isopropyl groups (R^5 = $(CH_3)_2CH$) (see Experimental Part). Furthermore, ^{13}C signals for only two different types of monosubstituted phenyl groups are observed, along with two resonances for C=N and one signal for a single sp^3 carbon at 97.7 ppm ($CDCl_3$). Structure 5c has been confirmed by an X-ray diffraction analysis (see below).

The formation of compounds 5 can be rationalized assuming a (probably stepwise) [2 + 2] cycloaddition of the carbodiimide 2 to the 2-azaallenium salt 1 to give a diazetidinium intermediate 3, which rearranges to 5 via a second intermediate 4. Instead of cyclization to 5e the guanidine 4e stabilizes itself by migration of a diphenylmethyl cation to a neighbouring nitrogen atom giving the guanidinium salt 6. The structure of 6 is supported by the ^{13}C NMR spectrum, which shows only one signal for an sp^3 carbon, two kinds of phenyl groups and two signals for C=N. For a structure 5e two resonances for sp^3 carbons and three types of phenyl groups

should be expected.

Triazinium compounds 11 are obtained when compounds 5 are boiled under reflux in acetonitrile in the presence of two further equivalents of diisopropylcarbodiimide, 2a, or when the 2-azaallenium salts 1 are treated with three equivalents of 2a. The formation of 11 apparently takes place via opening of the azetidinium ring 5, addition of one molecule of carbodiimide to 8, elimination of an azomethine to afford the cyanamidium salt 9 [16], which adds another molecule of carbodiimide. The cyanamidium salt 10 then cyclizes giving the formal 2-azaallenium salt 11. Hetero-substituted 2-azaallenium salts related to 11 have recently been prepared from 1-oxa-3-azabutatrienium salts and carbodiimides [17]. The structures of compounds 11 follow inter alia from the symmetries of their ^1H and ^{13}C NMR spectra, which show signals for three different isopropyl groups with integrals in the ratio of 1:2:2. In the ^{13}C NMR spectrum of 11a three C=N resonances and four lines for phenyl are observed. A strong band at 1690 cm^{-1} in the IR spectrum of 11a suggests a C=N=C bond angle for the formal 2-azaallenium unit of about 130° [6].

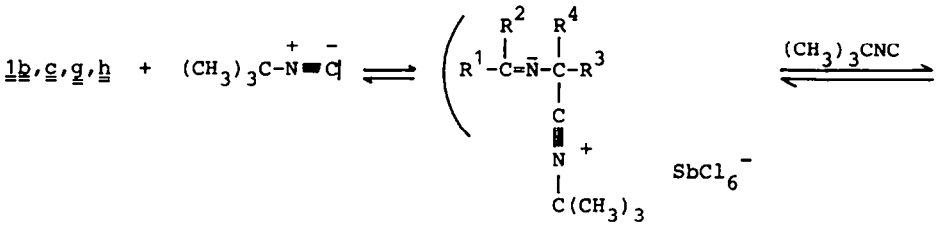




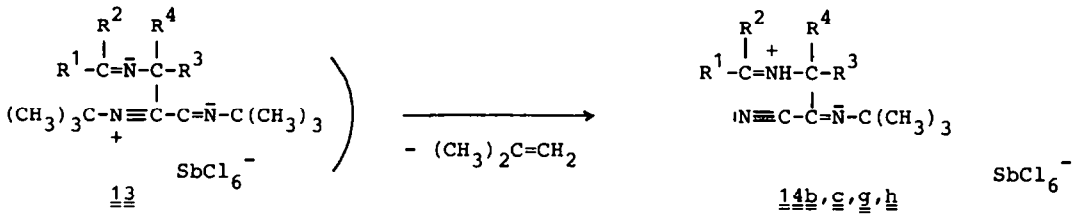
11a,d,f

Reactions of 2-azaallenium salts 1 with carbodiimides other than 2a,b, e.g. dicyclohexylcarbodiimide, proceed in the same way but the products were obtained as foams or oils. With di-p-anisylcarbodiimide 1b reacted to give a red foam, the structure of which remains to be elucidated. No reaction occurred between di-tert-butylcarbodiimide and 1a in boiling acetonitrile (40 hours).

