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REACTIONS OF 1-OXA-3-AZONIABUTATRIENE SALTS WITH 1,3-DIPOLES

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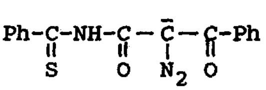
Abstract - The nitrile N-oxide **4** undergoes a reversible cycloaddition to the carbonyl group of the 1-oxa-3-azonia-butatriene salts **3a-c** to give the geminal dioxy substituted 2-azoniaallene salts **5a-c**. Azibenzil **7** and **3a,d** afford the 2-azoniaallene salts **8a,d**. With the nitrone **11** the cumulene **3d** reacts to yield the open-chain addition product **12**. The salt **3a** reacts with two equivalents of diazofluorene to give the β-lactamium salt **13**, which can be hydrolyzed to afford the N-formyl-β-lactam **15**. X-ray structural analyses of **5b** and **8d** confirm the proposed constitutions.[1]

1,3-Dipolar cycloaddition reactions [2] to isocyanates have been used to synthesize a variety of heterocycles and other compounds.[3-5] Usually, the 1,3-dipole adds across the C=N double bond of the isocyanate. Thus, benzonitrile oxide is reported [6-8] to react with phenyl isocyanate to yield 2,4-diphenyl-1,2,5-oxadiazole-3-one. On the other hand, nitrile oxides add to the C=O double bond rather than to the N=C bond of trichloroacetyl isocyanate.[9]

Similarly, α-ketocarbenes react across the C=N double bond of phenyl isocyanate to give N-phenyl-1,3-oxazole-2-ones.[10,11] From the reaction of diazoacetophenone with thiobenzoyl isocyanate compound **1** was obtained.[12] A related reaction was observed for chlorosulfonyl isocyanate.[13]

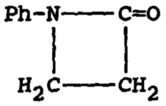
Nitrones usually react with the C=N double bond of isocyanates.[3,12-18] An interesting Beckmann-type rearrangement has recently been described for reactions of chlorosulfonyl isocyanate with nitrones.[19]

Phenyl isocyanate reacts with two molecules of diazomethane to yield **2**.[20] Corresponding β-lactams were obtained from the reaction of sulfonyl isocyanates with two molecules of 9-diazofluorene.[21] The addition of diazoalkanes to acyl isocyanates proceeds via diazonium betaines,[13] which either lose nitrogen to cyclize to 1,3-oxazoline-4-ones [22,23] or retain nitrogen affording diazoamides.[13]



$Ph{-}C({=}S){-}NH{-}C({=}O){-}\bar{C}(N_2){-}C({=}O){-}Ph$

1



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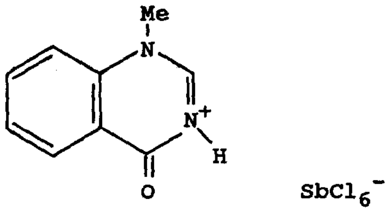

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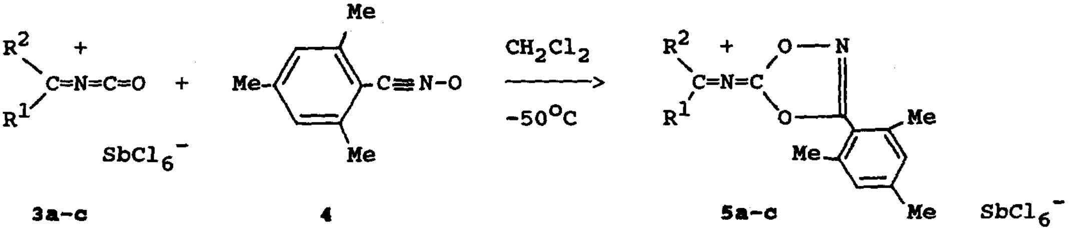


3a–c **4** **5a–c**

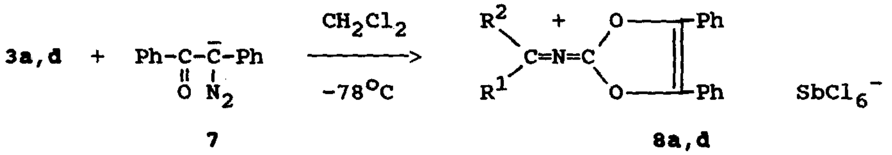
3,5,8	R^1	R^2
a	Me_2N	H
b	MeNPh	H
c	Me_2N	Ph
d	Ph	Ph

In this communication 1,3-dipolar cycloadditions of 1-oxa-3-azoniabutatriene salts **3a-d**, members of a new class of extremely electron deficient cumulated isocyanates,[24-26] are reported.

