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N-ACYLIMINIUM SALTS FROM THE REACTION OF NITRILIUM SALTS WITH ALDEHYDES

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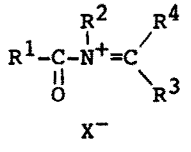
Abstract - The nitrilium hexachloroantimonates **2a,d,g,p** react with aromatic aldehydes to give isolable N-acyliminium hexachloroantimonates **10a-m**. The N-aroyliminium salts (**10g-m**) and acyliminium salts with an aliphatic N-acyl group (**10a-f**) are of remarkably different stability. Contrary to the N-aroyliminium salts, compounds **10a-f** are unstable in solution, e. g. react immediately with acetonitrile. With excess of aldehyde **10n,o** give insertion products of the probable structures **12a,b**. For **10b,f** X-ray structural analyses have been carried out. The N-acylcyanamidium hexachloroantimonate **2p** reacts with aldehydes to give new classes of cyclic N-acyliminium salts **13a-f**, and **14f**, respectively.

During the last years the versatile reactivity patterns of N-acyliminium ions **1** have been used for many synthetic purposes. The chemistry of reagents **1** has been reviewed comprehensively.[1-10]



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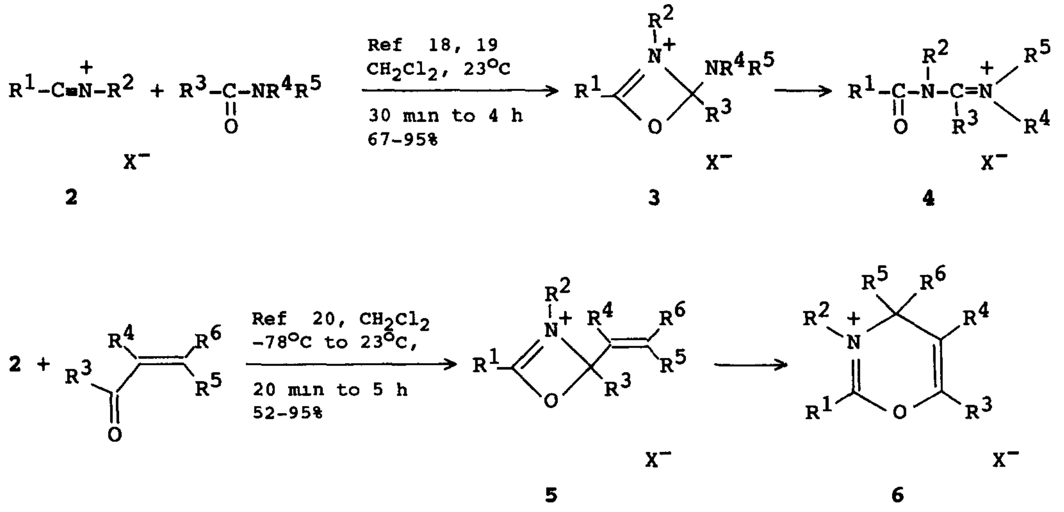
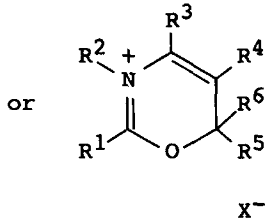
Acyliminium salts are generally considered to be of limited stability due to their high electrophilic reactivity. Therefore, in almost all applications the salts **1** are not isolated but generated *in situ*, although a few stable cyclic and open-chain chlorides and hexachloroantimonates **1** have been described in the literature.[11-16]

In preceding papers we reported on reactions of nitrilium salts[17] **2** with certain carbonyl compounds. With amides N-acylamidinium salts **4** were obtained.[18,19] With a,ß-unsaturated carbonyl compounds nitrilium salts **2** react to give, *inter alia*, the isomeric oxazinium salts **6** and **7**.[20] These reactions were interpreted as proceeding via oxazetium salts **3**, respectively **5**.



2 **3** **4**

5 **6**



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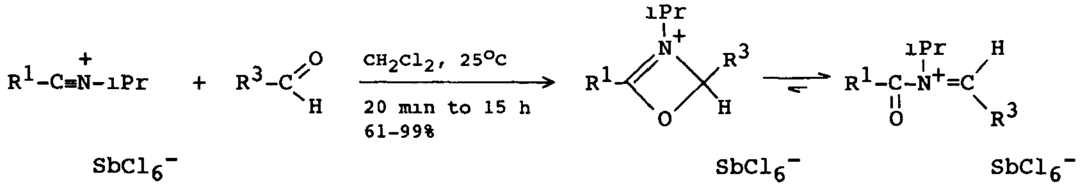
In this communication we wish to report on reactions of nitrilium hexachloroantimonates **2** with the aromatic aldehydes **8** to give isolable N-acyliminium salts **10**.



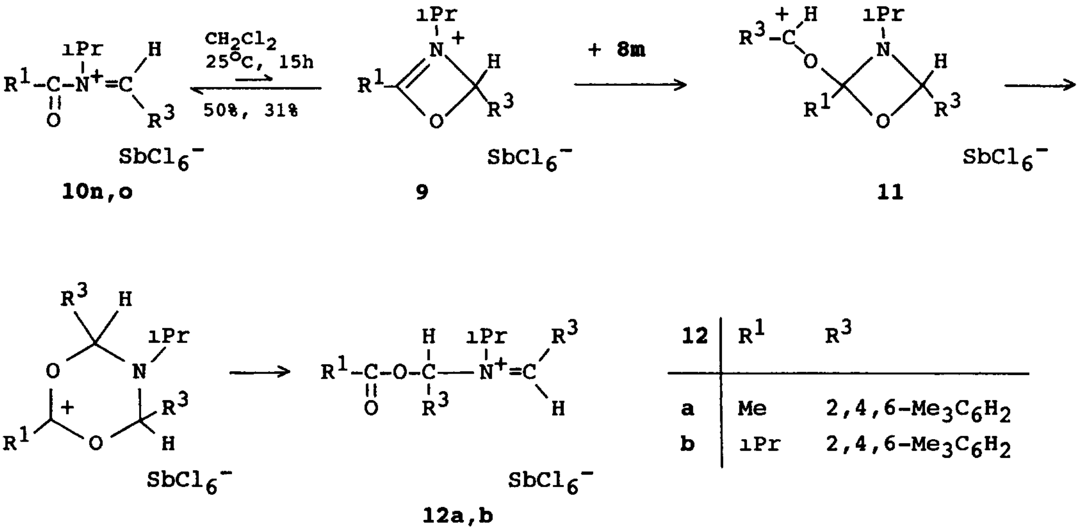
2a,d,g **8a-c,h-j,m** **9** **10a-m**

	R^1	R^3
a	Me	Ph
b	Me	$2\text{-MeOC}_6\text{H}_4$
c	Me	$2,5\text{-(MeO)}_2\text{C}_6\text{H}_3$
d	iPr	Ph
e	iPr	$2\text{-MeOC}_6\text{H}_4$
f	iPr	$2,5\text{-(MeO)}_2\text{C}_6\text{H}_3$
g	Ph	Ph
h	Ph	$4\text{-ClC}_6\text{H}_4$
i	Ph	$4\text{-MeC}_6\text{H}_4$
j	Ph	$4\text{-MeOC}_6\text{H}_4$
k	Ph	$2\text{-MeOC}_6\text{H}_4$
l	Ph	$2,5\text{-(MeO)}_2\text{C}_6\text{H}_3$
m	Ph	$2,4,6\text{-Me}_3\text{C}_6\text{H}_2$
n	Me	$2,4,6\text{-Me}_3\text{C}_6\text{H}_2$
o	iPr	$2,4,6\text{-Me}_3\text{C}_6\text{H}_2$