Stirring 1b with two equivalents of tert-butyl isocyanide in acetonitrile gave a crystalline salt, to which we assign structure 14b. Compounds 14c,g,h were prepared in a similar way. No reaction occurred with isopropyl isocyanide. In their



12



13

14b,c,g,h

IR spectra (in CH_2Cl_2) compounds **14** show weak nitrile bands at 2210-2220 cm^{-1}. According to the multiplicity of the NMR signals the phenyl groups of **14b,c,g** are inequivalent (e.g. for **14g** two OCH_3 signals are observed in the ^1H NMR spectra), while a plane of symmetry bisects the fluorene moiety (for all compounds **14** only six ^{13}C resonances for the fluorene sp^2 carbons are observed). A ^{13}C resonance at 109.3 ppm (CD_3CN) in the spectrum of **14b** can be assigned to the nitrile carbon. A signal at 184.4 ppm must arise from the iminium carbon and a line at 75.8 ppm from C-9 of the fluorene moiety. The ^1H NMR spectrum of **14b** shows a broad NH resonance at 12.47 ppm (CD_3CN). The formation of compounds **14** can be rationalized assuming an electrophilic attack of the isocyanide on the more positive and sterically less hindered end of the 2-azaallenium unit of **1**. The resulting nitrilium salt **12** adds another molecule of the isocyanide to give the nitrilium salt **13**, which loses a tert-butyl cation (von Braun cleavage) to give after proton transfer isobutene and **14**. The last step (**13** → **14**) is favourable only for the elimination of a stable tertiary carbenium ion. This is the reason why under mild conditions isopropyl isocyanide does not react with **1**. The reaction sequence can be regarded as a modification of the Ugi reaction [18], which comprises the addition of isocyanides to iminium salts.

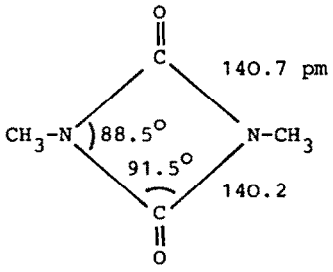
X-Ray Diffraction Analysis for **5c**

5c, $[C_{34}H_{34}N_3O]SbCl_6$, triclinic, space group $P\bar{1}$ (No. 2 [19]), Z = 2, a = 1074.4(3), b = 1231.2(4), c = 1491.9(4) pm, α = 112.63(2), β = 84.57(2), γ = 101.94(2)°, V = 178.2·10^6 pm^3, d_{calc} = 1.56 gcm^{-3}, μ_{Mo-K_α} = 12.6 cm^{-1}, T = 223 K, ω-scan, Δω = 1°, 2.2 < $\dot{\omega}$ < 29.3°min^{-1}, 2° < 2Θ < 42°, 3544 independent significant reflections ($I > 2\sigma$). The cell constants and the reflections were measured on a Syntex-P3-diffractiometer with a graphite monochromator, λ_{Mo-K_α} = 71.069 pm. The structure was solved using the program SHEL-XTL [20] by direct methods. Hydrogen atoms were fixed on calculated geometrically ideal positions. The independent unit contains one

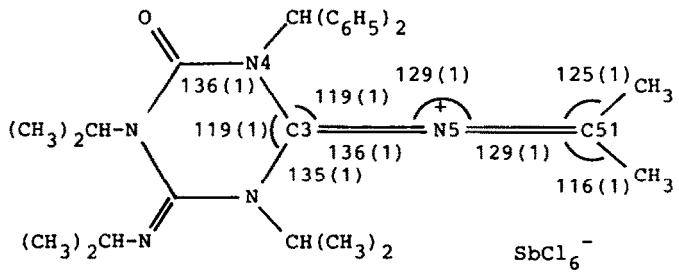
cation and two halves of the anion. The partially anisotropic refinement led to agreement factors R_1 = 0.050 and R_2 = 0.063.

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 for the cation of 5c. Selected bond angles and torsional angles for 5c are given in Table 2.

The crystals of 5c consist of discrete $[C_{34}H_{34}NO]^+$ cations and $SbCl_6^-$ anions. The structure of the cation may be compared with X-ray diffraction data for compounds 15 [21,22] and 16 [17].



15



16: N4-C3-N5-C51 = 100(1)°

Contrary to the isocyanate dimer 15 the four-membered ring in 5c shows long sp^3-C-N bonds (149(1), 151(1) pm) and shorter sp^2-C-N- bonds (135(1), 134(1) pm), the latter being almost equal to the corresponding bond distances for 16 (135(1), 136(1) pm) and to the sp^2-C-N- distance in dimethylformamide [23] (134 pm) indicating considerable double bond character for the bonds C1-N3 and C1-N2 in 5c. On the other hand, the four-membered ring of 5c is planar but the bonds from the ring nitrogen atoms to the isopropyl substituents do not lie in the plane of this ring as should be expected for a true resonance stabilized 1,3-diazetium cation. The 2-azaallenium unit of 5c is far from being linear (C1-N1-C2 127.3(7)°) and shows bond distances and torsional angles, which are similar to those observed for 16 and other 2-azaallenium salts [6,17].

