A Convenient Synthesis of Amino-substituted 1,3,5-Oxadiazinium Salts

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Diacyl chlorides react with dialkylcyanamide in the presence of a Lewis acid to give amino-substituted bis-1,3,5-oxadiazinium salts in excellent yields. A mechanism leads to the formation of the product has been postulated. All new compounds have been characterized by ^{1}H-nmr, ^{13}C-nmr, ir-spectroscopy and elemental analysis.

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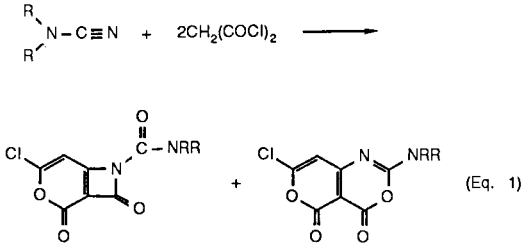
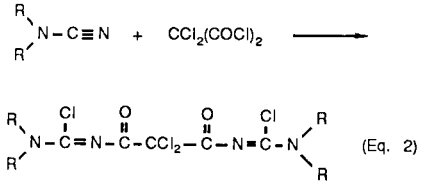
The reaction of dialkylcyanamide with acyl chlorides has attracted much attention in the past few years due to its versatile use in organic synthesis [1-4]. Malonyl chloride was reported [1] to react with dialkylcyanamide to afford pyranoazetedione **1** and pyranooxazinediones **2** (Eq 1). On the other hand, dichloromalonyl chloride was found to



(Eq. 1)

react with dialkylcyanamides to give the open chain derivative bischloroformamidine **3** (Eq 2) [2].



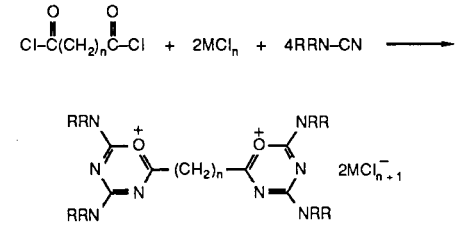
(Eq. 2)

In a recent communication [5], we showed that the presence of a Lewis acid changed the course of this reaction. Thus, diacyl chlorides react with dialkylcyanamide in the presence of a Lewis acid to afford amino-substituted bis-1,3,5-oxadiazinium salts, **4**, as the sole product (Scheme 1). In the present contribution we describe the scope and other details of this reaction.

Results and Discussion.

Adipoyl chloride was found to rapidly react at -20° with four equivalents of diisopropylcyanamide in the presence of two equivalents of antimony pentachloride to give a good yield of 1,4-butylene-bis-[4,6-bis(diisopropylamino)-1,3,5-oxadiazene-2-yl-1-ium] bis-hexachloroantimonate (**4f**)

Scheme 1



4a-m

Compound No.	n	R	MCl_n
4a	0	$(CH_3)_2CH$–	$SbCl_5$
b	2	$(CH_3)_2CH$–	$SbCl_5$
c	2	$-(CH_2)_2O(CH_2)_2-$	$SbCl_5$
d	2	$-(CH_2)_2O(CH_2)_2-$	$SnCl_4$
e	4	CH_3–	$SbCl_5$
f	4	$(CH_3)_2CH$–	$SbCl_5$
g	4	$(CH_3)_2CH$–	$FeCl_3$
h	4	$-(CH_2)_2O(CH_2)_2-$	$SbCl_5$
i	8	CH_3–	$SbCl_5$
j	8	$(CH_3)_2CH$–	$SbCl_5$
k	8	$(CH_3)_2CH$–	$FeCl_3$
l	8	$(CH_3)_2CH$–	$SnCl_4$
m	8	$-(CH_2)_2O(CH_2)_2-$	$SbCl_5$

as a pale yellow crystalline product. The reaction was clean and strongly promoted by the presence of the Lewis acid. The progress of the reaction was easily followed by the disappearance of the infrared bands between 2200-2300 cm^{-1} for the starting substrates. Similarly, adipoyl chloride was found to cleanly react with other dialkylcyanamides in the presence of antimony pentachloride to afford the corresponding amino-substituted bis-1,3,5-oxadiazinium salts **4e,h**. Other diacyl chlorides were found to react under the reaction conditions in the presence of different Lewis acids to afford the amino substituted bis-1,3,5-oxadiazinium salts in good yields. The details are shown in Scheme 1.