Scheme 1

On stirring a suspension of **2a** with a slight excess of benzaldehyde at room temperature in dichloromethane the nitrilium salt gradually dissolves. After 15 hours the acetyliminium hexachloroantimonate **10a** can be precipitated with ether in 78% yield. The salts **10b-m** are prepared correspondingly.

However, in the reaction of the alkanoyl nitrilium salts **2a,d** with 2,4,6-trimethylbenzaldehyde (**8m**) adducts **12a,b** are formed, which contain two molecules of the aldehyde per molecule of the nitrilium salt. According to the NMR spectra of these adducts the methyl groups of the isopropyl substituents are diastereotopic and the 1,2,4,6-tetrasubstituted aryl groups are inequivalent. One aryl groups shows hindered rotation (temperature dependent line broadening in the ^{1}H and ^{13}C NMR spectra). Furthermore, two signals for $H-\overset{|}{C}=$ fragments [^{1}H resonances at 7.85 and 8.93 ppm for **12a** in CD_2Cl_2 (263 K), and at 7.77 and 9.11 for **12b** in CD_3CN. ^{13}C signals at 167.7 and 180.7 ppm for **12a** in CD_2Cl_2 (263 K) and 174.8 and 182.3 for **12b** in CD_3CN (263 K)] and one resonance for a saturated HC-O carbon atom [86.1 ppm for **12a**, 87.1 ppm for **12b**] are observed in both cases. Based on these data we tentatively propose the structures shown in Scheme 2.



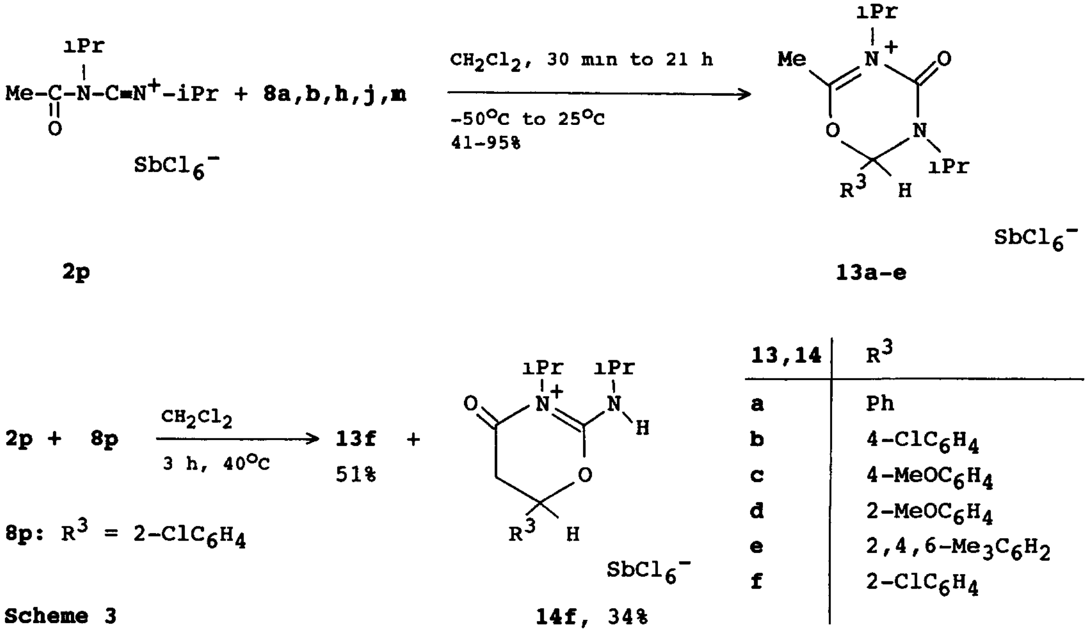
10n,o **9** **11** **12a,b**

12	R^1	R^3
a	Me	$2,4,6\text{-}Me_3C_6H_2$
b	iPr	$2,4,6\text{-}Me_3C_6H_2$

Scheme 2

Iwamura isolated 1,3-oxazetidine derivatives from the reaction of acetyl chloride with azomethines in the presence of triethylamine.[21] To explain the formation of these heterocycles the author postulated cyclisations of intermediate N-acyliminium ions to 1,3-oxazetium ions, very similar to the transformation **10**→**9**. Certain N-thioacylimines cyclize spontaneously to give stable 2*H*-1,3-thiazetenes.[22,23]

The formation of **12a,b** (Scheme 2) can be rationalized assuming an equilibrium **9** $\rightleftharpoons$ **10** lying far on the side of **10**. If attack of a nucleophile on N^+=C of **10** is sterically hindered by a bulky substituent R^3 the isomeric form **9** reacts preferentially. With a second molecule aldehyde as nucleophile intermediate **11** is formed, which rearranges to produce **12**. The acetylcyanamidium hexachloroantimonate[19] **2p** reacts readily with aromatic aldehydes to furnish the oxadiazinium hexachloroantimonates **13**, a new type of cyclic N-acyliminium salts.



2p

13a-e

$8p$: R^3 = 2-ClC_6H_4

Scheme 3

14f, 34%

13,14	R^3
a	Ph
b	4-ClC_6H_4
c	4-$MeOC_6H_4$
d	2-$MeOC_6H_4$
e	2,4,6-$Me_3C_6H_2$
f	2-ClC_6H_4

However, the reaction of **2p** with 2-chlorobenzaldehyde **8p** leads to a mixture of **13f** and **14f**.

No reactions were observed between the nitrilium salts **2a,d,g,p** and ketones like benzophenone. The starting materials were recovered unchanged. Reactions of nitrilium salts with non-enolizable aldehydes are not new in so far as the special case of the Ritter reaction (**2**, R^2 = H) has been known for a long time.[3,10,24-27] However, the N-protonated acyliminium salts have never been isolated. The intermediacy of nitrilium salts in these reactions has not always been considered.

The constitutions of the new compounds are derived from the IR and NMR spectra and the elemental analyses (see Experimental Section).