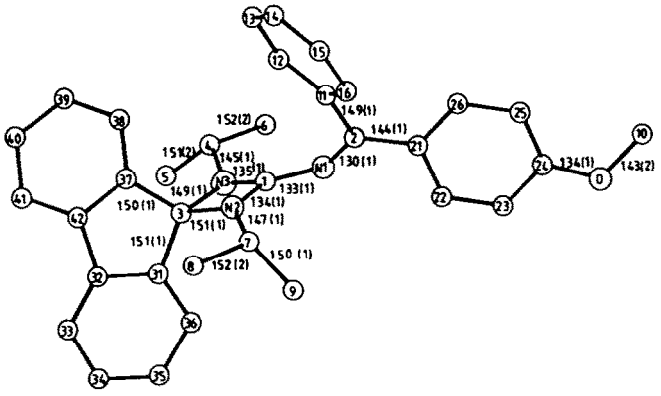


Figure 1. Molecular plot with selected bond lengths for the cation of 5c.

Table 1. Fractional Atomic Coordinates and Temperature Parameters for 5c [a)]

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Sb1 [b)]	1.0000	1.0000	0.5000	Cl1	0.9317(2)	1.0889(2)	0.4029(2)
Cl2	0.7963(2)	0.8764(2)	0.4868(2)	Cl3	1.0691(2)	0.8545(2)	0.3586(2)
Sb2 [b)]	1.0000	1.0000	0.0000	Cl1X	0.8110(2)	1.0049(2)	0.0938(2)
Cl2X	1.1134(3)	1.0282(3)	0.1380(2)	Cl3X	1.0289(3)	1.2100(2)	0.0453(2)
O	1.1695(6)	0.4410(5)	0.3980(5)	N1	0.6683(6)	0.5763(6)	0.3240(5)
N2	0.5802(6)	0.6328(6)	0.2064(5)	N3	0.5002(6)	0.6882(6)	0.3403(5)
C1	0.5877(8)	0.6208(7)	0.2914(6)	C2	0.7034(8)	0.4728(7)	0.2809(6)
C3	0.4804(8)	0.7091(7)	0.2508(6)	C4	0.4084(9)	0.6825(8)	0.4164(7)
C5	0.354(1)	0.7965(9)	0.4561(8)	C6	0.467(1)	0.6619(9)	0.4956(7)
C7	0.6724(9)	0.6258(8)	0.1264(7)	C8	0.6191(9)	0.6587(9)	0.0517(7)
C9	0.801(1)	0.701(1)	0.1612(9)	C10	1.199(1)	0.3301(9)	0.3917(8)
C11	0.6232(8)	0.3711(7)	0.2061(6)	C12	0.4925(9)	0.3511(8)	0.2185(7)
C13	0.416(1)	0.2554(9)	0.1486(7)	C14	0.473(1)	0.1814(9)	0.0693(8)
C15	0.601(1)	0.1996(9)	0.0552(8)	C16	0.6786(9)	0.2956(8)	0.1250(7)
C21	0.8209(7)	0.4593(7)	0.3114(6)	C22	0.9123(8)	0.5607(8)	0.3581(6)
C23	1.0263(9)	0.5522(8)	0.3863(7)	C24	1.0548(8)	0.4398(8)	0.3687(6)
C25	0.9656(8)	0.3374(8)	0.3238(6)	C26	0.8510(8)	0.3473(8)	0.2945(6)
C31	0.5084(8)	0.8374(7)	0.2571(6)	C32	0.4116(8)	0.8597(7)	0.2165(6)
C33	0.4172(8)	0.9722(8)	0.2136(6)	C34	0.5231(9)	0.9404(8)	0.2514(7)
C35	0.6196(8)	1.0369(8)	0.2917(6)	C36	0.6141(8)	0.9247(8)	0.2976(6)
C37	0.3524(8)	0.6614(7)	0.2040(6)	C38	0.2763(9)	0.5495(8)	0.1833(7)
C39	0.162(1)	0.5276(9)	0.1392(7)	C40	0.1222(9)	0.6131(9)	0.1150(7)
C41	0.1991(9)	0.7260(8)	0.1361(7)	C42	0.3132(8)	0.7500(7)	0.1833(6)

