Preparation of 3,4,5-Trisubstituted 1,2,4-Oxadiazolium Salts from Nitrilium Salts

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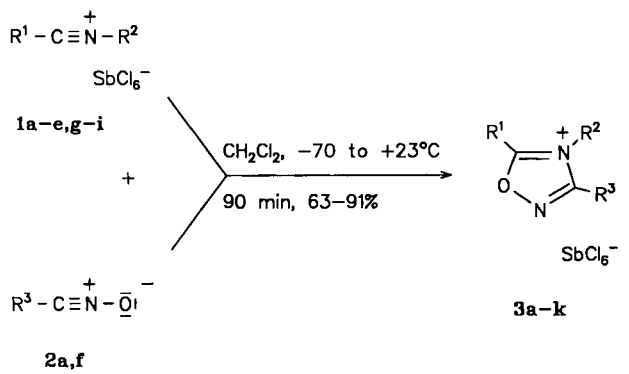
1,3-Cycloadditions of stable nitrile oxides **2** to nitrilium salts **1** afford high yields of 3,4,5-trisubstituted 1,2,4-oxadiazolium salts **3**. *N*-Hydroxycarboximidoyl chlorides **4** add to nitrilium salts **1** to give isolable [(chloroalkylidene)aminooxyalkylidene]ammonium salts **5**. A thermal stereomutation around the $C=N^+$ bond is observed. On heating neat or in solution most compounds **5** cyclize to oxadiazolium salts **3**. In cases where decomposition of **5** is faster than cyclization *O*-silylated *N*-hydroxycarboximidoyl chlorides **7** are treated with nitrilium salts **1** to furnish oxadiazolium salts **3**.

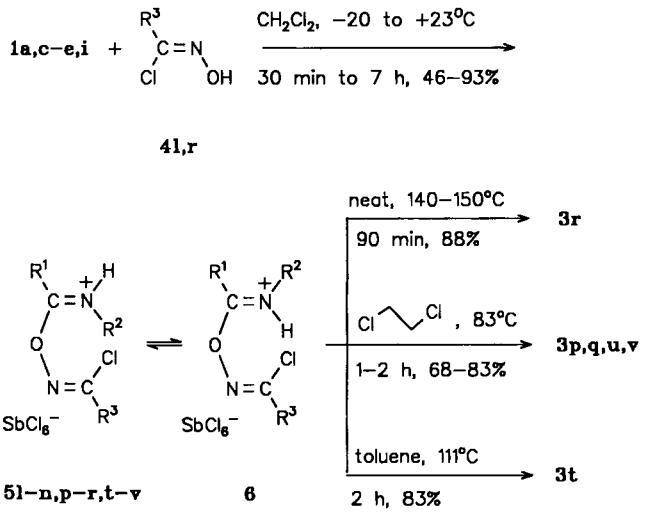
1,3-Dipolar cycloadditions to the nitrile triple bond are less common than the corresponding additions to acetylenes[1,2]. For instance, aliphatic nitriles show a low reactivity towards nitrile oxides[3]. In contrast, high dipolarophilic activities have been observed for nitrilium ions, although only few examples have been studied until now. The reaction of nitrilium ions with pyridine *N*-oxide has been reported[4]. While cycloadditions of inorganic azides to nitrilium ions are kinetically two-step reactions[5–7], additions of organic azides to nitrilium ions to give 1,4,5-trisubstituted tetrazolium ions may proceed in a concerted manner, as has first been shown by Quast et al.[8–10]. These reactions are dominated by interaction of the nitrilium LUMO with the azide HOMO[9]. In extreme cases, cycloadditions of nucleophilic 1,3-dipoles to very electron-deficient dipolarophiles[11–14] as well as of electrophilic 1,3-dipoles to especially nucleophilic dipolarophiles[15] have been found to be nonconcerted processes.

In this paper we would like to report that isolable nitrile oxides, e.g. **2a, f**[16] react with nitrilium salts **1** to give completely regioselectively 3,4,5-trisubstituted 1,2,4-oxadiazolium salts **3**, a class of heterocycles, which has previously not been reported[17] (Scheme 1).

Scheme 1



Scheme 2



In many cases the cyclizations are complete after a few minutes at temperatures as low as −50°C in dichloromethane.

Problems arise if the nitrile oxide is unstable and has to be prepared in situ. For instance, 1,3-eliminations from *N*-hydroxycarboximidoyl chlorides in the presence of a base like triethylamine are not compatible with the presence of a nitrilium hexachloroantimonate. Intractable mixture of compounds are formed.

Such problems can be overcome if the reaction is carried out in two steps. In the first step the *N*-hydroxycarboximidoyl chloride is added to the nitrilium salt to give an isolable adduct **5**. Compounds of type **5** have been unknown. In some cases (**5l, n, q, t, u**) mixtures of two geometrical isomers have been isolated. In other cases (**5p, r, s**) the products have

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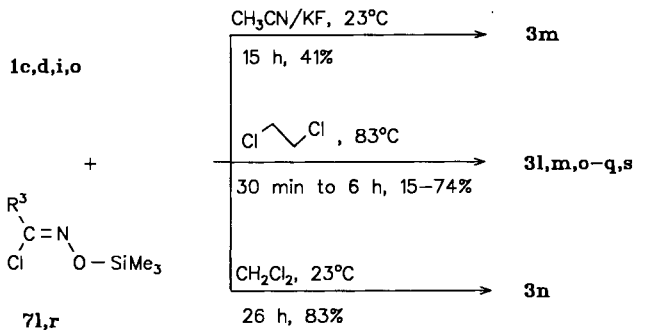
Scheme 3