Solutions of the aroyl substituted iminium salts **10g-m** (R^1 = phenyl) are stable in the absence of moisture. The NMR spectra of these compounds in CD_3CN can be measured without problems. In sharp contrast, solutions of the alkanoyl substituted salts **10a-f** (R^1 = alkyl) are thermally unstable, e.g. these salts react immediately with CD_3CN and decompose even at -20°C in CD_2Cl_2 within a few hours. It was not possible to obtain good NMR spectra for **10a-f**. The proposed constitutions were confirmed by crystal structure analyses of two representative examples (**10b,f**). Molecular plots for the cations of **10b,f** are shown in Figure 1. Selected bond lengths, bond angles and torsional angles together with fractional atomic coordinates are presented in Tables 1 and 2.

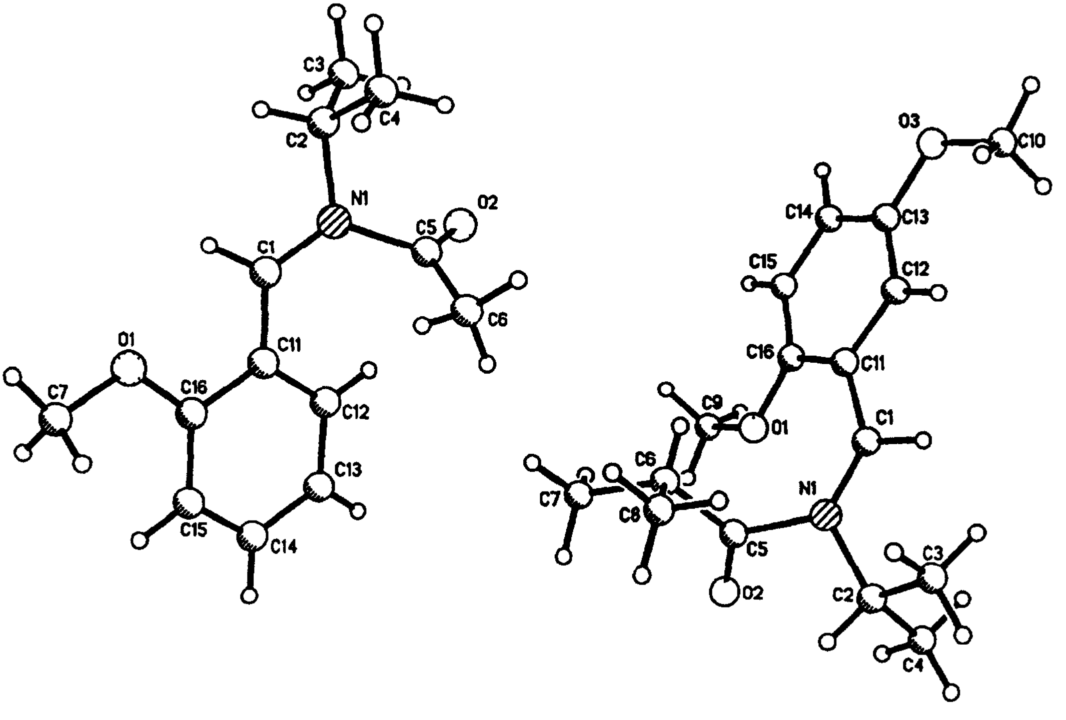


Figure 1. Molecular Plots for the Cations of **10b** (left) and **10f** (right).

X-ray structural analyses for simple N-acyliminium salts comparable to **10b,f** seem to be unreported in the literature. The large torsional angles between the planes through the atoms N1-C1-C2 and C5-O2-N1 of both cations **10b,f** [torsional angles C1-N1-C5-O2: 120° for **10b** and 129° for **10f**] indicate little conjugative interaction between the C=N and the C=O double bonds. This conclusion is confirmed by the rather long N1-C5 bonds

Table 1. Fractional Atomic Coordinates, Selected Bond Lengths [pm], Bond Angles, and Torsional Angles [°] for **10b** and **10f**

10b:

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Sb	0.05564(3)	0.74057(2)	0.72994(2)	C6	0.7008(6)	0.0048(3)	0.1584(3)
Cl1	0.3486(1)	0.75736(8)	0.74305(8)	C7	0.598(1)	0.1905(5)	0.4829(4)
Cl2	0.0365(2)	0.69728(9)	0.58848(8)	C11	0.5502(5)	0.0132(3)	0.3396(3)
Cl3	0.0139(2)	0.88012(7)	0.68500(8)	C12	0.6109(7)	-0.682(3)	0.3342(3)
Cl4	-0.2398(1)	0.72720(7)	0.71542(9)	C13	0.7219(8)	-0.1011(4)	0.4010(4)
Cl5	0.0728(2)	0.78368(8)	0.87234(7)	C14	0.7736(7)	-0.0545(5)	0.4731(4)
Cl6	0.0945(2)	0.60235(7)	0.77846(8)	C15	0.7146(7)	0.0241(4)	0.4815(3)
C1	0.4383(5)	0.0534(3)	0.2726(3)	C16	0.6011(6)	0.0594(3)	0.4152(3)
C2	0.2878(6)	0.0874(3)	0.1318(3)	N1	0.4174(4)	0.0392(2)	0.1922(2)
C3	0.1474(6)	0.0323(3)	0.0884(3)	O1	0.5328(5)	0.1351(2)	0.4153(2)
C4	0.3727(7)	0.1348(3)	0.0694(3)	O2	0.4535(4)	-0.0758(2)	0.1128(2)
C5	0.5224(5)	-0.0195(3)	0.1516(3)				

C1-N1	128.7(5)	C5-N1-C1	124.3(3)	C3-C2-N1-C1	-114.5(4)
C1-C11	143.0(6)	C5-N1-C2	115.6(3)	C6-C5-N1-C2	110.4(4)
N1-C5	149.8(6)	N1-C2-C3	111.6(3)	C6-C5-N1-C1	- 65.5(5)
C5-O2	118.3(5)	N1-C2-C4	109.8(4)	O2-C5-N1-C2	- 64.4(5)
C5-C6	148.0(6)	C2-N1-C1	120.0(3)	O2-C5-N1-C1	119.7(5)
N1-C2	150.9(5)	N1-C1-C11	128.3(4)	C5-N1-C2-C3	69.3(5)
C6-C5-O2	127.1(4)	C1-C11-C12	123.9(4)	C5-N1-C1-C11	- 5.9(7)
C6-C5-N1	114.9(4)	C2-N1-C1-C11	178.3(4)	N1-C1-C11-C12	- 25.6(7)
O2-C5-N1	117.7(4)				

10f:

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Sb	0.05181(2)	0.25892(1)	0.89248(1)	C8	0.7870(7)	0.9825(3)	0.8571(4)
Cl1	-0.2521(1)	0.25386(4)	0.8804(1)	C9	0.1574(6)	1.0760(2)	0.7213(3)
Cl2	0.3564(1)	0.2610(1))	0.9058(1)	C10	0.3978(6)	0.8539(2)	0.3864(2)
Cl3	0.0736(1)	0.15598(4)	0.9534(1)	C11	0.3648(4)	0.9395(1)	0.6365(2)
Cl4	0.0349(1)	0.36299(4)	0.8325(1)	C12	0.3834(4)	0.9109(1)	0.5539(2)
Cl5	0.0260(2)	0.22043(5)	0.7447(1)	C13	0.3241(4)	0.9408(1)	0.4728(2)
Cl6	0.0707(1)	0.30176(4)	1.0384(1)	C14	0.2453(4)	0.9993(2)	0.4735(2)
C1	0.4171(4)	0.9009(1)	0.7162(2)	C15	0.2213(5)	1.0274(1)	0.5530(2)
C2	0.4766(5)	0.8617(2)	0.8717(2)	C16	0.2792(5)	0.9973(1)	0.6353(2)
C3	0.5815(6)	0.8081(2)	0.8416(3)	N1	0.4495(4)	0.9141(1)	0.8017(2)
C4	0.3029(6)	0.8413(2)	0.8926(3)	O1	0.2535(4)	1.0192(1)	0.7172(2)
C5	0.4691(5)	0.9787(2)	0.8450(2)	O2	0.3866(4)	0.9895(1)	0.9025(2)
C6	0.6157(6)	1.0158(2)	0.8193(3)	O3	0.3359(3)	0.9169(1)	0.3891(1)
C7	0.6122(8)	1.0824(2)	0.8555(3)				

C1-N1	129.6(4)	C5-N1-C1	127.6(3)	C6-C5-N1-C2	117.5
C1-C11	145.1(4)	C5-N1-C2	112.1(2)	C6-C5-N1-C1	- 61.2
N1-C5	151.6(4)	N1-C2-C3	111.5(3)	C7-C6-C5-N1	172.8
C5-O2	118.2(4)	N1-C2-C4	109.2(3)	O2-C5-N1-C2	- 52.2
C5-C6	149.5(5)	C2-N1-C1	120.3(3)	O2-C5-N1-C1	129.0
N1-C2	152.2(4)	N1-C1-C11	132.3(3)	C5-N1-C2-C3	-139.0
C6-C5-O2	128.3(3)	C1-C11-C12	115.0(3)	C5-N1-C1-C11	- 10.4
C6-C5-N1	113.3(3)	C2-N1-C1-C11	171.0	N1-C1-C11-C12	165.0
O2-C5-N1	117.5(3)	C3-C2-N1-C1	39.9	C11-C16-O1-C9	-176.1

[149.8(6) pm in **10b**, 151.6(4) pm in **10f**]. For N,N-dimethylformamide a bond length for the N-C partial double bond of 143 pm was reported[28] and for the corresponding bonds in cyanuric acid 137 pm were observed.[29,30] While the C=N and the C=O bonds in **10b,f** are electronically decoupled resonance is still possible between the C=N bonds and the aryl groups. The deviations from coplanarity of the aryl planes and the planes through the atoms N1-C1-C2 are small in both cases [N1-C1-C11-C12: -26° for **10b** and 165° for **10f**]. The aryl groups are arranged antiperplanarly to the N-isopropyl groups (C2-N1-C1-C11: 178° for **10b**, 171° for **10f**). Sterical interactions may be important in determining the geometries of the cations **10b,f**.

EXPERIMENTAL SECTION

X-ray structural analyses of **10b** *and* **10f**:[31]
The cell constants and the reflections were measured with a Syntex P3 diffractometer (graphite monochromator, $\lambda(Mo\text{-}K_\alpha)$ = 71.069 pm).
The structures were solved by the Patterson method using the program SHELXTL.[32] All hydrogen atoms were included in calculated positions and treated as rigid groups.
10b, $[C_{13}H_{18}NO_2]^+SbCl_6^-$, M = 554.8, crystal size [mm]: 0.5 x 0.4 x 0.3, space group $P2_1/c$, Z = 4, monoclinic, a = 808.9(1), b = 1617.5(2), c = 1600.1(2) pm, β = 100.34(1)°, $V = 2060 \cdot 10^6$ pm^3, d_{calc} = 1.79 g cm^{-3}, $F(000)$ = 1088, $\mu(Mo\text{-}K_\alpha)$ = 21.4 cm^{-1}, T = 228 K, ω-scan, $\Delta\omega$ = 1.0°, $2.0 \le \omega \le 29.3°$ min^{-1}, $4.0 \le 2\Theta \le 52.0°$, 3779 independent significant reflections ($I > 1.5\sigma$). The anisotropic refinement converged to $R_F{}^1$ = 3.29% and $R_F{}^2$ = 3.73%
10f, $[C_{16}H_{24}NO_3]^+SbCl_6^-$, M = 612.8, crystal size [mm]: 0.5 x 0.3 x 0.2, space group $P2_1/c$, Z = 4, monoclinic, a = 781.2(2), b = 2128.2(5), c = 1500.0(4) pm, β = 99.66(2)°, $V = 2459 \cdot 10^6$ pm^3, d_{calc} = 1.66 g cm^{-3}, $F(000)$ = 1216, $\mu(Mo\text{-}K_\alpha)$ = 16.6 cm^{-1}, T = 223 K, ω-scan, $\Delta\omega$ = 1.0°, $0.5 \le \omega \le 29.3°$ min^{-1}, $4.0 \le 2\Theta \le 53.0°$, 5017 independent significant reflections ($I > 1.5\sigma$). The anisotropic refinement converged to $R_F{}^1$ = 3.17% and $R_F{}^2$ = 3.29%

IR spectra: Mattson Polaris FT-IR; solutions in CH_2Cl_2. *^1H and ^{13}C NMR spectra*: Bruker AC-250 and WM-250 spectrometers; δ-scale; coupling constants J in Hz; internal reference tetramethylsilane. All experiments were carried out with exclusion of moisture. The solvents were dried by standard methods. $SbCl_5$ was distilled before use. The melting points are uncorrected.

Acetylbenzylideneisopropylammonium Hexachloroantimonate (**10a**): A suspension of **2a**[33] (1.05 g, 2.5 mmol) and **8a** (0.32 g, 3.0 mmol) in CH_2Cl_2 (10 ml) is stirred at 25°C for 12 h. The yellow solution is poured with stirring into ether (50 ml) and the precipitate is filtered off. Yield: 1.02 g (78%) of a colourless very moisture-sensitive powder; mp 119-123°C (dec). IR: 1702, 1798 cm^{-1}. ^1H NMR (CD_2Cl_2, 273 K): 1.77 (d, J = 6.7), 2.59 (CH_3), 4.83 (sept, J = 6.7), 9.16 (CH). ^{13}C NMR (CD_2Cl_2, 273 K): 21.8 (2 CH_3), 27.9 (CH_3), 65.6 (NCH), 125.3 (i-C), 131.3, 134.2 (o,m-C), 140.1 (p-C), 169.2, 173.4 (C=N, C=O). (Found: C, 27.25; H, 3.22; N, 2.72. Calc for $[C_{12}H_{16}NO]SbCl_6$ (MW = 524.7): C, 27.47; H, 3.07; N, 2.67%).