atom	U11	U22	U33	U23	U13	U12
Sb1 [b)]	0.0215(5)	0.0133(4)	0.0318(5)	0.0095(4)	-0.0063(4)	0.0006(4)
Cl1	0.035(1)	0.043(2)	0.060(2)	0.037(1)	-0.012(1)	0.003(1)
Cl2	0.027(1)	0.031(1)	0.060(2)	0.024(1)	-0.012(1)	-0.007(1)
Cl3	0.046(2)	0.032(1)	0.045(2)	0.000(1)	-0.001(1)	0.012(1)
Sb2 [b)]	0.0214(5)	0.0132(4)	0.0319(5)	0.0070(4)	-0.0038(4)	0.0017(3)
Cl1X	0.031(1)	0.045(2)	0.054(2)	0.014(1)	0.010(1)	0.005(1)
Cl2X	0.052(2)	0.062(2)	0.047(2)	0.018(1)	-0.020(1)	0.011(1)
Cl3X	0.078(2)	0.016(1)	0.068(2)	0.014(1)	0.013(2)	0.007(1)
O	0.025(4)	0.031(4)	0.086(5)	0.036(4)	-0.019(3)	-0.001(3)
N1	0.025(4)	0.019(4)	0.030(4)	-0.008(3)	-0.007(3)	0.007(3)
N2	0.022(4)	0.015(4)	0.032(4)	0.007(3)	0.002(3)	0.010(3)
N3	0.021(4)	0.017(4)	0.025(4)	0.008(3)	0.001(3)	0.006(3)

atom	U	atom	U	atom	U	atom	U
C1	0.021(2)	C2	0.021(2)	C3	0.023(2)	C4	0.032(2)
C5	0.045(3)	C6	0.043(3)	C7	0.037(2)	C8	0.040(3)
C9	0.061(3)	C10	0.047(3)	C11	0.023(5)	C12	0.032(2)
C13	0.042(3)	C14	0.047(3)	C15	0.045(3)	C16	0.032(2)
C21	0.020(2)	C22	0.030(2)	C23	0.033(2)	C24	0.027(2)
C25	0.030(2)	C26	0.028(2)	C31	0.021(2)	C32	0.023(2)
C33	0.031(2)	C34	0.031(2)	C35	0.031(2)	C36	0.026(2)
C37	0.023(2)	C38	0.033(2)	C39	0.043(3)	C40	0.041(3)
C41	0.033(2)	C42	0.024(2)				

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) The independent unit contains one cation and two halves of the anion.

Table 2. Selected Bond Angles and Torsional Angles [°] for 5c

N2-C1-N3	96.7(8)	N1-C2-C21	117.3(6)	N2-C3-N3-C4	-149.8(7)
C1-N3-C3	48.1(5)	C11-C2-C21	121.2(7)	C3-N2-C1-N3	+ 0.4(6)
N3-C3-N2	84.4(7)	N2-C7-C8	109.5(8)	C3-N2-C1-N1	-170.0(8)
C3-N2-C1	48.7(5)	N2-C7-C9	112.4(8)	C3-N2-C7-C8	- 30(1)
C1-N2-C7	131.5(8)	N3-C4-C5	108.9(9)	C3-N3-C1-N1	+170.4(8)
C1-N3-C4	133.3(9)	N3-C4-C6	111.3(8)	C3-N3-C4-C5	- 55.4(9)
N2-C1-N1	132.5(7)	C1-N1-C2-C11	- 23(1)	N3-C1-N1-C2	+143.0(9)
N3-C1-N1	129.9(8)	C1-N1-C2-C21	+159.2(8)	N3-C1-N2-C7	+154.2(7)
C3-N2-C7	133.1(9)	C1-N2-C7-C8	-174.4(7)	N3-C3-N2-C7	-153.5(7)
C3-N3-C4	127.7(7)	C1-N2-C7-C9	- 49(1)	N1-C2-C11-C12	- 39(2)
N2-C3-C31	118.5(7)	C1-N2-C3-N3	+ 0.3(5)	N1-C2-C21-C22	- 21(1)
N3-C3-C31	117.2(6)	C1-N3-C3-N2	- 0.3(5)	N1-C1-N2-C7	- 15(1)
N2-C3-C37	115.7(6)	C1-N3-C4-C5	+168.9(8)	N1-C1-N3-C4	- 43(1)
N3-C3-C37	118.6(7)	C1-N3-C4-C6	+ 45(1)	C12-C11-C2-C21	+138(1)
C31-C3-C37	102.9(8)	N2-C1-N1-C2	- 51(1)	C22-C21-C2-C11	+160.9(8)
C1-N1-C2	127.3(7)	N2-C1-N3-C3	+ 0.4(6)	C23-C24-O-C10	+173.4(9)
N1-C2-C11	121.5(8)	N2-C1-N3-C4	+146.8(8)		