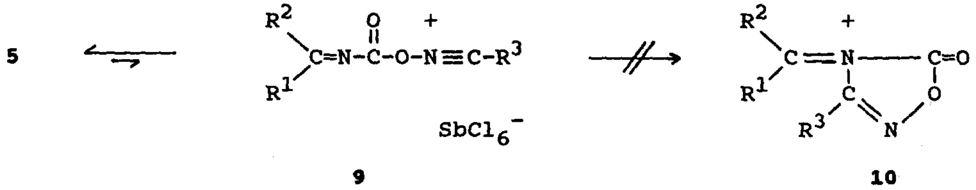
At -50°C vigorous reactions take place between the stable nitrile oxide **4** and the hexachloroantimonates **3a-c** affording the cycloadducts **5a-c**. The addition is reversible. When a solution of **5b** in 1,2-dichloroethane is boiled under reflux (83°C) **3b** is formed back, which cyclizes to give the quinazolinium salt **6**.[26] For **5b** an X-ray structural analysis has been carried out confirming the proposed constitution. With other nitrile oxides, e.g. 2,4,6-trimethoxybenzonitrile oxide, mixtures of compounds were obtained.

When the butatrienium hexachloroantimonate **3d** was treated with azibenzil **7** at -78°C a vigorous reaction with evolution of nitrogen took place and the moisture-sensitive 1,1-dioxy substituted 2-azoniaallene salt **8d** was isolated. Hydrolysis with aqueous sodium hydroxide gave benzoin and benzophenone. Similarly, from **3a** and azibenzil the 2-azoniaallene salt **8a** was obtained. The constitution of **8d** is confirmed by an X-ray structural analysis. Recently, Maas et al.[27] described a related acylation of azibenzil with benzoyl triflate.

The additions of nitrile oxides and diazoketones to the isocyanates **3** constitute a new method for the synthesis of oxy-substituted 2-azoniaallene salts.[28,29]

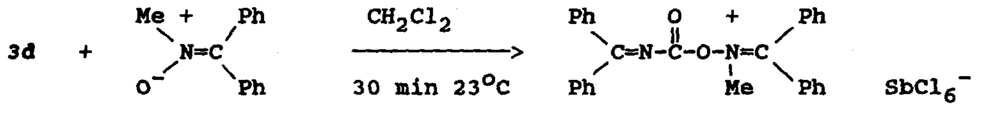


Possibly, these cycloadditions proceed thermodynamically controlled in two steps. Attack of the oxygen atom of the 1,3-dipol on the carbonyl group of the cumulene **3** yields a cation, e.g. **9** in the case of a nitrile oxide. In a second step this cation cyclizes reversibly to give as the most stable product a 2-azoniaallene cation **5** rather than an isomeric N-acyliminium cation **10**.

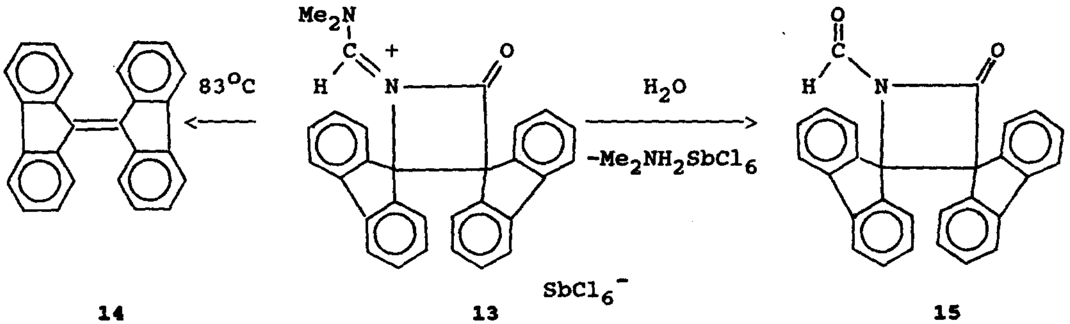


From the reaction of **3d** with the nitrone **11** a compound was isolated in almost quantitative yield, to which the constitution **12** must be assigned on account of the NMR spectra. In the ^{13}C NMR spectrum only a signal for one saturated carbon is found (CH_3 δ = 48.6 ppm, CD_3CN, 263 K) together with sixteen signals for phenyl carbons. Three resonances at 156.2, 181.2 and 181.8 ppm are interpreted as arising from two nonequivalent C=N carbons and a C=O carbon. Compound **12** survives two hours of boiling under reflux in anhydrous acetonitrile but decomposes quickly in boiling chlorobenzene. With nitrones derived from aldehydes the cumulenes **3** afforded only mixtures of unstable compounds.

Products similar to those isolated from the reaction of sulfonyl isocyanates with diazoalkanes [2] were obtained from the α-isocyanato carbenium salt **3a** with two equivalents of 9-diazofluorene.