Acetylisopropyl(2-methoxybenzylidene)ammonium Hexachloroantimonate (**10b**): A suspension of **2a** (4.18 g, 10 mmol) and **8b** (1.64 g, 12 mmol) in CH_2Cl_2 (20 ml) is stirred at 25°C for 1 h. On slow addition of ether (80 ml) a yellow powder (5.20 g, 94%) is precipitated; mp 112-113°C (dec). IR: 1601, 1663, 1686, 1798 cm^{-1}. ^1H NMR (CD_2Cl_2, 263 K): 1.71 (d, J = 6.7), 2.56, 4.06 (CH_3), 4.76 (sept, J = 6.7), 9.04 (CH). ^{13}C NMR (CD_2Cl_2, 263 K): 22.2, 26.8, 56.9 (CH_3), 64.3 (CH), 165.8, 172.9 (C=N, C=O). (Found: C, 27.95; H, 3.44; N, 2.55. Calc for $[C_{13}H_{18}NO_2]SbCl_6$ (MW = 554.8): C, 28.14; H, 3.27; N, 2.53%).

Acetyl(2,5-dimethoxybenzylidene)isopropylammonium Hexachloroantimonate (**10c**): From **8c** (1.99 g, 12 mmol) as described for **10b**. After 30 min the reaction mixture is poured into ether (80 ml) and the precipitate is filtered off. Yield: 5.32 g (91%) of an orange powder; mp 90-93°C (dec). IR: 1571, 1598 (shoulder), 1679 (shoulder), 1794 cm^{-1}. ^1H NMR (CD_2Cl_2, 263 K): 1.71 (d, J = 6.7), 2.53, 3.88, 3.99 (CH_3), 4.75 (sept, J = 6.7), 8.97 (CH). ^{13}C NMR (CD_2Cl_2, 263 K): 22.2, 26.5, 56.7, 56.9 (CH_3), 64.2 (CH), 165.7, 172.6 (C=N, C=O). (Found: C, 28.65; H, 3.47; N, 2.41. Calc for $[C_{14}H_{20}NO_3]SbCl_6$ (MW = 584.8): C, 28.75; H, 3.45; N, 2.40%).

Benzylideneisobutyrylisopropylammonium Hexachloroantimonate (**10d**): From **2d**[33] (1.12 g, 2.5 mmol) and **8a** (0.32 g, 3.0 mmol) as described for **10a**. Yield: 0.84 g (61%) of a colourless very moisture sensitive powder; mp 113-115°C (dec). IR: 1598, 1663 cm^{-1}. ^1H NMR (CD_2Cl_2, 273 K): 1.28 (d, J = 6.9), 1.82 (d, J = 6.7)(CH_3), 2.75 (sept, J = 6.9), 4.66 (sept, J = 6.7), 9.24 (CH). ^{13}C NMR (CD_2Cl_2, 273 K): 18.9, 23.0 (CH_3), 39.2, 64.8 (CH), 126.1, 131.4, 134.3, 140.3 (phenyl), 170.4, 181.3 (C=N, C=O). (Found: C, 29.68; H, 3.72; N, 2.62. Calc for $[C_{14}H_{20}NO]SbCl_6$ (MW = 552.8): C, 30.42; H, 3.65; N, 2.53%).

Isobutyrylisopropyl(2-methoxybenzylidene)ammonium Hexachloroantimonate (**10e**): From **2d** (4.47 g, 10 mmol) and **8b** (1.64 g, 12 mmol) as described for **10b**. Yield: 5.55 g (95%) of a yellow very moisture sensitive powder, mp 110-114°C (dec). IR: 1598, 1787 cm^{-1}. ^1H NMR (CD_2Cl_2, 263 K): 1.24

(d, J = 6.8), 1.71 (d, J = 6.6), 4.07 (CH_3), 2.83 (m, broad), 4.63 (m, broad), 9.06 (CH). (Found: C, 30.67; H, 3.89; N, 2.40. Calc for $[C_{15}H_{22}NO_2]SbCl_6$ (MW = 582.8): C, 30.91; H, 3.81; N, 2.40%).

(2,5-Dimethoxybenzylidene)isobutyrylisopropylammonium Hexachloroantimonate (**10f**): From **2d** (4.47 g, 10 mmol) and **8c** (1.99 g, 12 mmol) as described for **10b**. Yield: 6.05 g (99%) of an orange unstable powder; mp 93-97°C (dec). IR: 1566, 1593, 1787 cm^{-1}. ^1H NMR (CD_2Cl_2, 263 K): 1.22 (d, J = 6.7), 1.73 (d, J = 6.7), 3.89, 3.99 (CH_3), 2.87 (sept., J = 6.7), 4.66 (sept, J = 6.7), 9.08 (broad) (CH). ^{13}C NMR (CD_2Cl_2, 263 K): 18.8, 23.1 (CH_3), 37.2, 63.9 (CH). (Found: C, 31.18; H, 3.91, N, 2.27. Calc for $[C_{16}H_{24}NO_3]SbCl_6$ (MW = 612.8): C, 31.36; H, 3.95; N, 2.29%).

Benzoylbenzylideneisopropylammonium Hexachloroantimonate (**10g**): A solution of **8a** (0.32 g, 3.0 mmol) in CH_2Cl_2 (5 ml) is added dropwise to a suspension of **2g**[34] (1.20 g, 2.5 mmol) in CH_2Cl_2 (10 ml). After stirring at 25°C for 15 h the red solution is poured into ether (50 ml) affording a precipi-tate, which is reprecipitated at -30°C from CH_3CN (3 ml)/ether (40 ml) giving a colourless powder (0.94 g, 64%); mp 120-122°C (dec). IR: 1575, 1600 (shoulder), 1640 (shoulder), 1695, 1740 cm^{-1}. ^1H NMR (CD_3CN): 1.69 (d, J = 6.7) (CH_3), 4.81 (sept, J = 6.7), 9.34 (CH). ^{13}C NMR (CD_3CN, 263 K): 21.6 (CH_3), 66.0 (CH), 126.9, 127.8, 138.8, 139.4 (i,p-C), 131.1, 132.5, 134.8 (o,m-C), 170.1, 172.7 (C=N, C=O). (Found: C, 34.58; H, 2.95; N, 2.52. Calc for $[C_{17}H_{18}NO]SbCl_6$ (MW = 586.8): C, 34.80; H, 3.09; N, 2.39%).