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

EXPERIMENTAL SECTION

IR spectra: Perkin-Elmer IR 299, always solutions in CH_2Cl_2. ^1H and ^{13}C NMR spectra: Jeol JNM-MH-100 and Bruker WM-250 instruments; δ-scale; internal reference tetramethylsilane. The melting points are uncorrected.

4--Diphenylmethylenamino-2,3-dihydro-1,3-diisopropyl-2,2-diphenyl-1,3-diazetium Hexachloroantimonate (5a): A mixture of 1a [5] (3.41 g, 5.00 mmol) and 2a (0.64 g, 5.05 mmol) in absol acetonitrile (25 ml) was stirred at +23°C till complete disappearance of the 2-azaallenium band at 1860 cm^{-1} in the IR spectra of the solution (about 5 h). The solvent was evaporated under reduced pressure. The oily residue crystallized from absol dichloromethane (10 ml) after dropwise addition of dry ether (30 ml) affording pale yellow crystals (2.86 g, 71%); m.p. 117-121°C (dec). IR: 1640, 1590 cm^{-1}. ^1H NMR($CDCl_3$): CH_3 δ = 0.97 (d, J = 7 Hz), CH 3.53 (sept, J = 7 Hz). ^{13}C NMR($CDCl_3$): CH_3 δ = 21.1, CH 49.0, C2 97.7, C=N 163.7, 181.2, phenyl 128.5, 129.5, 129.6, 130.8, 131.5, 132.6, 134.5, 134.8. (Found: C, 48.79; H, 4.25; N, 5.12. Calc for $[C_{33}H_{34}N_3]SbCl_6$ (MW = 807.1): C, 49.11; H, 4.25; N, 5.21%).

2,2-(Biphenyl-2,2'-diyl)-4-diphenylmethylenamino-2,3-dihydro-1,3-diisopropyl-1,3-diazetium Hexachloroantimonate (5b): A mixture of 1b [24] (3.39 g, 5.00 mmol) and 2a (0.64 g, 5.05 mmol) in absol dichloromethane (30 ml) was boiled under reflux for 5 h. Slow addition of dry ether (50 ml) afforded a yellow powder (3.25 g, 81%); m.p. 147-151°C (dec). IR: 1640, 1590 cm^{-1}. ^1H NMR(CD_2Cl_2): CH_3 δ = 0.89 (d, J =

7 Hz), CH 3.61 (sept, J = 7 Hz). ^{13}C NMR(CD_2Cl_2): CH_3 δ = 21.2, CH 49.8, C-2 94.0, C=N 165.0, 182.5, ten signals for aromatic C's. (Found: C, 49.48; H, 4.03; N, 5.23. Calc for $[C_{33}H_{32}N_3]SbCl_6$ (MW = 805.1): C, 49.23; H, 4.01; N, 5.22%).

2,2-(Biphenyl-2,2'-diyl)-2,3-dihydro-1,3-diisopropyl-4-(4-methoxyphenyl)phenylmethylenamino-1,3-diazetium Hexachloroantimonate (5c): A mixture of 1c [5] (3.55 g, 5.00 mmol) and 2a (0.64 g, 5.05 mmol) in absol acetonitrile (25 ml) was boiled under reflux for 2 h. Evaporation of the solvent and crystallization of the residue from dichloromethane (10 ml)/ether (30 ml)/pentane (10 ml) afforded yellow prisms (1.96 g, 47%); m.p. 159-164°C (dec). IR: 1640, 1580 cm^{-1}. ^{1}H NMR(CD_3CN/CD_2Cl_2 (3:2), 263 K): CH_3 δ = 0.80 (d, J = 7 Hz), 3.98, CH 3.61 (sept, J = 7 Hz). ^{13}C NMR(CD_3CN/CD_2Cl_2 (3:2), 263 K): CH_3 δ = 21.1, 56.8, CH 49.5, C-2 93.1, C=N, O-C= 165.2, 166.3, 181.2, thirteen signals for aromatic C's. (Found: C, 48.74; H, 4.13; N, 4.94. Calc for $[C_{34}H_{34}N_3O]SbCl_6$ (MW = 835.1): C, 48.90; H, 4.10; N, 5.03%).