1–7	R^1	R^2	R^3	1–7	R^1	R^2	R^3
a	Me	Me	2,4,6-$Me_3C_6H_2$	**l**	Me	Me	Ph
b	Me	i-Pr	2,4,6-$Me_3C_6H_2$	**m**	Ph	Me	Ph
c	Ph	i-Pr	2,4,6-$Me_3C_6H_2$	**n**	Ph	i-Pr	Ph
d	Me	Ph	2,4,6-$Me_3C_6H_2$	**o**	4-ClC_6H_4	Me	Ph
e	Ph	Ph	2,4,6-$Me_3C_6H_2$	**p**	Me	Ph	Ph
f	Me	Me	2,4,6-$(MeO_3)C_6H_2$	**q**	Ph	Ph	Ph
g	Et	i-Pr	2,4,6-$(MeO)_3C_6H_2$	**r**	Me	Me	Me
h	i-Pr	i-Pr	2,4,6-$(MeO)_3C_6H_2$	**s**	Ph	Me	Me
i	Ph	Me	2,4,6-$(MeO)_3C_6H_2$	**t**	Ph	i-Pr	Me
j	Ph	i-Pr	2,4,6-$(MeO)_3C_6H_2$	**u**	Me	Ph	Me
k	Me	Ph	2,4,6-$(MeO)_3C_6H_2$	**v**	Ph	Ph	Me

been obtained stereochemically homogeneously. Prolonged heating in boiling 1,2-dichloroethane results in stereomutation. However, we have never observed more than two stereoisomers. *N*-Hydroxybenzenecarboximidoyl chloride is known to have (*Z*) configuration. Attempts to isomerize the (*Z*) form to the (*E*) form photochemically or thermally have failed[18]. An X-ray structural analysis of an *N*-hydroxycarboximidoyl chloride showing the (*Z*) configuration has been reported[19]. The configuration of *N*-hydroxyethanimidoyl chloride is not known. We assume that all compounds **5** are (*Z*)-configurated around the C=N bond of the carboximidoyl chloride moiety, and that the barrier to *cis/trans* isomerization around this double bond is high. Consequently, the stereoisomerization observed for compounds **5** on heating in boiling 1,2-dichloroethane (83°C) should be a *cis/trans* isomerization around the alkylideneammonium ($C=N^+$) bond. Nucleophilic additions to nitrilium ions have been shown by Hegarty et al.[20,21] to be stereoelectronically controlled. The nitrogen lone pair develops always *trans* to the intruding nucleophile. In the resulting imines the nucleophile and the *N*-substituent are *cis* with respect to each other. It is likely, therefore, that the addition of the *N*-hydroxycarboximidoyl chloride to a nitrilium ion gives the (*Z*) adduct **5** as the primary product. Thermal isomerization around the $R^1C=N^+R^2$ bond furnishes the (*E*) form **6**, which may readily undergo ring closure. On heating compounds **5** either neat (**5r**) or in boiling 1,2-dichloroethane (**5p**, **q**, **u**, **v**) or in toluene (**5t**) HCl is eliminated, and the oxadiazolium salts **3** are formed in good yields (Scheme 2).

However, for R^2 = Me the salts **5** decompose on heating. In this case another technique is applied to the preparation of heterocycles **3** (Scheme 3). It has been shown by Akimova[22] and Cunico[23] et al. that *N*-hydroxycarboximidoyl chlorides can be *O*-silylated. Heating of the silyl compounds **7** in an inert solvent like dichloromethane or 1,2-dichloroethane in the presence of a nitrilium salt results in the formation of oxadiazolium salts **3** in good yields. Cunico et al. have treated **7** with olefins in acetonitrile in the presence of KF to obtain isoxazolines. The authors have found the presence of potassium fluoride to be crucial to the generation of the nitrile oxide, which is intercepted by the olefin. The application of Cunico's technique afforded the oxadiazolium salts in moderate yields. The presence of KF is not required for the formation of **3** (Scheme 3). The constitutions of the new compounds are derived from the spectra (Table 1).

The oxadiazolium salts **3** exhibit ^{13}C-NMR resonances for C-3 at δ = 161–163 (δ = 167–168 for R^3 = 2,4,6-trimethoxyphenyl) and signals for C-5 at δ = 180–185 (δ = 175–177 for R^1 = aryl). The IR spectra of compounds **3** all show a very strong absorption at $\tilde{\nu} \approx 1600\ cm^{-1}$, while for the salts **5** a very strong band is observed between $\tilde{\nu}$ = 1640 and 1690 cm^{-1} (in CH_2Cl_2). The similarities of the NMR and IR spectra suggest that the reactions outlined in Schemes 1–3 all proceed with the same regioselectivity to furnish heterocycles **3**.

Finally, it should be mentioned that after stirring a mixture of the nitrilium salt **1a** and azoxybenzene at 23°C for 24 hours in dichloromethane the starting components are isolated unchanged. On addition of a solution of the nitrone *N*-benzylideneaniline *N*-oxide in dichloromethane to a cold (−78°C) suspension of the nitrilium salt **1a** in dichloromethane a black tar is formed within 30 minutes.

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Experimental

All experiments were carried out with the exclusion of moisture. – All solvents were dried by conventional methods. – The melting points are uncorrected.

Preparation of the 1,2,4-Oxadiazolium Hexachloroantimonates **3a–k**. – *General Procedures:* A solution of **2** (10.0 mmol) in CH_2Cl_2 (20 ml) is added dropwise to a cold (−70°C) suspension of **1** (10.0 mmol) in CH_2Cl_2 (30 ml). After stirring at −70°C for 30 min and then at 23°C for 1 h, the solution is cooled to −50°C, and the product is precipitated by slow addition of ether (100 ml). The products are analytically pure or are reprecipitated from CH_2Cl_2 (20 ml)/ether (150 ml).