Benzoyl(4-chlorobenzylidene)isopropylammonium Hexachloroantimonate (**10h**): A mixture of **2g** (9.61 g, 20 mmol) and **8h** (3.51 g, 25 mmol) in CH_2Cl_2 (20 ml) is stirred at 25°C for 14 h. Slow addition of ether (80 ml) affords a colourless precipitate (12.04 g, 97%); mp 114-117°C (dec). IR: 1586, 1610 (shoulder), 1744 cm^{-1}. ^1H NMR CD_3CN): 1.68 (d, J = 6.7) (CH_3), 4.80 (sept, J = 6.7), 9.31 (CH). ^{13}C NMR (CD_3CN, 273 K): 21.6 (CH_3), 66.2 (CH), 125.5, 127.6, 138.9, 145.8 (i,p-C), 131.1, 131.4, 132.6, 136.2 (o,m-C), 169.9, 171.5 (C=N, C=O). (Found: C, 32.78; H, 2.69; N, 2.26. Calc for $[C_{17}H_{17}ClNO]SbCl_6$ (MW = 621.2): C, 32.87, H, 2.76; N, 2.26%).

Benzoylisopropyl(4-methylbenzylidene)ammonium Hexachloroantimonate (**10i**): A solution of benzonitrile (5.16 g, 50 mmol) in CH_2Cl_2 (20 ml) is added dropwise to a cold (-50°C) solution of $SbCl_5$ (14.95 g, 50 mmol) in CH_2Cl_2 (30 ml). After stirring at -50°C for 10 min isopropyl chloride (10 ml) is added dropwise. The reaction mixture is warmed to 25°C and stirred at this temperature for 1 h. A solution of **8i** (6.61 g, 55 mmol) in CH_2Cl_2 (20 ml) is added dropwise. After stirring for 20 min ether (100 ml) is added dropwise affording a yellow powder (24.92 g, 83%); mp 144-147°C (dec).

IR: 1586, 1744 cm^{-1}. ^{1}H NMR (CD_3CN, 263 K): 1.67 (d, J = 6.7), 2.39 (CH_3), 4.77 (sept, J = 6.7), 9.24 (CH). ^{13}C NMR (CD_3CN, 263 K): 21.6, 22.5 (CH_3), 65.5 (CH), 170.7, 171.6 (C=N, C=O). (Found: C, 35.81; H, 3.38; N, 2.35. Calc for $[C_{18}H_{20}NO]SbCl_6$ (MW = 600.8): C, 35.98; H, 3.36; N, 2.33%).

Benzoylisopropyl(4-methoxybenzylidene)ammonium Hexachloroantimonate (**10j**): A solution of **8j** (0.41 g, 3.0 mmol) in CH_2Cl_2 (5 ml) is added dropwise to a cold (-50°C) suspension of **2g** (1.20 g, 2.5 mmol) in CH_2Cl_2 (10 ml). The mixture is stirred at temperatures between -50°C and 25°C for 2 h. Slow addition of ether (70 ml) affords a colourless powder (1.35 g, 88%), which is reprecipitated from ethyl acetate (10 ml)/ether (50 ml); mp 104-106°C (dec). IR: 1517, 1578, 1740 cm^{-1}. ^{1}H NMR (CD_3CN): 1.64 (d, J = 6.7), 3.90 (CH_3), 4.67 (sept, J = 6.7), 9.86 (CH). ^{13}C NMR (CD_3CN, 263 K): 21.8, 57.5 (CH_3), 64.8 (CH), 168.9, 169.6, 171.2 (C-O, C=N, C=O). (Found: C, 34.78; H, 3.28; N, 2.27. Calc for $[C_{18}H_{20}NO_2]SbCl_6$ (MW = 616.8): C, 35.05; H, 3.27; N, 2.27%).

Benzoylisopropyl(2-methoxybenzylidene)ammonium Hexachloroantimonate (**10k**): From **8b** (0.41 g, 3.0 mmol) as described for **10j**. The product is precipitated at -50°C with ether (50 ml), stirred with charcoal in CH_2Cl_2 (20 ml), and reprecipitated at 25°C from CH_2Cl_2 (20 ml)/ ether (80 ml) affording a yellow powder (1.08 g, 70%); mp 121-124°C (dec). IR: 1482, 1598, 1744 cm^{-1}. ^{1}H NMR (CD_3CN): 1.66 (d, J = 6.7), 3.73 (CH_3), 4.77 (sept, J = 6.7), 9.29 (CH). ^{13}C NMR (CD_3CN, 273 K): 21.9, 56.7 (CH_3), 65.2 (CH), 161.8 (C-O), 169.5, 170.0 (C=N, C=O). (Found: C, 34.98; H, 3.31; N, 2.26. Calc for $[C_{18}H_{20}NO_2]SbCl_6$ (MW = 616.8): C, 35.05; H, 3.27; N, 2.27%).

Benzoyl(2,5-dimethoxybenzylidene)isopropylammonium Hexachloroantimonate (**10l**): A mixture of **2g** (1.20 g, 2.5 mmol) and **8c** (0.50 g, 3.0 mmol) in CH_2Cl_2 (15 ml) is stirred at 25°C for 1 h. The red solution is poured into ether (50 ml) affording an orange powder (1.55 g, 96%); mp 87-91°C (dec). IR: 1497, 1571, 1594 (shoulder), 1744 cm^{-1}. ^{1}H NMR (CD_3CN): 1.66 (d, J = 6.7), 3.68, 3.70 (CH_3), 4.76 (sept, J = 6.7), 9.23 (CH). ^{13}C NMR (CD_3CN, 273 K): 21.9, 56.7, 56.8 (CH_3), 65.0 (CH), 169.0, 170.1 (C=N, C=O). (Found: C, 35.26; H, 3.49; N, 2.21. Calc for $[C_{19}H_{22}NO_3]SbCl_6$ (MW = 646.9): C, 35.28; H, 3.43; N, 2.17%).

Benzoylisopropyl(2,4,6-trimethylbenzylidene)ammonium Hexachloroantimonate (**10m**): From **2g** (1.20 g, 2.5 mmol) and **8m** (0.89 g, 6 mmol) as described for **10g** but without reprecipitation. Yield: 0.98 g (62%) of a colourless powder; mp 114-115°C (dec). IR: 1598, 1752 cm^{-1}. ^{1}H NMR (CD_3CN): 1.79 (d, J = 6.7), 2.13 (3 H), 2.30 (6 H) (CH_3), 5.06 (sept, J = 6.7), 6.83, 9.84 (CH). ^{13}C NMR (CD_3CN, 273 K): 20.8, 21.5, 22.1 (CH_3), 66.3 (CH), 170.2, 179.6 (C=O, C=N). (Found: C, 37.98; H, 3.78; N, 2.26. Calc for $[C_{20}H_{24}NO]SbCl_6$ (MW = 628.9): C, 38.20; H, 3.85; N, 2.23%).