11 **12**



14 **13** **15**

According to the NMR spectra the orange product has the constitution of a β-lactamium salt **13**. Compound **13** decomposes to 9,9'-bifluorenylidene **14** when heated in boiling 1,2-dichloroethane. Mild hydrolysis in acetonitrile/water affords the N-formyl-β-lactam **15**. Only a few N-formyl-β-lactams seem to be described in the literature.[30]

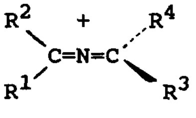
X-Ray Diffraction Analyses of 5b and 8d [1]

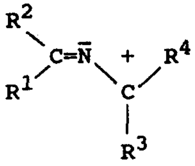
The cell constants and the reflections were measured on a Syntex-P3 diffractometer with a graphite monochromator, $\lambda_{Mo-K\alpha}$ = 71.069 pm. The structures were solved using the program SHELXTL [31] by direct methods. The hydrogen atoms were fixed on calculated geometrically ideal positions.

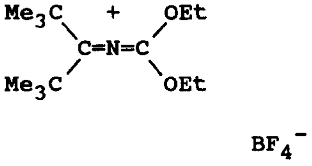
5b, $[C_{19}H_{20}N_3O_2]^+[SbCl_6]^-$, monoclinic, space group $P2_1/c$, Z = 4, a = 1657(1), b = 912(5), c = 2043(1) pm, β = 125.25(5)°, V = $2522\cdot10^6$ pm^3, d_{calc}= 1.73 gcm^{-3}, $\mu_{Mo-K\alpha}$= 17.52 cm^{-1}, T = 243 K, ω-scan, $\Delta\omega$= 1.3°, 2.0 ≤ $\dot{\omega}$ ≤ 29.3°min^{-1}, 2° < 2θ < 48°, 3176 independent significant reflections (I ≥ 2σ). The partially anisotropic refinement led to agreement factors R_1 = 0.042 and R_2 = 0.044.

8d, $[C_{28}H_{20}NO_2]^+[SbCl_6]^-$, triclinic, space group P1, Z = 2, a = 1042.0(6), b = 1171.1(7), c = 1246.5(6) pm, α = 96.45(4), β = 110.64(4), γ = 8.05(5)°, V = $1414.4\cdot10^6$ pm^3, d_{calc} = 1.73 gcm^{-3}, $\mu_{Mo-K\alpha}$ = 15.8 cm^{-1}, T = 228 K, ω-scan, $\Delta\omega$= 1.8 ≤ $\dot{\omega}$ ≤ 29.3°min^{-1}, 2° ≤ 2θ ≤ 42°, 3617 independent significant reflections (I ≥ 2σ). The partially anisotropic refinement led to agreement factors R_1 = 0.065 and R_2 = 0.074.

The crystals of **5b** and **8d** consist of discrete $[C_{19}H_{20}N_3O_2]^+$, respectively $[C_{28}H_{20}NO_2]^+$ cations and $SbCl_6^-$ anions. Valence-bond arguments suggest for the ground-state geometry of 2-azoniallene cations $C{=}N{=}C^+$ either the topology **16** of allene (D_{2d} symmetry) or **17** of the valence-tautomeric allylium cation (C_{2v} symmetry). According to calculations of Würthwein et al. the unsubstituted 2-azoniaallene cation prefers the allene topology **16**.[32,33] However, electron-releasing substituents diminish the energy difference between **16** and **17**. The most stable conformation of 2-azoniallene cations with two amino substituents is predicted to be the allylium geometry **17**. Substituted 2-azoniaallene cations are predicted to be conformationally flexible, the ground-state geometry being mainly determined by sterical interactions of the substituents rather than by electronic factors of the C=N=C moiety. These predictions have been verified experimentally.[34,35] Most 2-azoniaallene cations assume geometries between those of **16** and **17**. For instance, in the crystal the sterically crowded geminal dialkoxy substituted 2-azoniaallene salt **18** [28] shows more or less allene topology with a slightly bent C=N=C unit (α = 149.8(5)°) and planes through the two C=N units, which are almost perpendicular with respect to one another (torsional angles β = 96(1) and β = -94(1) for the O-C-N-C- chains). In contrast, the less sterically demanding substituted cations **5b** and **8a** crystallize in almost ideal allylium conformations. Both cations are essentially planar (torsional angles β = 178.3(6) for N2-C2-N1-C1 in **5b** and -176(1) for C13-N-C14-O2 in **8d**). The central C-N-C units are bent (α = 116.2(5)° for C2-N1-C1 in **5b** and 124.2(8)° for C13-N-C14 in **8d**). The bond lengths of the central nitrogen atoms to the adjacent carbon atoms are unequal in both compounds. In **5b** the N1-C1 bond to the five-membered ring has more of a double-bond character (127(1) pm) than the N1-C2 bond (134(1) pm), contrary to **8d** where the longer bond is the one leading to the dioxole ring (N-C14 135(1) pm, N-C13 128(1) pm).