4,5-Dimethyl-3-(2,4,6-trimethylphenyl)-1,2,4-oxadiazolium Hexachloroantimonate (**3a**): From **1a**[10] (3.91 g, 10.0 mmol) and **2a**[16] (1.61 g, 10.0 mmol); yield 4.75 g (86%) of a yellow powder; m.p. 158–165°C (dec.).

$C_{13}H_{17}Cl_6N_2OSb$ (551.8) Calcd. C 28.30 H 3.11 N 5.08
Found C 28.00 H 3.07 N 4.95

4-Isopropyl-5-methyl-3-(2,3,6-trimethylphenyl)-1,2,4-oxadiazolium Hexachloroantimonate (**3b**): From **1b**[24] (4.19 g, 10.0 mmol)

Tab. 1. Selected NMR and IR data of the new compounds

Product	^{1}H-NMR[a] δ, J(Hz)	^{13}C-NMR[a] δ	IR[b] ν[cm^{-1}]
3a	2.16(6H), 2.39, 3.11, 3.56(CH_3), 7.18(CH)	14.2, 19.9(2C), 21.5, 33.7(CH_3), 114.4(i-C), 130.2(m-C), 140.1(o-C), 145.1(p-C), 161.9(C-3), 181.7(C-5)	1582(sh), 1609
3b	1.48(d,J=7.0), 2.18(6H), 2.39, 3.18(CH_3), 4.37 (sept,J=7.0,CH), 7.19 (CH) [c]	15.4, 20.2(2C), 20.3(2C), 21.5(CH_3), 55.4(CH), 115.1(i-C), 130.2(m-C), 140.1(o-C), 144.8(p-C), 161.4(C-3), 181.1(C-5)[c]	1590, 1605(sh)
3c	1.43(d,J=7.0), 2.29(6H), 2.41(CH_3), 4.98(sept, J=7.0,CH), 7.22(CH)[c]	20.8(2C), 20.9(2C), 21.5(CH_3), 57.3(CH), 116.2, 130.3, 130.8, 132.3, 137.6, 140.3, 144.8(aryl), 161.7(C-3), 177.3(C-5)[c]	1565, 1575(sh), 1590, 1605
3d	2.20(6H), 2.26, 3.06 (CH_3), 7.02(CH)	14.9, 20.3(2C), 21.4(CH_3), 114.6, 126.7, 129.4, 130.1, 131.9, 133.8, 140.1, 145.1(aryl), 161.6(C-3), 182.2(C-5)	1590, 1605(sh)
3e	2.26(6H), 2.27(CH_3)	20.4(2C), 21.4(CH_3), 114.6, 118.4, 126.9, 129.4, 130.3, 130.9, 132.1, 132.2, 133.9, 138.8, 140.2, 144.9 (aryl), 162.7(C-3), 175.4(C-5)	1532, 1582(sh), 1594
3f	3.03, 3.59, 3.84(6H), 3.92(CH_3), 6.38(CH)	13.8, 34.0, 56.9, 57.3(2C)(CH_3), 87.7(i-C), 92.5(m-C), 159.0(C-3), 161.8(o-C), 167.8(p-C), 180.6(C-5)	1586, 1617
3g	1.41(d,J=6.6,6H), 1.55 (t,J=7.3), 3.82(6H), 3.92(CH_3), 3.40(q,J=7.1, CH_2), 4.49(sept,J=6.6, CH), 5.47(CH_2Cl_2), 6.38 (CH)[c]	7.9, 19.9(2C), 23.2, 54.9, 55.4, 56.9, 57.0(CH_3,CH_2,CH,CH_2Cl_2), 88.1 (i-C), 92.1(m-C), 158.2(C-3), 161.4 (o-C), 167.3 (p-C), 182.6 (C-5)[c]	1580, 1600(sh)
3h	1.41(d,J=7.0,6H), 1.58 (d,J=7.0,6H), 3.83(6H), 3.93(CH_3), 3.81(sept, J=7.0), 4.67(sept,J= 7.0), 6.38(CH)[c]	19.4, 20.5, 29.0, 55.2, 56.8, 56.9 (CH_3,CH), 88.2(i-C), 92.0(m-C), 157.9(C-3), 161.4(o-C), 167.4(p-C), 185.0(C-5)[c]	1575, 1600
3i	3.82, 3.89(6H), 3.95 (CH_3), 6.42(CH)[c]	35.8, 56.9, 57.2(2C)(CH_3), 87.5 (i-C), 92.2(m-C), 118.6, 130.9, 131.6, 137.9(phenyl), 159.8(C-3), 161.7(o-C), 167.6(p-C), 175.3(C-5)[c]	1540(sh), 1575(sh), 1605
3j	1.39(d,J=6.7), 3.85(6H), 3.94(CH_3), 4.93(sept, J=6.7), 6.41(CH)[c]	20.6, 56.7, 56.9(CH_3,CH), 88.9(i-C), 92.1(m-C), 118.5, 130.8, 132.0, 137.3(phenyl), 159.6(C-3), 161.5 (o-C), 167.5(p-C), 176.8(C-5)[c]	1525, 1580(sh), 1605
3k	2.94, 3.71(6H), 3.81 (CH_3), 6.17(CH)	14.4, 56.8, 57.1(2C)(CH_3), 87.7(i-C), 91.9(m-C), 126.8, 130.1, 131.3, 133.4(phenyl), 158.8(C-3), 161.5 (o-C), 167.6(p-C), 181.1(C-5)	1547(sh), 1594(sh), 1617
3l	3.08, 3.81(CH_3)	13.4, 34.9(CH_3), 118.9(i-C), 130.6, 131.0(o,m-C), 135.1(p-C), 162.7 (C-3), 181.2(C-5)	1578(sh), 1617
3m	4.00(CH_3)	37.0(CH_3), 118.0, 119.0(i-C), 130.8, 131.1, 131.5, 131.7(o,m-C), 135.2, 138.6(p-C), 163.9(C-3), 176.5(C-5)	1571, 1601
3n	1.43(d,J=6.9,CH_3), 4.92 (sept,J=6.9,CH)	21.7(CH_3), 57.6(CH), 162.9(C-3), 176.8(C-5)	1532, 1570, 1601