2:1-Adduct of 2,4,6-Trimethylbenzaldehyde to N-Isopropyl Acetonitrilium Hexachloroantimonate (**12a**): From **2a** (1.05 g, 2.5 mmol) and **8m** (0.74 g, 5.0 mmol) as described for **10g**. The oily precipitate solidifies when stirred under pentane (40 ml) affording a yellow powder (0.90 g, 50%), which is recrystallized at -30°C from CH_3CN (3 ml)/ether (200 ml) giving pale yellow prisms; mp 102-104°C (dec). IR: 1609, 1771 cm^{-1}. ^1H NMR (CD_2Cl_2, 263 K): 1.62 (d, J = 6.7), 1.63 (d, J = 6.7), 2.08 (broad), 2.29 (broad), 2.34, 2.35, 2.37, 2.47 (6 H) (CH_3), 4.82 (sept, J = 6.7), 7.10 (broad, 4 H), 7.85, 8.93 (CH). ^{13}C NMR (CD_2Cl_2, 263 K): 20.0, 20.3 (broad), 21.0, 21.1, 21.3, 21.6, 22.2 (CH_3), 60.8 (CH-N), 86.1 (CH-O), 167.7, 180.7 (C=N, C=O). (Found: C, 41.76; H, 4.72; N, 2.01. Calc for $[C_{25}H_{34}NO_2]SbCl_6$ (MW = 715.0): C, 41.99; H, 4.79; N, 1.96%).

2:1-Adduct of 2,4,6-Trimethylbenzaldehyde to N-Isopropyl Isobutyronitrilium Hexachloroantimonate (**12b**): From **2d** (1.12 g, 2.5 mmol) as described for **12a**. The oily product solidifies when reprecipitated from CH_3CN (3 ml)/ ether (60 ml) affording a colourless powder (0.57 g, 31%); mp 118-119°C (dec). IR: 1613, 1760 cm^{-1}. ^1H NMR (CD_3CN): 1.20 (d, J = 7.0), 1.25 (d, J = 7.0), 1.52 (d, J = 6.7), 1.54 (d, J = 6.7), 2.16 (broad, 6 H), 2.32, 2.33, 2.48 (6 H)(CH_3), 2.86 (sept, J = 7.0), 4.77 (sept, J = 6.7), 7.10 (2 H), 7.11 (2 H), 7.77, 9.11 (CH). ^{13}C NMR (CD_3CN, 263 K): 18.7, 18.9, 19.7, 20.3, 20.7, 21.2, 21.3, 21.7, 22.0 (CH_3), 34.7, 61.6, 87.1 (CH), 174.8, 182.3 (C=O, C=N). (Found: C, 43.38; H, 5.05; N, 1.94. Calc for $[C_{27}H_{38}NO_2]SbCl_6$ (MW = 743.1): C, 43.64; H, 5.15; N, 1.89%).

3,4-Dihydro-3,5-diisopropyl-6-methyl-4-oxo-2-phenyl-*2H*-1,3,5-oxadiazinium Hexachloroantimonate (**13a**): A solution of **8a** (0.32 g, 3.0 mmol) in CH_2Cl_2 (5 ml) is added at 25°C dropwise to a solution of **2p**[19] (1.26 g, 2.5 mmol) in CH_2Cl_2 (10 ml). After stirring for 2 h the product is precipitated at -20°C with pentane (25 ml). Reprecipitation first from CH_2Cl_2 (6 ml)/ pentane (25 ml) and then at -20°C from CH_2Cl_2 (10 ml)/ether (40 ml) affords a colourless powder (1.04 g, 68%); mp 139-141°C (dec). IR: 1560, 1700 (shoulder), 1765 cm^{-1}. ^1H NMR (CD_3CN): 1.14 (d, J = 7.0), 1.39 (d, J = 7.0), 1.46 (d, J = 6.7), 1.56 (d, J = 6.7), 2.58 (CH_3), 4.22 (sept, J = 6.7), 4.46 (sept, J = 7.0), 7.01 (CH). ^{13}C NMR (CD_3CN, 263 K): 19.6, 19.7, 19.8, 20.1, 21.8 (CH_3), 50.6, 57.2 (HCN), 88.5 (HCO), 128.2, 130.2 (o,m-C), 132.4, 133.0 (p,i-C), 144.4 (C=O), 182.8 (C=N). (Found: C, 31.33; H, 3.85; N, 4.50. Calc for $[C_{16}H_{23}N_2O_2]SbCl_6$ (MW = 609.8): C, 31.51; H, 3.80; N, 4.59%).

2-(4-Chlorophenyl)-3,4-dihydro-3,5-diisopropyl-6-methyl-4-oxo-*2H*-1,3,5-oxadiazinium Hexachloroantimonate (**13b**): A mixture of **2p** (1.26 g, 2.5 mmol) and **8h** (0.42 g, 3.0 mmol) in CH_2Cl_2 (10 ml) is stirred at 25°C for 21 h. The mixture is poured into ether (80 ml). A colourless powder

(1.30 g, 81%) precipitates; mp 153-158°C (dec). IR: 1567, 1767 cm^{-1}. ^{1}H NMR (CD_3CN): 1.14 (d, J = 6.7), 1.38 (d, J = 6.7), 1.47 (d, J = 6.7), 1.58 (d, J = 6.7), 2.59 (CH_3), 4.22 (sept, J = 6.7), 4.48 (sept, J = 6.7), 7.00 (CH). ^{13}C NMR (CD_3CN, 263 K): 19.8, 20.1, 21.9 (CH_3), 51.1, 57.4 (HCN), 88.1 (HCO), 130.0, 130.4 (o,m-C), 132.0, 138.0 (p,i-C), 144.2 (C=O), 182.9 (C=N). (Found: C, 29.77; H, 3.38; N, 4.27. Calc for $[C_{16}H_{22}ClN_2O_2]SbCl_6$ (MW = 644.3): C, 29.83; H, 3.44; N, 4.35%).

3,4-Dihydro-3,5-diisopropyl-2-(4-methoxyphenyl)-6-methyl-4-oxo-2*H*-1,3,5-oxadiazinium Hexachloroantimonate (**13c**): A solution of **8j** (0.41 g, 3.0 mmol) ir CH_2Cl_2 (5 ml) is added dropwise at -50°C to a solution of **2p** (1.26 g, 2.5 mmol) in CH_2Cl_2 (10 ml). After stirring between -50°C and 0°C for 2 h ether (80 ml) is added dropwise. The oily precipitate solidifies when stirred under pentane (30 ml). Reprecipitation from ethyl acetate (10 ml)/ether (50 ml) furnishes a colourless powder (0.66 g, 41%); mp 130-132°C (dec). IR: 1567, 1580 (shoulder), 1609 (shoulder), 1767 cm^{-1}. ^{1}H NMR (CD_3CN): 1.13 (d, J = 7.0), 1.38 (d, J = 7.0), 1.50 (d, J = 6.7), 1.58 (d, J = 7.0), 2.57, 3.84 (CH_3), 4.25 (sept, J = 6.7), 4.42 (sept, J = 6.7), 6.95 (CH). ^{13}C NMR (CD_3CN, 263 K): 19.8, 19.9, 20.1, 21.8 (CH_3), 50.9, 56.3, 57.2 (HCN, OCH_3), 89.5 (HCO), 115.5 (m-C), 124.8 (i-C), 130.0 (o-C), 162.9 (p-C), 144.4 (C=O), 182.5 (C=N). (Found: C, 31.62; H, 3.93; N, 4.32. Calc for $[C_{17}H_{25}N_2O_3]SbCl_6$ (MW = 639.9): C, 31.91; H, 3.94; N, 4.38%).