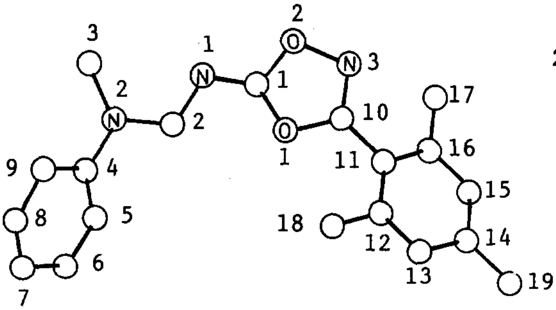


16, $\alpha = 0^\circ$, $\beta = 90^\circ$ **17**, $\alpha = 120^\circ$, $\beta = 0^\circ$ **18**, α = 149.8(5), $\beta \approx 94^\circ$

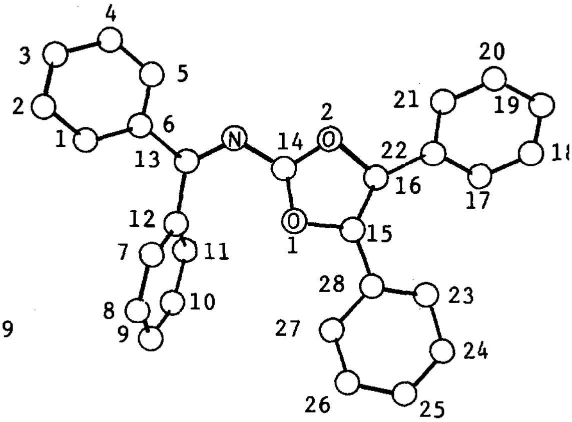
α: bond angle C=N=C β: angle between the planes through R^1-C-R^2 and R^3-C-R^4

Table 1. Selected Bond Lengths [pm], Bond Angles and Torsional Angles [°] of the Cations of **5b** and **8d**.

5b				**8d**			
N1-C1	127(1)	N2-C2-N1-C1	178.3(6)	C13-N	128(1)	C6-C13-N-C14	163(1)
N1-C2	134(1)	C2-N1-C1-O1	4.3(9)	N-C14	135(1)	C12-C13-N-C14	- 12(2)
C2-N2	131(1)	C2-N1-C1-O2	-174.7(6)	C14-O1	130(1)	C13-N-C14-O2	-176(1)
C1-O1	133.7(6)	N1-C2-N2-C3	1.3(9)	C14-O2	129(1)	C13-N-C14-O1	- 4(2)
C1-O2	131(1)	N1-C2-N2-C4	-177.5(5)	O1-C15	140(1)	N-C14-O2-C16	-172(1)
O2-N3	143.4(8)	C2-N2-C4-C5	-49.8(9)	C15-C16	133(1)	N-C14-O1-C15	-170(1)
O1-C10	139(1)	O1-C10-C11-C12	40.7(9)	C16-O2	141(1)	C14-O2-C16-C22	-179(1)
N3-C10	126.9(9)					C14-O1-C15-C28	175(1)
C10-C11	144.9(7)					O2-C16-C22-C17	-143(1)
N1-C2-N2	120.9(5)	C1-O2-N3	109.3(5)			O1-C15-C28-C23	-171(1)
C2-N1-C1	116.2(5)	O2-N3-C10	104.0(7)			N-C13-C6-C1	162(1)
C2-N2-C4	119.5(5)	N3-C10-O1	112.4(5)			N-C13-C12-C7	119(1)
C2-N2-C3	121.2(8)	C10-O1-C1	105.8(6)	C13-N-C14	124.2(8)	O2-C16-C10	6.3(7)
N1-C1-O1	128.8(8)	O1-C10-C11	120.2(6)	N-C14-O1	129.4(9)	C16-C15-O1	107.6(7)
N1-C1-O2	122.8(5)	N3-C10-C11	127.4(8)	N-C14-O2	118.1(8)	C15-O1-C14	106.8(7)
				O1-C14-O2	112.0(7)	C6-C13-N	116.5(8)
				C14-O2-C16	107.2(7)	C12-C13-N	25.8(7)



5b



8d

Figure 1. Molecular Plots for the Cations **5b** and **8d**.

Table 2. Fractional Atomic Coordinates and Temperature Parameters for 5b [a]