Tab. 1 *(Continued)*

Product	^{1}H-NMR[a] δ, J(Hz)	^{13}C-NMR[a] δ	IR[b] ν[cm^{-1}]
3o	3.98(CH_3)	37.0(CH_3), 116.5, 118.8(i-C), 130.7, 131.0, 131.8, 133.2(o,m-C), 135.1, 144.8(p-C), 163.9(C-3), 175.6(C-5)	1571(sh), 1598
3p	3.00(CH_3)	13.9(CH_3), 118.8, 130.0(i-C), 127.6, 130.5, 130.7, 132.1(o,m-C), 134.0, 135.0(p-C), 161.8(C-3), 181.6(C-5)	1567, 1605
3q		117.9, 118.8, 128.0, 130.5, 130.6, 130.7, 131.3, 131.8, 132.5, 134.2, 134.8, 138.9(phenyl), 162.9(C-3), 175.2(C-5)	1524, 1560, 1598
3r	2.63, 2.99, 3.78(CH_3)	9.2, 13.2, 33.8(CH_3), 162.0(C-3), 180.3(C-5)	1374, 1420, 1470, 1551, 1628[d]
3s	2.72, 3.98(CH_3)	9.5, 35.4(CH_3), 118.1(i-C), 131.3, 131.5(o,m-C), 138.2(p-C), 163.1 (C-3), 176.1(C-5)	1547, 1617
3t	1.66(d,J=7.0), 2.85(CH_3), 5.02(sept,J= 7.0,CH)	11.1, 20.7(2C)(CH_3), 56.4(CH), 118.3(?), 131.1, 131.5, 137.4 (phenyl), 161.7(C-3), 176.6(C-5)	1532, 1601
3u	2.48, 2.90(CH_3)	9.5, 13.7(CH_3), 127.3, 132.2(o,m-C), 129.2, 134.1(i,p-C), 161.6(C-3), 180.8(C-5)	1536, 1613
3v	2.51(CH_3)	9.6(CH_3), 118.0, 130.4, 134.3, 138.9(o,p-C), 127.6, 131.2, 131.7, 132.7(o,m-C), 162.8(C-3), 174.6(C-5)	1528, 1605
5l	main component[e]: 2.73 (d,J=0.8), 3.24(d,J=4.3) (CH_3), NH 9.84; minor component: 2.60, 3.29 (d,J=5.2)(CH_3), NH 9.84	main component: 19.8, 30.9(CH_3), 153.7, 179.7(C=N); minor component: 16.9, 32.8(CH_3), 155.3, 176.8(C=N)	1690
5m	3.47(d,J=5.3,CH_3), 10.06(NH)	32.2(CH_3), 153.6, 175.9(C=N)	1598, 1659
5n	main component[f]: 1.54 (d,J=6.6,CH_3), 4.64(m, CH), 10.08(NH); minor component: 1.48(d,J= 6.5,CH_3), 4.29(m,CH), 10.08(NH)	main component: 21.3(CH_3), 51.2(CH), 153.4, 174.9(C=N); minor component: 22.0(CH_3), 53.7(CH), 155.9, 171.4 (C=N)	1559, 1598, 1640
5p	2.95(CH_3), 11.38 (NH)	20.7(CH_3), 154.2, 178.8(C=N)	1594, 1659
5q	main component[g]: 11.81 (NH); minor component: 11.62(NH)	main component: 156.8(C-3), 171.8 (C-5); minor component: 153.9(C-3), 174.2(C-5)	1555, 1589, 1632
5r	2.50, 2.58(q,J=1.0), 3.14 (br,coupled to 2.58) (CH_3), 9.64(NH)	19.6, 23.8, 30.7(CH_3), 154.6, 179.3(C=N)	1621, 1690
5t	1.48(d,J=6.6), 2.39(CH_3), 4.53(m,CH), 9.93(NH)	21.2(2 C), 23.7(CH_3), 50.9(CH), 124.8, 129.6, 131.6, 136.1(phenyl), 154.1(C-3), 174.4(C-5)	1582(sh), 1621(sh), 1640
5u	main component[d]: 2.45, 2.63(CH_3), 11.50(NH); minor component: 2.51, 2.81(CH_3), 11.50(NH)	main component: 18.0, 24.4(CH_3), 156.8, 177.6(C=N); minor component: 20.7, 23.7(CH_3), 155.0, 178.2(C=N)	1509, 1520(sh), 1594, 1621, 1659

Tab. 1 *(Continued)*

Product	^{1}H-NMR[a] δ, J(Hz)	^{13}C-NMR[a] δ	IR[b] ν[cm^{-1}]
5v	2.69(CH_3), 11.68(NH)	main component[h]: 24.4(CH_3), 157.7, 171.8(C=N); minor component: 23.6 (CH_3), 155.0, 174.3(C=N)	1580(sh), 1600(sh), 1613, 1640(sh)
7l	0.33(CH_3)[i]	-0.7(CH_3), 127.4, 128.4, 130.5, 133.0(phenyl), 141.7(C=N)[i]	1254(vs), 1447, 1563, 1721(w)[j]
7r	0.25(9H), 2.26(CH_3)[i]	-0.5, 23.3(CH_3), 139.7(C=N)[i]	1621(vs)

[a] At 250 MHz at 295 K in CD_3CN with TMS as internal standard; Bruker AC-250 and WM-250 spectrometers. — [b] Mattson Polaris FTIR spectrometer; solutions in CH_2Cl_2. — [c] At 263 K. — [d] In KBr. — [e] 2:1 mixture of two geometrical isomers. — [f] 3:1 mixture of two geometrical isomers. — [g] 6:1 mixture of two geometrical isomers. — [h] 8:1 mixture of two isomers. — [i] In $CDCl_3$. — [j] Neat.

and **2a** (1.61 g, 10.0 mmol); yield 4.70 g (81%) of a yellow powder; dec. >135°C.