Among the tested Lewis acids, antimony pentachloride was found to be the most effective in promoting the reaction of diacyl chloride with dialkylcyanamide.

Table 1

Spectral Data of Substituted Bis-1,3,5-Oxadiazinium Salts **4a-m** and **5a-c**

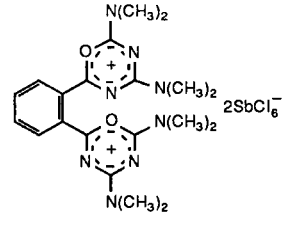
Compound No.	^{1}H NMR [a] Solvent, δ	^{13}C NMR [a]	IR (cm^{-1}) KBr disc
4a	CD_3CN/acetone-d_6 (1:1) 4.68 (m, 4H, CH), 4.40 (m, 4H, CH), 1.55 (d, 24H, J = 7.0 Hz, $(CH_3)_2CH$), 1.45 (d, 24H, J = 7.0 Hz, $(CH_3)_2CH$)	166.2, 158.6 (2C) (C=O, C=N), 52.1, 51.9 (CH) 20.3, 19.8 (CH_3)	1650, 1585
b	CD_3CN/DMSO-d_6 (5:1) 4.62 (m, 4H, CH), 4.19 (m, 4H, CH), 3.52 (s, 4H, $-CH_2-$), 1.39-1.26 (m, 48H, $(CH_3)_2CH$)	[b]	1680, 1620, 1560
c	CD_3CN/DMSO-d_6 (5:1) 3.81-3.47 (m, 32H, $-OCH_2CH_2N-$), 2.75 (s, 4H, $-CH_2-$)	[b]	1690, 1635, 1580
d	CD_3CN/DMSO-d_6 (3:1) 3.82-3.50 (m, 32H, $-OCH_2CH_2N-$), 2.72 (s, 4H, $-CH_2-$)	[b]	1680, 1630, 1570
e	CD_3CN/acetone-d_6 (1:1) 3.70 (s, 6H, CH_3), 3.67 (s, 6H, CH_3), 3.60 (s, 6H, CH_3), 3.57 (s, 6H, CH_3), 2.72 (t, 4H, J = 6.5 Hz, $-CH_2-$), 1.84 (broad, 4H, $-CH_2-$)	165.9, 158.0, 154.3 (C=O, C=N), 39.1, 38.8, 38.3 37.9 (CH_3), 34.5, 24.3 ($-CH_2-$)	1700, 1655, 1605
f	CD_3CN/DMSO-d_6 (5:1) 4.47 (m, 4H, CH), 4.03 (m, 4H, CH), 2.78 (t, 4H, J= 7.0 Hz, $-CH_2-$), 1.72 (broad, 4H, $-CH_2-$), 1.44-1.16 (m, 48H, $(CH_3)_2CH$)	173.5, 157.1, 155.4 (C=O, C=N), 50.2, 49.3, 48.0, 47.0 (CH), 35.8, 24.0 ($-CH_2-$), 20.7, 19.7, 19.6, 19.5, 19.3, 19.1 (CH_3)	1680, 1620, 1550
g	—	—	1680, 1625, 1545
h	CD_3CN/DMSO-d_6 (3:1) 3.80-3.47 (m, 32H, $-OCH_2CH_2N-$), 2.47 (t, 4H, J = 7.0 Hz, $-CH_2-$), 1.64 (broad, 4H, $-CH_2-$)	172.7, 157.3, 155.8 (C=O, C=N), 66.4 66.2, 66.1, 65.9 ($-OCH_2-$), 46.3, 45.9, 45.7, 45.1 ($-NCH_2-$), 36.5, 23.6 ($-CH_2-$)	1682, 1630, 1575
i	CD_3CN 3.34 (s, 6H, CH_3), 3.28 (s, 6H, CH_3), 3.22 (s, 6H, CH_3), 3.17 (s, 6H, CH_3), 2.73 (t, 4H, J = 7.0 Hz, $-CH_2-$), 1.39 (m, 12H, $-CH_2-$)	164.9, 158.1, 156.0 (C=O, C=N), 39.2, 38.9 38.6, 37.9 (CH_3), 34.2, 24.1, 22.3, 20.7 ($-CH_2-$)	1690, 1635, 1590
j	CD_3CN 4.60 (m, 4H, CH), 4.13 (m, 4H, CH), 2.11 (t, 4H, J = 7.0 Hz, $-CH_2-$), 1.44-1.28 (m, 60H, $(CH_3)_2CH$ and $-CH_2-$)	[b]	1682, 1625, 1550
k	—	—	1670, 1610, 1545
l	CD_3CN/DMSO-d_6 (3:1) 4.29 (m, 4H, CH), 3.75 (m, 4H, CH), 2.56 (broad, 4H, $-CH_2-$), 1.40-1.20 (m, 60H, $(CH_3)_2CH$ and $-CH_2-$)	[b]	1685, 1628, 1580