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Sb	0.22091(3)	0.63769(4)	0.23667(2)	C5	0.3384(5)	0.1674(8)	0.1233(4)
Cl1	0.1157(2)	0.5421(2)	0.1067(1)	C6	0.4163(6)	0.1228(9)	0.1222(5)
Cl2	0.3289(1)	0.7364(2)	0.36546(9)	C7	0.3996(7)	0.023(1)	0.0647(5)
Cl3	0.2901(2)	0.7991(2)	0.1915(1)	C8	0.3101(7)	-0.025(1)	0.0131(5)
Cl4	0.1538(1)	0.4823(2)	0.2851(1)	C9	0.2287(6)	0.0142(9)	0.0111(5)
Cl5	0.3375(1)	0.4563(2)	0.2636(1)	C10	0.1848(5)	0.1079(6)	0.3442(3)
Cl6	0.1001(1)	0.8132(2)	0.2073(1)	C11	0.2603(4)	0.0617(6)	0.4254(3)
O1	0.2063(3)	0.1176(4)	0.2879(2)	C12	0.3568(5)	0.1105(6)	0.4646(3)
O2	0.0528(3)	0.1665(5)	0.2318(3)	C13	0.4266(5)	0.0612(7)	0.5420(4)
N1	0.1036(4)	0.1689(5)	0.1498(3)	C14	0.4007(5)	-0.0341(7)	0.5798(4)
N2	0.1669(4)	0.1497(6)	0.0754(3)	C15	0.3051(5)	-0.0792(7)	0.5396(4)
N3	0.0954(4)	0.1392(6)	0.3149(3)	C16	0.2331(5)	-0.0359(7)	0.4625(4)
C1	0.1212(5)	0.1525(7)	0.2187(4)	C17	0.1309(5)	-0.0994(8)	0.4218(4)
C2	0.1783(5)	0.1396(7)	0.1440(4)	C18	0.3889(5)	0.2196(8)	0.4287(4)
C3	0.0733(6)	0.196(1)	0.0032(5)	C19	0.4756(6)	-0.0831(9)	0.6627(4)
C4	0.2470(5)	0.1118(7)	0.0706(4)				

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sb	0.0436(3)	0.0268(2)	0.0323(2)	0.0011(2)	0.0210(2)	-0.0002(2)
Cl1	0.082(1)	0.049(1)	0.0374(9)	-0.0077(8)	0.0216(9)	0.001(1)
Cl2	0.048(1)	0.066(1)	0.0395(9)	-0.0123(8)	0.0207(8)	-0.0162(9)
Cl3	0.095(2)	0.0418(9)	0.075(1)	0.0038(9)	0.067(1)	-0.0036(9)
Cl4	0.054(1)	0.0374(8)	0.062(1)	0.0058(8)	0.0364(9)	-0.0038(8)
Cl5	0.062(1)	0.046(1)	0.071(1)	0.0100(9)	0.044(1)	0.0156(9)
Cl6	0.049(1)	0.0332(8)	0.054(1)	-0.0006(7)	0.0226(8)	0.0037(7)
O1	0.031(2)	0.033(2)	0.033(2)	0.001(2)	0.013(2)	0.001(2)
O2	0.038(3)	0.049(3)	0.058(3)	0.015(2)	0.019(2)	0.005(2)
N1	0.052(4)	0.036(3)	0.038(3)	0.005(2)	0.014(3)	-0.001(3)
N2	0.067(4)	0.037(3)	0.026(3)	0.008(2)	0.007(3)	0.001(3)
N3	0.041(3)	0.056(3)	0.057(4)	0.011(3)	0.027(3)	0.007(3)

Atom	U	Atom	U	Atom	U	Atom	U
C1	0.043(2)	C2	0.043(2)	C3	0.080(3)	C4	0.049(2)
C5	0.056(2)	C6	0.072(2)	C7	0.086(3)	C8	0.083(3)
C9	0.071(2)	C10	0.038(1)	C11	0.036(1)	C12	0.039(1)
C13	0.048(2)	C14	0.047(2)	C15	0.049(2)	C16	0.042(2)
C17	0.063(2)	C18	0.056(2)	C19	0.067(2)		

Table 3. Fractional Atomic Coordinates and Temperature Parameters for 8d [a]