3,4-Dihydro-3,5-diisopropyl-2-(2-methoxyphenyl)-6-methyl-4-oxo-2*H*-1,3,5-oxadiazinium Hexachloroantimonate (**13d**): A mixture of **2p** (1.26 g, 2.5 mmol) and **8b** (0.41 g, 3.0 mmol) in CH_2Cl_2 (15 ml) is stirred at 25° for 30 min. On cooling to -50°C the colour of the reaction mixture changes from red to yellow. On slow addition of ether (50 ml) a yellow powder (1.52 g, 95%) is precipitated; mp 128-131°C (dec). IR: 1470, 1485, 1567, 1597, 1764 cm^{-1}. ^{1}H NMR (CD_3CN): 1.10 (d, J = 7.0), 1.34 (d, J = 7.0), 1,57 (J = 6.7), 1.59 (d, J = 7.0), 2.58, 3.94 (CH_3), 4.29 (sept, J = 6.7), 4.32 (sept, J = 6.7), 7.02 (CH). ^{13}C NMR (CD_3CN, 263 K): 19.7, 19.9, 20.0, 21.8 (CH_3), 51.1, 56.9, 57.0 (HCN, OCH_3), 86.9 (HCO), 113.2, 120.5 (i-C), 121.3, 129.1, 134.5, 158.9 (aryl), 144.5 (C=O), 182.1 (C=N). (Found: C, 31.86; H, 3.85; N, 4.29. Calc for $[C_{17}H_{25}N_2O_3]SbCl_6$ (MW = 639.9): C, 31.91; H, 3.94; N, 4.38%).

3,4-Dihydro-3,5-diisopropyl-6-methyl-4-oxo-2-(2,4,6-trimethylphenyl)-2*H*-1,3,5-oxadiazinium Hexachloroantimonate (**13e**): From **8m** (0.89 g, 6.0 mmol) and **2p** (1.26 g, 2.5 mmol) as described for **13b**. Yield: 1.59 g (98%) of a yellow powder ; mp 146-148°C (dec). IR: 1478, 1563, 1771 cm^{-1}. ^{1}H NMR (CD_3CN): 1.22 (d, J = 6.7), 1.42 (d, J = 6.7), 1.65 (d, J = 6.7, 6 H), 2.32, 2.42 (6 H), 2.73 (CH_3), 3.22 (sept, J = 6.7), 4.53 (sept, J = 6.7),

6.94, 7.07 (2 H) (CH). ^{13}C NMR (CD_3CN, 273 K): 19.8, 20.2, 20.3, 20.5, 20.6, 21.2, 21.8 (CH_3), 52.2, 56.6 (HCN), 91.9 (HCO), 122.2, 131.6 (broad), 140.0, 143.2 (aryl), 146.2 (C=O), 184.6 (C=N). (Found: C, 34.95; H, 4.49; N, 4.23. Calc for $[C_{19}H_{29}N_2O_2]SbCl_6$ (MW = 651.9): C, 35.00; H, 4.48; N, 4.30%).

2-(2-Chlorophenyl)-3,4-dihydro-3,5-diisopropyl-6-methyl-4-oxo-*2H*-1,3,5-oxadiazinium Hexachloroantimonate (**13f**): A mixture of **2p** (1.26 g, 2.5 mmol) and **8p** (0.42 g, 3.0 mmol) in CH_2Cl_2 (10 ml) is boiled under reflux for 3 h. Slow addition of ether (60 ml) affords a colourless precipitate (1.45 g, 90%), which is dissolved in ethyl acetate (10 ml). On addition of ether (50 ml) a pale yellow powder (0.82 g, 51%) precipitates; mp 153-155°C (dec). IR: 1571, 1767 cm^{-1}. ^{1}H NMR (CD_3CN): 1.16 (d, J = 7.0), 1.40 (d, J = 6.7), 1.54 (d, J = 6.7), 1.59 (d, J = 7.0), 2.61 (CH_3), 4.27 (sept, J = 6.7), 4.35 (sept, J = 7.0), 7.09 (CH). ^{13}C NMR (CD_3CN, 263 K): 19.6, 19.7, 19.8, 19.9, 21.8 (CH_3), 51.8, 57.5 (HCN), 87.2 (HCO), 144.4 (C=O), 182.7 (C=N). (Found: C, 29.51; H, 3.31; N, 4.25. Calc for $[C_{16}H_{22}ClN_2O_2]SbCl_6$ (MW = 644.3): C, 29.83; H, 3.44; N, 4.35%).

6-(2-Chlorophenyl)-5,6-dihydro-2-(isopropylamino)-3-isopropyl-4-oxo-*4H*-1,3-oxazinium Hexachloroantimonate (**14f**): Pentane (50 ml) is added dropwise to the mother liquor of the preparation of **13f**. The precipitating oil solidifies when stirred under pentane (30 ml). Purification by flash chromatography (silica gel, CH_2Cl_2 as eluent) and precipitation at -30°C from CH_2Cl_2 (5 ml)/ether (5 ml) furnishes a colourless powder (0.54 g, 34%); mp 151-153°C (dec). IR: 1517, 1617, 1767 cm^{-1}. ^{1}H NMR (CD_3CN): 1.33 (d, J = 6.4), 1.34 (d, J = 6.7), 1.52 (d, J = 7.0), 1.61 (d, J = 6.7) (CH_3), 3.20 (AB part of ABX system, J_{AB} = 17.8, J_{AX} = 3.4, J_{BX} = 12.6) (CH_2), 4.15 (m) (2 CH), 6.30 (X part of ABX system, J_{AX} = 3.4, J_{BX} = 12.6) (HCO), 7.89 (broad, coupled to 4.15). ^{13}C NMR (CD_3CN, 273 K): 19.3, 20.5, 21.6, 21.8 (CH_3), 38.2 (CH_2), 49.0, 53.2 (HCN), 77.9 (HCO), 128.9, 129.0, 131.1, 132.5, 132.6, 133.6 (aryl), 159.4, 165.9 (C=O, C=N). (Found: C, 29.76; H, 3.46; N, 4.28. Calc for $[C_{16}H_{22}ClN_2O_2]SbCl_6$ (MW = 644.3): C, 29.83; H, 3.44; N, 4.35%).

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