Table 1 (continued)

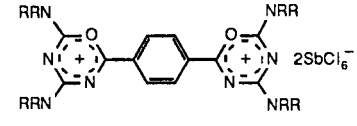
Compound No.	^{1}H NMR [a] Solvent, δ	^{13}C NMR [a]	IR (cm^{-1}) KBr disc
m	CD_3CN/DMSO-d_6 (3:1) 3.81-3.46 (m, 32H, $-OCH_2CH_2N-$), 2.42 (t, 4H, J = 7.0 Hz, $-CH_2-$), 1.61 (broad, 4H, $-CH_2-$), 1.32 (broad, 8H, $-CH_2-$)	172.3, 158.0, 155.7 (C=O, C=N), 66.3 66.1, 65.9, 65.7 ($-OCH_2-$), 46.6, 46.3, 45.9, 45.5 ($-NCH_2-$), 36.5, 23.6, 22.5, 21.9 ($-CH_2-$)	1688, 1620, 1575
5a	CD_3CN 8.02 (broad 4H, aromatic), 3.43 (s, 3H, CH_3), 3.34 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 3.13 (s, 6H, CH_3), 2.98 (s, 3H, CH_3), 2.84 (s, 3H, CH_3), 2.69 (s, 3H, CH_3)	[b]	1685, 1630, 1590
b	CD_3CN/DMSO-d_6 (1:1) 8.30-8.00 (m, 4H, aromatic), 4.65 (m, 4H, CH), 4.30 (m, 4H, CH), 1.65-1.25 (m, 48H, $(CH_3)_2CH$)	165.1, 157.7, 155.2 (C=O, C=N), 139.2, 133.0, 132.3, 131.0 (aromatic), 48.3, 47.2, 46.5, 45.8 (CH), 20.5, 19.8, 19.6, 19.4, 19.3, 19.2 (broad) (CH_3)	1665, 1605, 1550
c	CD_3CN 8.84-8.31 (m, 4H, aromatic), 4.20-3.72 (m, 32H, $-OCH_2CH_2N-$)	164.1, 157.9, 155.1 (C=O, C=N), 139.5, 133.5, 132.5, 131.1 (aromatic), 67.2, 66.8, 66.4, 66.3 ($-OCH_2-$), 47.4, 47.0, 46.1, 46.0 ($-NCH_2-$)	1682, 1615 1570

[a] NMR spectra were recorded at 303°K. [b] The solubility is too low for ^{13}C-nmr to be determined. The compounds showed a significant decomposition in DMSO after 1 hour.

In comparison with other diacyl chlorides, phthaloyl chloride was found to react slowly with dialkylcyanamide. Thus its reaction with dimethylcyanamide in the presence of antimony pentachloride proceeded slowly (22 hours) and gave a low yield (46%) of the corresponding bis-1,3,5-oxadiazinium salt **5a**. The reaction can be enhanced by heating the reaction mixture under reflux in dichloroethane (10 hours) with little improvement in the yield (58%). On the other hand, the reaction of phthaloyl chloride with diisopropylcyanamide in the presence of antimony pentachloride failed to proceed under the reaction condition. The slowness or the failure of the reaction of phthaloyl chloride could be attributed to steric hindrance in the product. Terephthaloyl chloride reacts normally with dialkylcyanamides to give good yields of the corresponding products **5b-c**.