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Sb	0.76900(6)	0.75364(5)	0.16866(5)	C13	0.9346(9)	0.7287(8)	0.7312(8)
Cl1	0.8817(3)	0.6662(3)	0.0480(2)	N	0.9427(8)	0.6362(7)	0.6686(7)
Cl2	0.9542(3)	0.8821(2)	0.2574(3)	C14	0.841(1)	0.5947(8)	0.5724(8)
Cl3	0.8785(3)	0.6286(2)	0.3071(2)	O1	0.7170(6)	0.6321(5)	0.5275(5)
Cl4	0.6630(3)	0.8819(2)	0.0334(2)	O2	0.8590(6)	0.4969(6)	0.5206(5)
Cl5	0.6550(3)	0.8401(3)	0.2892(3)	C15	0.646(1)	0.5485(8)	0.4396(8)
Cl6	0.5884(3)	0.6229(2)	0.0821(3)	C16	0.733(1)	0.4648(8)	0.4337(8)
C1	1.063(1)	0.8522(9)	0.9114(9)	C17	0.660(1)	0.3377(9)	0.2514(9)
C2	1.164(1)	0.866(1)	1.015(1)	C18	0.655(1)	0.2338(9)	0.194(1)
C3	1.240(1)	0.7742(9)	1.059(1)	C19	0.721(1)	0.142(1)	0.246(1)
C4	1.215(1)	0.665(1)	0.9985(9)	C20	0.800(1)	0.160(1)	0.364(1)
C5	1.114(1)	0.6509(9)	0.8915(9)	C21	0.805(1)	0.2655(9)	0.424(1)
C6	1.036(1)	0.7440(8)	0.8472(8)	C22	0.733(1)	0.3554(8)	0.3677(8)
C7	0.743(1)	0.8421(9)	0.7640(9)	C23	0.417(1)	0.4880(9)	0.3082(9)
C8	0.640(1)	0.922(1)	0.735(1)	C24	0.277(1)	0.514(1)	0.253(1)
C9	0.625(1)	0.981(1)	0.641(1)	C25	0.227(1)	0.619(1)	0.272(1)
C10	0.710(1)	0.9573(9)	0.576(1)	C26	0.313(1)	0.703(1)	0.352(1)
C11	0.808(1)	0.8743(9)	0.6029(9)	C27	0.450(1)	0.6790(9)	0.4028(9)
C12	0.826(1)	0.8169(8)	0.6988(8)	C28	0.499(1)	0.5703(8)	0.3832(8)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sb	0.0236(4)	0.0228(4)	0.0255(4)	0.0032(3)	0.0060(3)	0.0002(3)
Cl1	0.049(2)	0.052(2)	0.038(2)	0.001(1)	0.022(1)	0.009(1)
Cl2	0.039(2)	0.038(2)	0.055(2)	0.000(1)	0.003(1)	-0.011(1)
Cl3	0.039(2)	0.046(2)	0.042(2)	0.022(1)	0.010(1)	0.008(1)
Cl4	0.051(2)	0.036(1)	0.035(1)	0.012(1)	0.001(1)	0.004(1)
Cl5	0.061(2)	0.058(2)	0.049(2)	0.006(1)	0.034(2)	0.016(2)
Cl6	0.033(2)	0.038(2)	0.070(2)	0.006(1)	0.003(1)	-0.010(1)
N	0.019(4)	0.029(4)	0.031(5)	0.002(4)	0.002(3)	0.001(3)
O1	0.021(3)	0.021(3)	0.032(4)	-0.001(3)	0.004(3)	-0.002(3)
O2	0.024(3)	0.032(4)	0.023(3)	0.001(3)	0.001(3)	0.003(3)

Atom	U	Atom	U	Atom	U	Atom	U
C1	0.032(2)	C2	0.043(3)	C3	0.041(3)	C4	0.039(3)
C5	0.035(2)	C6	0.029(2)	C7	0.032(2)	C8	0.047(3)
C9	0.043(3)	C10	0.039(3)	C11	0.035(2)	C12	0.030(2)
C13	0.025(2)	C14	0.026(2)	C15	0.028(2)	C16	0.026(2)
C17	0.032(2)	C18	0.038(3)	C19	0.052(3)	C20	0.043(3)
C21	0.037(2)	C22	0.030(2)	C23	0.034(2)	C24	0.045(3)
C25	0.048(3)	C26	0.041(3)	C27	0.035(2)	C28	0.029(2)

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

EXPERIMENTAL SECTION

IR spectra: Perkin-Elmer IR 299 and Mattson Polaris FT-IR; solutions were always in CH_2Cl_2. ^1H and ^{13}C NMR spectra: Bruker WM-250 spectrometer; δ-scale; internal reference tetramethylsilane; solutions in CD_3CN if not stated otherwise. All experiments were carried out under exclusion of moisture. The solvents were dried by standard methods, antimony pentachloride was distilled before use. The melting points are uncorrected.

3-[5-(2,4,6-Trimethylphenyl)-1,3,4-dioxazol-2-ylidene)]-1,1-dimethylformamidinium Hexachloroantimonate (5a)

A solution of **4**[36] (1.61 g, 10 mmol) in dichloromethane (15 ml) is added dropwise to a stirred suspension of **3a**[26] (4.34 g, 10 mmol) in dichloromethane (25 ml) at -50°C. Stirring is continued for 30 min at -50°C. The reaction mixture is filtered, and ether is added dropwise to the filtrate at -50°C affording a pale yellow precipitate (5.54 g, 93%), which is recrystallized from dichloromethane (15 ml) at -20°C giving pale yellow prisms (4.51 g, 76%); mp 112-114°C (dec). IR: 1580, 1630 cm^{-1}. ^1H NMR: CH_3 δ = 2.36, 2.44 (2 CH_3), 3.40 (d, J = 1.3 Hz), 3.51 (d, J = 0.7 Hz), phenyl 7.14, HC=N 8.69. ^{13}C NMR(263 K): CH_3 δ = 20.9 (2 CH_3), 21.6, 38.8, 44.9, C=N 162.7, 165.1, 168.1, phenyl 114.6, 130.7, 140.9, 145.5. (Found: C, 27.16; H, 3.26; N, 7.03. Calc for $[C_{14}H_{18}N_3O_2]SbCl_6$ (MW = 594.8): C, 28.27; H, 3.05; N, 7.06%).