$C_{15}H_{21}Cl_6N_2OSb$ (579.8) Calcd. C 31.07 H 3.65 N 4.83
Found C 31.16 H 3.81 N 4.69

4-Isopropyl-5-phenyl-3-(2,4,6-trimethylphenyl)-1,2,4-oxadiazolium Hexachloroantimonate (**3c**): From **1c**[25] (4.81 g, 10.0 mmol) and **2a** (1.61 g, 10.0 mmol); yield 4.69 g (73%) of a yellow powder; dec. >138°C.

$C_{20}H_{23}Cl_6N_2OSb$ (641.9) Calcd. C 37.42 H 3.61 N 4.37
Found C 37.59 H 3.62 N 4.29

5-Methyl-4-phenyl-3-(2,4,6-trimethylphenyl)-1,2,4-oxadiazolium Hexachloroantimonate (**3d**): From **1d**[26] (4.53 g, 10.0 mmol) and **2a** (1.61 g, 10.0 mmol). Crystallization at −20°C from CH_2Cl_2 (40 ml)/CCl_4 (20 ml) yields a pale yellow powder (4.73 g, 77%); m.p. 148−150°C (dec.).

$C_{18}H_{19}Cl_6N_2OSb$ (613.8) Calcd. C 35.22 H 3.12 N 4.56
Found C 34.99 H 3.10 N 4.38

4,5-Diphenyl-3-(2,4,6-trimethylphenyl)-1,2,4-oxadiazolium Hexachloroantimonate (**3e**): From **1e**[26] (5.15 g, 10.0 mmol) and **2a** (1.61 g, 10.0 mmol). Crystallization at −20°C from CH_2Cl_2 (20 ml)/CCl_4 (10 ml) affords pale yellow prisms (4.28 g, 63%); dec. >138°C.

$C_{23}H_{21}Cl_6N_2OSb$ (675.9) Calcd. C 40.87 H 3.13 N 4.15
Found C 40.64 H 3.15 N 3.89

4,5-Dimethyl-3-(2,4,6-trimethoxyphenyl)-1,2,4-oxadiazolium Hexachloroantimonate (**3f**): From **1a** (3.91 g, 10.0 mmol) and **2f**[16] (2.09 g, 10.0 mmol); yield 5.46 g (91%) of a yellow powder; dec >130°C.

$C_{13}H_{17}Cl_6N_2O_4Sb$ (599.8) Calcd. C 26.03 H 2.86 N 4.67
Found C 25.88 H 2.74 N 4.50

5-Ethyl-4-isopropyl-3-(2,4,6-trimethoxyphenyl)-1,2,4-oxadiazolium Hexachloroantimonate−Dichloromethane (**3g**): From **1g**[27] (4.33 g, 10.0 mmol) and **2f** (2.09 g, 10.0 mmol). Washing with CH_2Cl_2 (5 ml)/pentane (50 ml) affords an orange powder (5.67 g, 78%), which contains 1 equiv. of CH_2Cl_2; m.p. 80−82°C (dec.).

$C_{17}H_{25}Cl_8N_2O_4Sb$ (726.8) Calcd. C 28.09 H 3.47 N 3.85
Found C 27.82 H 3.33 N 3.91

4,5-Diisopropyl-3-(2,4,6-trimethoxyphenyl)-1,2,4-oxadiazolium Hexachloroantimonate (**3h**): From **1h**[24] (4.47 g, 10.0 mmol) and **2f** (2.09 g, 10.0 mmol); yield after reprecipitation 5.58 g (85%) of an orange powder; dec. >95°C.

$C_{17}H_{25}Cl_6N_2O_4Sb$ (655.9) Calcd. C 31.13 H 3.84 N 4.27
Found C 31.27 H 3.56 N 4.29

4-Methyl-5-phenyl-3-(2,4,6-trimethoxyphenyl)-1,2,4-oxadiazinium Hexachloroantimonate (**3i**): From **1i**[24] (4.53 g, 10.0 mmol) and **2f** (2.09 g, 10.0 mmol); yield after reprecipitation 5.89 g (89%) of a yellow powder; dec. >128°C.

$C_{18}H_{19}Cl_6N_2O_4Sb$ (661.8) Calcd. C 32.67 H 2.84 N 4.23
Found C 32.39 H 2.83 N 4.08

4-Isopropyl-5-phenyl-3-(2,4,6-trimethoxyphenyl)-1,2,4-oxadiazolium Hexachloroantimonate (**3j**): From **1c** (4.81 g, 10.0 mmol) and **2f** (2.09 g, 10.0 mmol); yield after reprecipitation 5.86 g (85%) of a yellow powder; m.p. 126−128°C (dec.).

$C_{20}H_{23}Cl_6N_2O_4Sb$ (689.9) Calcd. C 34.82 H 3.36 N 4.06
Found C 34.70 H 3.22 N 4.03

5-Methyl-4-phenyl-3-(2,4,6-trimethoxyphenyl)-1,2,4-oxadiazolium Hexachloroantimonate (**3k**): From **1d** (4.53 g, 10.0 mmol) and **2f** (2.09 g, 10.0 mmol); yield after reprecipitation 5.03 g (76%) of a pale green powder; m.p. 125−132°C (dec.).