2,2-(Biphenyl-2,2'-diyl)-2,3-dihydro-1,3-diisopropyl-4-(4-methylphenyl)phenylmethylenamino-1,3-diazetium Hexachloroantimonate (5d): A mixture of 1d [5] (3.47 g, 5.00 mmol) and 2a (1.91 g, 15.10 mmol) was boiled under reflux for 4 h. Evaporation of the solvent and crystallization of the residue from dichloromethane (10 ml)/ether (20 ml) at -25°C afforded yellow prisms (0.76 g, 19%); m.p. 160-168°C (dec). IR: 1630, 1590 cm^{-1}. ^{1}H NMR(CD_3CN): CH_3 δ = 0.80 (d, J = 7 Hz), 2.54, CH 3.64 (sept, J = 7 Hz). ^{13}C NMR(CD_3CN): CH_3 δ = 21.4, 22.0, CH 50.0, C 94.0, C=N 165.6, 183.0, fourteen signals for aromatic C's. (Found: C, 50.00; H, 4.30; N, 5.13. Calc for $[C_{34}H_{34}N_3]SbCl_6$ (MW = 819.1): C, 49.85; H, 4.18; N, 5.13%).

2,2-Bis(diphenylmethyl)-1,3-bis(diphenylmethylene)guanidinium Hexachloroantimonate (6): A mixture of 1a (3.41 g, 5.00 mmol) and 2e [25] (1.89 g, 5.05 mmol) in absol acetonitrile (25 ml) was boiled under reflux for 30 h. Evaporation of the solvent and crystallization from dichloromethane (10 ml)/ pentane (30 ml) at -25°C afforded pale yellow prisms (2.69 g, 51%); m.p. 181-185°C (dec). IR: 1610, 1590, 1570 cm^{-1}. ^{13}C NMR(CD_2Cl_2, 263 K): C=N δ = 165.0, 177.7. (Found: C, 59.69; H, 3.83; N, 3.88. Calc for $[C_{53}H_{42}N_3]SbCl_6$ (MW = 1055.4): C, 60.31; H, 4.01; N, 3.98%).

2-Diphenylmethylenamino-3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-1,3,5-triazinium Hexachloroantimonate (11a): A mixture of 1a [5] (3.41 g, 5.00 mmol) and 2a (1.91 g, 15.10 mmol) in absol acetonitrile (25 ml) was boiled under reflux for 1 h. Evaporation of the solvent and crystallization of the residue from dichloromethane (10 ml)/ ether (40 ml) afforded nearly colourless prisms (3.05 g, 73%); m.p. 177-179°C(dec). IR: 1690, 1650, 1620, 1590, 1570 cm^{-1}. ^{1}H NMR(CD_3CN): CH_3 δ = 0.89 (6 H, d, J = 6 Hz), 1.14 (12 H, d, J = 6 Hz), 1.43 (12 H, broad), CH 2.40 (1 H, sept, J = 6 Hz), 4.31 (4 H, m). ^{13}C NMR(CD_3CN): CH_3 δ = 20.0(broad), 21.1, 23.7, CH 50.7, 55.1, 56.1, C=N 161.0, 178.7, phenyl, C=N 130.2, 130.5 (broad), 134.7 (broad), 135.3, 137.3. (Found: C, 44.54; H, 5.38; N, 9.94. Calc for $[C_{31}H_{45}N_6]SbCl_6$ (MW = 836.2): C, 44.52; H, 5.42; N, 10.05%).

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-2-(4-methylphenyl)-phenylmethylenamino-1,3,5-triazinium Hexachloroantimonate (11d): To the filtrate of the crystallization of 5d (see above) ether (20 ml) was added. The precipitate was recrystallized from dichloromethane/ether yielding pale yellow prisms (1.44 g, 34%); m.p. 165-167°C (dec). IR: 1690, 1650, 1620, 1590 cm^{-1}. ^{1}H NMR(CD_3CN): CH_3 δ = 0.89 (6 H, d, J = 6 Hz), 1.14 (12 H, broad), 1.41 (12 H, broad), 2.47, CH 2.41 (1 H, broad), 4.31 (4 H, m). ^{13}C NMR(CD_3CN): CH_3 δ = 19.9 (broad), 20.1 (broad), 21.1, 21.8, 23.6, 23.7, CH 50.7, 55.0, 56.0, C=N 178.5, 161.0, 134.3 (broad). (Found: C, 45.62; H, 5.37; N, 9.63. Calc for $[C_{32}H_{47}N_6]SbCl_6$ (MW = 850.2): C, 45.20; H, 5.57; N, 9.89%).