3-[5-(2,4,6-Trimethylphenyl)-1,3,4-dioxazol-2-ylidene]-1-methyl-1-phenylformamidinium Hexachloroantimonate (5b)

A mixture of **3b**[26] (0.99 g, 2 mmol) and 2,4,6-trimethylbenzonitrile oxide (0.32 g, 2 mmol) in dichloromethane (10 ml) is stirred at -70°C for 3 h. The solvent is evaporated and the residue is stirred under hexane (10 ml) at -50°C for 30 min. Filtration and crystallization of the residue from dichloromethane (15 ml)/ ether (5 ml) at -20°C affords pale green cubes (0.88 g, 67%); mp 109-111°C (dec). IR: 1570, 1590, 1620, 1660 cm^{-1}. ^1H-NMR (263 K): CH_3 δ = 2.36, 2.46 (2 CH_3), 3.85, trimethylphenyl 7.15, HC=N 8.98. ^{13}C NMR(263 K): CH_3 δ = 20.9 (2 CH_3), 21.6, 40.4, C=N 163.8, 165.6, 169.7. (Found: C, 34.48; H, 2.85; N, 6.25. Calc for $[C_{19}H_{20}N_3O_2]SbCl_6$ (MW = 656.9): C, 34.74; H, 3.07; N, 6.40%).

3-[5-(2,4,6-Trimethylphenyl)-1,3,4-dioxazol-2-ylidene]-1,1-dimethylbenzamidinium Hexachloroantimonate (5c)

Antimony pentachloride (2.99g, 10 mmol) in 1,2-dichloroethane (5 ml) is added to a stirred solution of **3c**[26] (2.04 g, 10 mmol) in 1,2-dichloroethane (10 ml) at -30°C. After stirring for 1 h at 23°C a solution of 2,4,6-tris(trimethylsiloxy)-1,3,5-triazine[37,38] (1.38 g, 4 mmol) in 1,2-dichloroethane (10 ml) is added. The reaction mixture is boiled under reflux for 15 h. After cooling to -50°C a solution of 2,4,6-trimethylbenzonitrile oxide (1.61 g, 10 mmol) in 1,2-dichloroethane (10 ml) is added dropwise. The reaction mixture is stirred for 5 h at -50°C. The solvent is evaporated. The oily residue solidifies when stirred under pentane (50 ml) for 1 h affording a yellow powder (5.57 g, 83%), which is recrystallized from dichloromethane (10 ml)/ether (5 ml) at 0°C to yield pale yellow prisms (2.68 g, 40%); mp 112-114°C (dec). IR: 1590, 1680. ^1H NMR: CH_3 δ = 2.15 (2 CH_3), 2.29, 3.36, 3.62, trimethylphenyl 7.02. ^{13}C NMR: CH_3 δ = 20.6 (2 CH_3), 21.4, 42.9, 44.7, C=N 162.0, 164.7, 170.9. (Found: C, 35.53; H, 3.12; N, 6.34. Calc for $[C_{20}H_{22}N_3O_2]SbCl_6$ (MW = 670.9): C, 35.81; H, 3.31; N, 6.26%).

1-Methyl-4-oxoquinazolinium Hexachloroantimonate[26] (6)

A solution of **5b** (1.31 g, 2 mmol) in 1,2-dichloroethane (15 ml) is boiled under reflux for 30 min. After cooling to 23°C the colourless precipitate (0.64 g, 76%) is filtered. The spectra of the residue are identical with those of an authentic[26] sample; mp 258-260°C (Ref [26]: mp 258-261°C).

1,1-Dimethyl-3-(4,5-diphenyl-1,3-dioxol-2-ylidene)formamidinium Hexachloroantimonate (8a)

A solution of **7** (4.34 g, 10 mmol) in dichloromethane (20 ml) is added dropwise at -20°C to a stirred solution of **3a**[26] in CH_2Cl_2 (20 ml). Stirring at -20°C is continued for 1 h. The product is precipitated by slow addition of carbon tetrachloride (70 ml). Crystallization from dichloromethane (60 ml)/ ether (60 ml) affords yellow prisms (3.20 g, 51%); mp 154-156°C (dec). IR: 1595, 1665 cm^{-1}. ^1H NMR: CH_3 δ = 3.35 (d, J = 1.2 Hz), 3.46 (d, J = 0.6 Hz), CH 8.79. ^{13}C NMR: CH_3 δ = 38.3, 44.3, C=N 163.1, 164.9, phenyl 124.5, 128.0, 130.3, 132.3, 141.2. (Found: C, 34.46; H, 2.57; N, 4.45. Calc for $[C_{18}H_{17}N_2O_2]SbCl_6$ (MW = 627.8): C, 34.44; H, 2.73; N, 4.46%).