$C_{18}H_{19}Cl_6N_2O_4Sb$ (661.8) Calcd. C 32.67 H 2.89 N 4.23
Found C 32.53 H 3.02 N 4.28

4,5-Dimethyl-3-phenyl-1,2,4-oxadiazolium Hexachloroantimonate (**3l**): A mixture of **7l** (0.46 g, 2.00 mmol) and **1a** (0.78 g, 2.00 mmol) in $ClCH_2CH_2Cl$ (10 ml) is boiled under reflux for 1 h. After cooling to −20°C, ether (40 ml) is added to the red solution. A pale yellow precipitate is filtered off and stirred in CH_2Cl_2 (10 ml) for 15 min. After filtration from an impurity, ether (5 ml) is added. At −20°C colorless crystals are formed (0.67 g, 66%); m.p. 148−150°C (dec.).

$C_{10}H_{11}Cl_6N_2OSb$ (509.7) Calcd. C 23.56 H 2.18 N 5.50
Found C 23.67 H 2.23 N 5.48

4-Methyl-3,5-diphenyl-1,2,4-oxadiazolium Hexachloroantimonate (**3m**). — a) A mixture of **7l** (2.28 g, 10.0 mmol), **1i** (4.53 g, 10.0 mmol) and dry KF (2 g) in CH_3CN (35 ml) is stirred at 23°C for 15 h. The solvent is evaporated, and the residue is suspended in CH_2Cl_2 (100 ml). Extraction with water and usual workup afford a pale yellow powder, which is crystallized at −20°C from CH_2Cl_2 (50 ml)/ether (15 ml) to furnish pale yellow prisms (2.34 g, 41%); m.p. 230−232°C (dec.).

b) A mixture of **7l** (2.51 g, 11.0 mmol) and **1i** (4.53 g, 10.0 mmol) in $ClCH_2CH_2Cl$ (50 ml) is boiled under reflux for 30 min. After cooling, a pale yellow powder (3.43 g, 60%) is precipitated with ether (200 ml).

$C_{15}H_{13}Cl_6N_2OSb$ (571.7) Calcd. C 31.51 H 2.29 N 4.90
Found C 31.53 H 2.30 N 4.82

4-Isopropyl-3,5-diphenyl-1,2,4-oxadiazolium Hexachloroantimonate (**3n**): A mixture of **7l** (2.51 g, 11.0 mmol) and **1c** (4.81 g, 10.0 mmol) in CH_2Cl_2 (30 ml) is stirred at 23 °C for 26 h. After cooling to −20 °C, ether (150 ml) is added dropwise. A pale yellow powder (4.97 g, 83%) is filtered off, which is crystallized at −20 °C from CH_2Cl_2 (100 ml)/ether (20 ml) to afford colorless prisms; m.p. 149−151 °C (dec.).

$C_{17}H_{17}Cl_6N_2OSb$ (599.8) Calcd. C 34.04 H 2.86 N 4.67
Found C 33.91 H 2.85 N 4.54

In CH_3CN in the presence of KF **3n** is obtained in less than 20% yield.

5-(4-Chlorophenyl)-4-methyl-3-phenyl-1,2,4-oxadiazolium Hexachloroantimonate (**3o**): A mixture of **7l** (2.51 g, 11.0 mmol) and **1o**[28] (4.87 g, 10.0 mmol) in $ClCH_2CH_2Cl$ (50 ml) is boiled under reflux for 30 min. After cooling, a yellow powder (4.24 g, 70%) is precipitated with ether (200 ml). Crystallization at −20 °C from CH_2Cl_2 (25 ml)/CH_3CN (10 ml)/ether (15 ml) affords a colorless powder; m.p. 225−230 °C (dec.).

$C_{15}H_{12}Cl_7N_2OSb$ (606.2) Calcd. C 29.72 H 2.00 N 4.62
Found C 29.79 H 2.03 N 4.61

5-Methyl-3,4-diphenyl-1,2,4-oxadiazolium Hexachloroantimonate (**3p**). – a) From **7l** (2.51 g, 11.0 mmol) and **1d** (4.53 g, 10.0 mmol) as described for **3m** (procedure b); yield 4.23 g (74%) of a brown powder, which is crystallized at −20 °C from CH_2Cl_2 (50 ml)/ether (50 ml) to give colorless needles (3.51 g); m.p. 145−148 °C (dec.).

$C_{15}H_{13}Cl_6N_2OSb$ (571.7) Calcd. C 31.51 H 2.29 N 4.90
Found C 31.22 H 2.28 N 4.87

b) A suspension of **5p** (0.61 g, 1.00 mmol) in $ClCH_2CH_2Cl$ (10 ml) is boiled under reflux for 1 h. After cooling to −20 °C, ether (60 ml) is added, and a colorless powder (0.39 g, 68%) showing the spectra of pure **3p** is filtered off.

3,4,5-Triphenyl-1,2,4-oxadiazolium Hexachloroantimonate (**3q**). – a) From **7l** (2.51 g, 11.0 mmol) and **1e** (5.15 g, 10.0 mmol) as described for **3m** (procedure b); yield 4.25 g (67%) of a colorless powder, which is crystallized at −20 °C from CH_2Cl_2 (30 ml)/CH_3CN (15 ml)/ether (15 ml) to give a colorless powder (3.49 g); m.p. 200−202 °C (dec.).

$C_{20}H_{15}Cl_6N_2OSb$ (633.8) Calcd. C 37.90 H 2.39 N 4.42
Found C 37.75 H 2.37 N 4.20

b) From **5q** (0.67 g, 1.00 mmol) as described for **3p** (procedure b); yield 0.44 g (70%) of a colorless powder showing the spectra of pure **3q**.

3,4,5-Trimethyl-1,2,4-oxadiazolium Hexachloroantimonate (**3r**): Compound **5r** (4.84 g, 10 mmol) is kept at 140−150 °C for 90 min. After cooling to 23 °C, the yellow product is triturated with CH_2Cl_2 (15 ml) and filtered off; yield 3.94 g (88%) of a colorless powder, which can be crystallized at −20 °C from CH_2Cl_2 (30 ml)/CH_3CN (6 ml)/ether (15 ml) to give a colorless powder (3.12 g); m.p. 153−155 °C.