5a



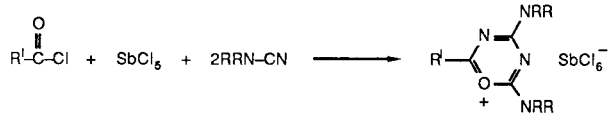
5b R = $(CH_3)_2CH-$
5c R = $-(CH_2)_2O(CH_2)_2-$

All new products were characterized by ir, ^{1}H-nmr, ^{13}C-nmr spectroscopy and elemental analysis. Despite the low solubility of these salts in most polar solvents, ^{1}H-nmr spectra of these compounds have been recorded. However, ^{13}C-nmr spectra could not be recorded for some compounds due to their low solubilities. In general, ^{13}C-nmr

spectra of these salts exhibit characteristic signals between 173-155 ppm for the aromatic heterocyclic ring carbons. The ^{1}H-nmr, ^{13}C-nmr and ir data for bis-1,3,5-oxadiazinium salts are presented in Table 1.

It is worth mentioning that the reaction of acyl chloride with dialkylcyanamide, without Lewis acids, has been previously reported [6]. However, the reaction proceeded only under drastic conditions and gave low yields of 1,3,5-oxadiazinium salts. We have found that the above reaction is greatly enhanced by the use of Lewis acids. Thus, acetyl chloride was found to react at -20° with dimethylcyanamide in the presence of antimony pentachloride to give an

Scheme 2



6a-g

Compound No.	R^1	R
6a	CH_3–	CH_3–
b	C_6H_5–	CH_3–
c	**p** -$O_2NC_6H_4$–	-$(CH_2)_2$-O-$(CH_2)_2$
d	**m** -$CH_3OC_6H_4$–	CH_3–
e	**p** -$CH_3OC_6H_4$–	-$(CH_2)_2$-O-$(CH_2)_2$
f	α -$C_{10}H_7$–	$(CH_3)_2CH$–
g	α -$C_{10}H_7$–	CH_3–

Table 2

Spectral Data of Substituted-1,3,5-Oxadiazinium Salts **6a-g**

Compound No.	^{1}H NMR [a] Solvent, δ	^{13}C NMR [a]	IR (cm^{-1}) KBr disc
6a	CD_3CN 3.33 (s, 3H, NCH_3), 3.27 (s, 3H, NCH_3), 3.21 (s, 3H, NCH_3), 3.16 (s, 3H, NCH_3), 2.45 (s, 3H, CH_3)	[b]	1700, 1650, 1595
c	DMSO-d_6 8.49 (d, 4H, J = 4.0 Hz, aromatic), 3.52 (s, 3H, CH_3), 3.38 (s, 3H, CH_3), 3.37 (s, 3H, CH_3), 3.32 (s, 3H, CH_3)	[b]	1690, 1600, 1520
d	CD_3CN 8.12-7.26 (m, 4H, aromatic), 3.90, 3.88 (two singlets, 3H, -OCH_3), 3.47, 3.45, 3.34, 3.32, 3.31, 3.29 (singlets, 12H, -NCH_3) [c]	173.2, 171.7, 164.7 158.8, 156.9, 135.3, 131.6, 131.0, 129.1, 123.8, 122.8, 122.3, (C=O, C=N, and aromatic), 56.6, 56.4 (OCH_3), 39.1, 38.7, 38.6, 38.2, 37.7, 37.4 (NCH_3) [c]	1695, 1615, (broad)
e	CD_3CN/DMSO-d_6 (1:1) 8.28 (d, 2H, J = 9.0 Hz, aromatic), 7.16 (d, 2H, J = 9.0 Hz, aromatic), 4.16-3.75 (m, 16H, -OCH_2CH_2N-), 3.94 (s, 3H, -OCH_3)	[b]	1675, 1575, (broad)
f	CD_3CN/DMSO-d_6 (1:1) 8.97 (d, 1H, J= 8.5 Hz), 8.42 (d, 1H, J = 8.0 Hz), 8.37 (d, 1H, J = 8.0 Hz), 8.12 (d, 1H, J = 8.0 Hz), 7.83-7.60 (m, 3H) aromatic, 3.48 (s, 3H, CH_3), 3.38 (s, 3H, CH_3), 3.31 (s, 3H, CH_3), 3.30 (s, 3H, CH_3)	163.8, 158.1, 156.3 (C=O, C=N), 136.9, 134.1, 132.9, 132.7, 130.6, 129.8, 129.4, 128.9, 127.5, 125.4 (aromatic), 38.3, 38.0, 37.4, 36.8 (CH_3)	1690, 1600, (broad)
g	CD_3CN 8.79 (d, 1H, J = 8.5 Hz), 8.29 (d, 1H, J = 8.0 Hz), 8.27 (d, 1H, J = 8.0 Hz), 8.08 (d, 1H, J = 8.0 Hz), 7.80-7.66 (m, 3H) aromatic, 4.66 (m, 2H, CH), 4.28 (m, 2H, CH), 1.56-1.41 (m, 24H, $(CH_3)_2CH$)	164.6, 157.7, 156.0 (C=O, C=N), 136.4 134.7, 131.9, 130.8, 130.1, 129.5, 128.1, 126.0, 125.7, 125.4, (aromatic), 50.4, 50.3, 50.2, 49.2 (CH), 21.2, 20.9, 20.1, 19.8 (CH_3)	1660, 1600, 1550