(4,5-Diphenyl-1,3-dioxol-2-ylidene)(diphenylmethylene)ammonium Hexachloroantimonate (8d)

A solution of antimony pentachloride (2.99 g, 10 mmol) in dichloromethane (5 ml) was added at -79°C to a solution of chloroisocyanatodiphenylmethane[39] in dichloromethane (30 ml). A solution of **7** (2.23 g, 10 mmol) in dichloromethane (20 ml) was added dropwise at -50°C. When the evolution of nitrogen had ceased the product was precipitated by slow addition of ether (25 ml)/pentane (25 ml) affording a moisture-sensitive red powder (6.45 g (86%), which can be recrystallized from dichloromethane/ether at -20°C; mp 140-143°C (dec). IR: 1560 (broad), 1605. ^{13}C NMR ($CD_3CN/CDCl_3$(2:1), 263 K): C=N δ = 164.8, 194.1, phenyl 122.4, 127.3, 130.0, 130.2, 132.6, 133.7, 134.6, 137.6, 143.1. (Found: C, 45.14; H, 2.52; N, 1.91. Calc for $[C_{28}H_{20}NO_2]SbCl_6$ (MW = 737.0): C, 45.64; H, 2.74; N, 1.90%).

(Diphenylmethylene)[N-(diphenylmethylene)carbamoyloxy]methylammonium Hexachloroantimonate (12)

To antimony pentachloride (2.99g, 10 mmol) in dichloromethane (10 ml) a solution of chloroisocyanatodiphenylmethane [39] (2.44 g, 10 mmol) in dichloromethane (10 ml) is added dropwise at -78°C. The temperature is raised to 0°C and a solution of **11** [40] (2.11 g, 10 mmol) in dichloromethane (10 ml) is added dropwise. After stirring for 30 min at 23°C the reaction mixture is cooled to -30°C, and the product is precipitated by slow addition of ether (50 ml) affording a yellow powder (7.09 g, 94%), which can be recrystallized from dichloromethane or dichloromethane/carbon tetrachloride; dec above 132°C. IR: 1570, 1590, 1600 (shoulder), 1780 cm^{-1}. ^1H NMR: CH_3 δ = 3.77. ^{13}C NMR(263 K): CH_3 δ = 48.6, C=N, C=O 156.1, 181.2, 181.8. (Found: C, 44.70; H, 3.35; N, 3.75. Calc for $[C_{28}H_{23}N_2O_2]SbCl_6$ (MW = 754.0): C, 44.61; H, 3.07; N, 3.72%).

Fluorene-9-spiro-3'-[1-(dimethylaminomethylene)-2-oxoazetidinium]-4'-spiro-9"-fluorene Hexachloroantimonate (13)

A solution of diazofluorene (3.85 g, 20 mmol) in dichloromethane (20 ml) is added dropwise to a stirred solution of **3a** (4.34 g, 10 mmol) in acetonitrile (30 ml) at +23°C. After 30 min of stirring, the product is precipitated by slow addition of pentane (20 ml) affording an orange powder (3.56 g, 47%); mp 148-150°C (dec). IR(KBr): 1690, 1815 cm^{-1}. ^1H NMR: CH_3 δ = 2.67 (broad), 3.45 (d, J = 0.6 Hz). (Found: C, 47.12; H, 3.26; N, 3.75. Calc for $[C_{30}H_{23}N_2O]SbCl_6$ (MW = 762.0): C, 47.29; H, 3.04; N, 3.68%).

Thermolysis of 13

A solution of **13** (0.76 g, 1 mmol) in 1,2-dichloroethane (20 ml) is boiled under reflux for 4 h. Evaporation of the solvent and chromatography of the residue on silica gel with dichloromethane / carbon tetrachloride (1:1) as eluent affords **14** (0.22g, 70%); mp 186-187°C (Ref [41]: mp 186-187°C).

Fluorene-9-spiro-3'-(1-formylazetidinone)-4'-spiro-9"-fluorene (15)

A solution of **13** (3.05 g, 4 mmol) in acetonitrile (50 ml) + water (5 ml) is stirred at 23°C for 24 h. After evaporation of the solvent the residue is extracted twice with ether (50 ml). The residue is stirred under CH_2Cl_2 (40 ml) for 15 min. Filtration and evaporation of the solvent yields a colourless powder (0.97 g, 61%); mp 164-167 (dec). IR (CH_2Cl_2): 1705, 1790 cm^{-1}. ^1H NMR (CD_2Cl_2): CH δ = 9.22. ^{13}C NMR (CD_2Cl_2, 263 K): C δ = 75.5, 78.2, C=O 155.9, 168.9. (Found: C, 83.94; H, 4.35; N, 3.77. Calc for $C_{28}H_{17}NO_2$ (MW = 399.5): C, 84.19; H, 4.29; N, 3.51%).

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