$C_5H_9Cl_6N_2OSb$ (447.6) Calcd. C 13.42 H 2.03 N 6.26
Found C 13.58 H 2.04 N 6.30

3,4-Dimethyl-5-phenyl-1,2,4-oxadiazolium Hexachloroantimonate (**3s**): From **7r** (1.66 g, 10.0 mmol) and **1i** (4.53 g, 10.0 mmol) as described for **3m** (procedure a). However, the reaction time is 6 h. The crude product is precipitated from CH_2Cl_2 (12 ml)/ether (50 ml) to furnish a colorless powder (0.77 g, 15%); m.p. 158−160 °C (dec.).

$C_{10}H_{11}Cl_6N_2OSb$ (509.7) Calcd. C 23.56 H 2.18 N 5.50
Found C 23.58 H 2.20 N 5.44

4-Isopropyl-3-methyl-5-phenyl-1,2,4-oxadiazolium Hexachloroantimonate (**3t**): A suspension of **5t** (5.74 g, 10.0 mmol) in toluene (25 ml) is boiled under reflux for 75 min. After cooling to 23 °C, the solvent is decanted, and the residue is precipitated from CH_2Cl_2 (25 ml)/ether (100 ml) to afford a colorless powder (4.46 g, 83%). Reprecipitation at −20 °C from CH_2Cl_2/ether gives a colorless crystalline powder; m.p. 152−154 °C (dec.).

$C_{12}H_{15}Cl_6N_2OSb$ (537.7) Calcd. C 26.80 H 2.81 N 5.21
Found C 26.95 H 2.83 N 5.10

3,5-Dimethyl-4-phenyl-1,2,4-oxadiazolium Hexachloroantimonate (**3u**): A suspension of **5u** (5.46 g, 10.0 mmol) in $ClCH_2CH_2Cl$ (50 ml) is boiled under reflux for 2 h. The clear brown solution is cooled to 23 °C, and ether (300 ml) is added. At −20 °C colorless needles (4.08 g, 80%) are formed; m.p. 160−162 °C (dec.).

$C_{10}H_{11}Cl_6N_2OSb$ (509.7) Calcd. C 23.56 H 2.18 N 5.50
Found C 23.50 H 2.19 N 5.58

3-Methyl-4,5-diphenyl-1,2,4-oxadiazolium Hexachloroantimonate (**3v**): From **5v** (6.08 g, 10.0 mmol) as described for **3u**; yield 4.52 g (79%) of a colorless powder, which is reprecipitated at −20 °C from CH_2Cl_2/ether; m.p. 156−158 °C (dec.).

$C_{15}H_{13}Cl_6N_2OSb$ (571.6) Calcd. C 31.51 H 2.29 N 4.90
Found C 31.51 H 2.30 N 4.85

(1-{[Chloro(phenyl)methylene]aminooxy}ethylidene)methylammonium Hexachloroantimonate (**5l**): A solution of **4l**[29,30] (1.56 g, 10.0 mmol) in CH_2Cl_2 (20 ml) is added to a suspension of **1a** (3.91 g, 10.0 mmol) in CH_2Cl_2 (20 ml). After stirring at 23 °C for 7 h and cooling to −10 °C, ether (150 ml) is added, and the precipitate (5.41 g, 99%) is filtered off. Crystallization at −20 °C from CH_2Cl_2 (10 ml)/CH_3CN (10 ml) affords colorless crystals (2.51 g, 46%); m.p. 190−192 °C (dec.).

$C_{10}H_{12}Cl_7N_2OSb$ (546.1) Calcd. C 21.99 H 2.21 N 5.13
Found C 21.89 H 2.27 N 4.99

On heating **5l** in boiling chlorobenzene a mixture of compounds is formed.

({[Chloro(phenyl)methylene]aminooxy}phenylmethylene)methylammonium Hexachloroantimonate (**5m**): From **4l** (1.56 g, 10.0 mmol) and **1i** (4.53 g, 10.0 mmol) as described for **5l**. However, the reaction time is 2 h; yield 5.35 g (88%) of an orange-yellow powder, which is crystallized at −20 °C from CH_2Cl_2 (30 ml)/ether (10 ml) to afford a brownish powder; m.p. 133−135 °C (dec.).

$C_{15}H_{14}Cl_7N_2OSb$ (608.2) Calcd. C 29.62 H 2.32 N 4.61
Found C 29.50 H 2.35 N 4.63

({[Chloro(phenyl)methylene]aminooxy}phenylmethylene)isopropylammonium Hexachloroantimonate (**5n**): From **4l** (1.56 g, 10.0 mmol) and **1c** (4.81 g, 10.0 mmol) as described for **5l**. However, the reaction mixture is stirred first at 0 °C for 2 h and then at 23 °C for 3 h; yield 5.92 g (91%) of a colorless powder; m.p. 135−137 °C (dec.).

$C_{17}H_{18}Cl_7N_2OSb$ (636.3) Calcd. C 32.09 H 2.85 N 4.40
Found C 32.16 H 2.90 N 4.34

(1-{[Chloro(phenyl)methylene]aminooxy}ethylidene)anilinium Hexachloroantimonate (**5p**): From **4l** (1.56 g, 10.0 mmol) and **1d**

(4.53 g, 10.0 mmol) as described for **5l**. However, the reaction mixture is stirred at 0°C for 90 min. Cooling to −30°C and slow addition of pentane (150 ml) afford a pale yellow powder (5.66 g, 93%), which is crystallized at −20°C from CH_2Cl_2 (12 ml)/CH_3CN (2 ml)/pentane (5 ml) to give pale yellow prisms; m.p. 135−137°C (dec.).