2-(9-Fluorenylidenamino)-3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-1,3,5-triazinium Hexachloroantimonate (11f): A mixture of 1f [5] (3.39 g,

5.00 mmol) and 2a (1.91 g, 15.10 mmol) in absol acetonitrile (30 ml) was boiled under reflux for 4 h. Evaporation of the solvent and crystallization of the residue from dichloromethane (10 ml)/ether (20 ml) at -25°C afforded deep yellow prisms (2.13 g, 51%); m.p. 162-163°C (dec). IR: 1660, 1590 cm^{-1}. ^1H NMR(CD_3CN, 263 K): CH_3 δ = 1.22 (12 H, d, J = 6 Hz), 1.33 (6 H, d, J = 6 Hz), 1.36 (12 H, d, J = 7 Hz), CH 3.55 (1 H, sept, J = 6 Hz), 4.36 (4 H, m). ^{13}C NMR(CD_3CN, 263 K): CH_3 δ = 20.9 (broad), 21.3, 23.7, CH 50.8, 55.6, 56.6, C=N 133.2(?)(broad), 159.8, 171.8, aryl 122.9, 127.3, 130.5, 137.7, 137.9, 145.1. (Found: C, 44.94; H, 5.28; N, 9.91. Calc for $[C_{31}H_{43}N_6]SbCl_6$ (MW = 834.0): C, 44.63; H, 5.20; N, 10.08%).

[9-[(tert-Butylimino)cyanomethyl]-9-fluorenyl](diphenylmethylen)ammonium Hexachloroantimonate (14b): A mixture of 1b [24] (3.39 g, 5.00 mmol) and tert-butyl isocyanide (0.85 g, 10.23 mmol) in absol acetonitrile (30 ml) was boiled under reflux for 4 h. Evaporation of the solvent and crystallization and recrystallization from dichloromethane (10 ml)/ether (30 ml) afforded a yellow powder (2.76 g, 70%); dec above 185°C. IR: 2220, 1640, 1570 cm^{-1}. ^1H NMR(CD_3CN): CH_3 δ = 1.64, NH 12.47. ^{13}C NMR(CD_3CN): CH_3 δ = 29.4, C 61.4, 75.8, C≡N 109.3, C=NH 184.4, C=N and aromatic C's: fifteen signals. (Found: C, 48.95; H, 3.63; N, 5.24. Calc for $[C_{32}H_{28}N_3]SbCl_6$ (MW = 789.0): C, 48.71; H, 3.58; N, 5.33%).

[9-[(tert-Butylimino)cyanomethyl]-9-fluorenyl][(4-methoxyphenyl)phenylmethylen]-ammonium Hexachloroantimonate (14c): As described for 14b from 1c [5] (3.55 g, 5.00 mmol) and tert-butyl isocyanide (0.85 g, 10.23 mmol). The product was crystallized from dichloromethane (10 ml)/ether (30 ml)/pentane (10 ml) and recrystallized from dichloromethane/ether affording yellow prisms (2.50 g, 60%); m.p. 201-203°C (dec). IR: 2210(weak), 1640, 1600, 1550 cm^{-1}. ^1H NMR(CD_2Cl_2, 263 K): CH_3 δ = 1.65, 4.00, NH 12.17. ^{13}C NMR(CD_2Cl_2, 263 K): CH_3 δ = 29.5, 57.2, C 60.8, 73.8, C≡N 108.4, C=N 135.6(?)(broad), 180.6, C-O 169.3, thirteen signals for aryl C's. (Found: C, 48.74; H, 3.58; N, 5.10. Calc for $[C_{33}H_{30}N_3O]SbCl_6$ (MW = 819.1): C, 48.39; H, 3.69; N, 5.13%).

[9-[(tert-Butylimino)cyanomethyl]-9-fluorenyl][bis(4-methoxyphenyl)methylen]ammonium Hexachloroantimonate (14g): A mixture of 1g [5] (3.70 g, 5.00 mmol) and tert-butyl isocyanide (0.85 g, 10.23 mmol) was stirred at +23°C for 10 h. Evaporation of the solvent afforded an oil, which crystallized from dichloromethane (10 ml)/pentane (30 ml). Recrystallization from dichloromethane/pentane gave a yellow powder (2.84 g, 67%); m.p. 207-210°C (dec). IR: 1630, 1590 cm^{-1}. ^1H NMR(CD_2Cl_2): CH_3 δ = 1.64, OCH_3 3.74, 4.00, NH 11.65. ^{13}C NMR(CD_2Cl_2): CH_3 δ = 29.6, 56.3, 57.1, C 61.0, 74.8, C≡N 108.5, C=N 181.2, C-O 169.1, 164.8, thirteen signals for aromatic C's and C=N. (Found: C, 48.27; H, 3.73; N, 4.93. Calc for $[C_{34}H_{32}N_3O_2]SbCl_6$ (MW = 848.1): C, 48.15; H, 3.68; N, 4.95%).

N-[9-[(tert-Butylimino)cyanomethyl]-9-fluorenyl]-N'-dimethylformamidinium Hexachloroantimonate (14h): A mixture of 1h [6] (2.85 g, 5.00 mmol) and tert-butyl isocyanide (0.85 g, 10.22 mmol) in dry acetonitrile (25 ml) was stirred for 12 h at +22°C. After evaporation of the solvent the oily residue was crystallized from dichloromethane (10 ml)/ether (15 ml). After two recrystallizations from dichloromethane/ether deep yellow prisms were obtained (1.46 g, 43%); m.p. 200-202°C (dec). IR: 2210 (weak), 1700, 1640, 1600 cm^{-1}. ^1H NMR(CD_3CN, 263 K): CH_3 δ = 1.50, 3.02, 3.15, CH 7.23 (d, J = 14 Hz), NH 8.63 (d, J = 14 Hz). ^{13}C NMR (CD_3CN, 263 K): CH_3 δ = 29.2, 37.4, 44.4, C 60.3, 73.2, C≡N 110.0, C=N, aryl-C 122.3, 126.1, 130.4, 132.7, 136.6, 141.2, 142.6, 153.6. (Found: C, 39.08; H, 3.60; N, 8.09. Calc for $[C_{22}H_{25}N_4]SbCl_6$ (MW = 679.9): C, 38.86; H, 3.71; N, 8.24%).

ACKNOWLEDGEMENTS

This investigation was supported by the Fonds der Chemischen Industrie and the Deutscher Akademischer Austauschdienst.

REFERENCES

1 B.Samuel and K.Wade, J.Chem.Soc. A 1969, 1742.

2 D.H.R.Barton, R.D.Bracho, A.A.Gunatilaka, and D.A.Widdowson, J.Chem.Soc., Perkin Trans.1, 1975, 579.

3 M.T.Reetz, W.Stephan, and W.F.Maier, Synth.Commun. 10, 867 (1981).

4 E.-U.Würthwein, Angew.Chem 93, 110 (1981); Angew.Chem., Int.Ed.Engl. 20, 99 (1981).

5 M.Al-Talib and J.C.Jochims, Chem.Ber., submitted for publication.

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

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

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

9 J.T.Gupton and D.E.Polk, Synth.Commun. 11, 571 (1981).

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

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

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

13 R.Gompper and C.S.Schneider, Synthesis 1979, 215.

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

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

16 R.Abu-El-Halawa and J.C.Jochims, Chem.Ber. 116, 1834 (1983).

17 M.Al-Talib, J.C.Jochims, L.Zsolnai, and G.Huttner, Chem.Ber., submitted for publication.

18 G.Gokel, G.Lüdke, and I.Ugi, Isonitrile Chemistry, p.145, I.Ugi Ed., Academic Press 1971.

19 International Tables for X-Ray Crystallography. The Kynoch Press, Birmingham 1969.

20 SHELL-XTL, program system of W.S.Sheldrick, Göttingen, revision 1979.

21 N.Kuhn, W.Schwarz, and A.Schmidt, Chem.Ber. 110, 1130 (1977).

22 J.-L.Baudour, Y.Delugeard, and M.Sanquer, Acta Crystallogr., Sect.B 30, 691 (1974).

23 L.Brun and C.I.Bränden, Acta Crystallogr. 20, 749 (1966).

24 M.Al-Talib, I.Jibril, E.-U.Würthwein, J.C.Jochims, and G.Huttner, Chem.Ber., submitted for publication.

25 J.C.Jochims, Chem.Ber. 98, 2128 (1965).