$C_{15}H_{14}Cl_7N_2OSb$ (608.2) Calcd. C 29.62 H 2.32 N 4.61
Found C 29.69 H 2.43 N 4.48

({[Chloro(phenyl)methylene]aminooxy}phenylmethylene)anilinium Hexachloroantimonate (**5q**): A mixture of **4l** (1.56 g, 10.0 mmol) and **1e** (5.15 g, 10.0 mmol) in CH_2Cl_2 (80 ml) is stirred at −10°C for 2 h. Slow addition of pentane (150 ml) affords a colorless powder (4.83 g, 72%). Crystallization at −20°C from CH_2Cl_2 (25 ml)/CH_3CN (5 ml)/ether (50 ml) gives colorless prisms; m.p. 150−152°C (dec.).

$C_{20}H_{16}Cl_7N_2OSb$ (670.3) Calcd. C 35.84 H 2.41 N 4.18
Found C 35.70 H 2.43 N 4.21

{1-[(1-Chloroethylidene)aminooxy]ethylidene}methylammonium Hexachloroantimonate (**5r**): A solution of **4r**[29,30] (0.94 g, 10.0 mmol) in CH_2Cl_2 (20 ml) is added to a cold (−10°C) suspension of **1a** (3.91 g, 10.0 mmol) in CH_2Cl_2 (20 ml). The reaction mixture is stirred at 23°C for 1 h. Cooling to −20°C and slow addition of ether (150 ml) afford a colourless powder (4.02 g, 83%), which can be crystallized at −20°C from CH_2Cl_2 (20 ml)/ether (10 ml) to give colorless needles (3.84 g); m.p. 145−150°C.

$C_5H_{10}Cl_7N_2OSb$ (484.1) Calcd. C 12.41 H 2.08 N 5.79
Found C 12.54 H 2.13 N 5.77

[(1-Chloroethylidene)aminooxy(phenyl)methylene]isopropylammonium Hexachloroantimonate (**5t**): From **4r** (0.94 g, 10.0 mmol) and **1c** (4.81 g, 10.0 mmol) as described for **5r**. However, the reaction time is 90 min at 23°C; yield 4.59 g (80%) of a colorless powder, which can be crystallized at −20°C from CH_2Cl_2 (50 ml)/ether (50 ml) to give colorless fine prisms; m.p. 134−138°C (dec.).

$C_{12}H_{16}Cl_7N_2OSb$ (574.2) Calcd. C 25.10 H 2.81 N 4.88
Found C 25.17 H 2.85 N 4.84

{1-[(1-Chloroethylidene)aminooxy]ethylidene}anilinium Hexachloroantimonate (**5u**): A mixture of **4r** (0.94 g, 10.0 mmol) and **1d** (4.53 g, 10.0 mmol) in CH_2Cl_2 (40 ml) is stirred at −20°C for 30 min. Cooling to −40°C and slow addition of ether (250 ml) afford a pale yellow powder (3.86 g, 71%), which consists of only one isomer according to the ^{1}H-NMR spectrum; m.p. 132−135°C. Reprecipitation at −20°C from CH_2Cl_2 (40 ml)/ether (160 ml) affords a crystalline 1:2 mixture of the original and a second isomer.

$C_{10}H_{12}Cl_7N_2OSb$ (546.1) Calcd. C 21.99 H 2.21 N 5.13
Found C 21.96 H 2.18 N 5.10

[(1-Chloroethylidene)aminooxy(phenyl)methylene]anilinium Hexachloroantimonate (**5v**): A solution of **4r** (0.94 g, 10.0 mmol) in CH_2Cl_2 (20 ml) is added to a cold (−10°C) suspension of **1e** (5.15 g, 10.0 mmol) in CH_2Cl_2 (20 ml). The reaction mixture is stirred at 0°C for 1 h. Cooling to −30°C and slow addition of ether (100 ml) afford a colorless powder (4.99 g, 82%), which can be crystallized at −20°C from CH_2Cl_2 (60 ml)/ether (60 ml) to give colorless fine prisms (4.16 g); m.p. 145−147°C.

$C_{15}H_{14}Cl_7N_2OSb$ (608.2) Calcd. C 29.62 H 2.32 N 4.61
Found C 29.77 H 2.35 N 4.53

N-(Trimethylsilyloxy)benzenecarboximidic Chloride (**7l**)[22,23]: A solution of triethylamine (5.05 g, 50.0 mmol) in toluene (50 ml) is added dropwise at −50°C to a solution of **4l** (7.78 g, 50.0 mmol) in toluene (50 ml). Then, a solution of trimethylsilyl chloride (6.00 g, 55.0 mmol) in toluene (50 ml) is added dropwise. The suspension is stirred at 45°C for 2 h. After cooling to 23°C, triethylammonium chloride is filtered off and washed with toluene. The solvent of the filtrate is removed in vacuo. Kugelrohr distillation of the residue affords a colorless oil (6.04 g, 53%); b.p. ca. 90°C/1 Torr.

N-(Trimethylsilyloxy)ethenimidoyl Chloride (**7r**)[23]: A solution of triethylamine (5.05 g, 50.0 mmol) in ether (100 ml) is added dropwise at −70°C to a solution of **4r** (4.68 g, 50.0 mmol) in ether (100 ml). Then, a solution of trimethylsilyl chloride (10.9 g, 100 mmol) in ether (100 ml) is added dropwise. The suspension is stirred at −20°C for 8 h and then at 23°C for 2 h. Filtration from triethylammonium chloride and evaporation of the solvent at 0°C/13 Torr afford a pale yellow oil, which is subjected to kugelrohr distillation at 18°C/10^{-1} Torr; yield 5.10 g (62%) of a colorless moisture-sensitive oil (b.p.[23] 34°C/11 Torr).

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