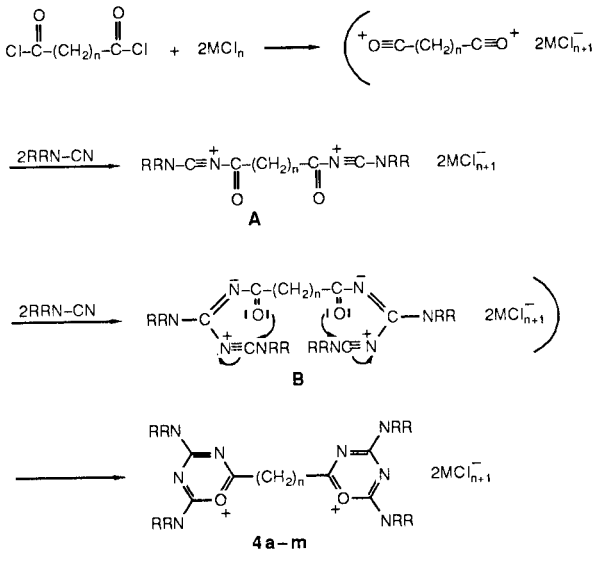
[a] NMR spectra were recorded at 303°K. [b] Footnote [b], Table 1. [c] According to the nmr spectra the substance is a mixture of two regioisomers.

excellent yield of (**6a**). The details of the Lewis-acid promoted reactions of acyl chlorides with dialkylcyanamides are presented in Scheme 2. Table 2 summarized the ir, ^{1}H-nmr and ^{13}C-nmr spectral data of compounds **6a-g**.

Mechanism.

The Lewis acid promoted reaction of diacyl chlorides with dialkylcyanamides is believed to proceed *via* a stepwise cycloaddition mechanism, Scheme 3. The addition of each acylium unit of the substrate into one equivalent of cyanamide yields a nitrilium salt intermediate **A**. Intermediate **A** reacts further with two equivalents of dialkylcyanamide to afford intermediate **B**. The latter intermediate undergoes cyclization to give the products **4a-m** and **5a-c**. The driving force behind the cyclization is believed to be the formation of the aromatic 1,3,5-oxadiazinium moieties in the products.

Scheme 3



Evidence to support the involvement of the acylium salt in the above reaction stems from the fact that the addition of the Lewis acid to the acyl chloride solution in dichloro methane leads to a precipitate formation of the acylium salts. In addition, ir spectroscopy at this stage reveals the existence of this intermediate by exhibiting strong absorption bands between 2200-2300 cm^{-1} characteristic of $-C\equiv{}^{+}O$ unit.

In the reaction of aromatic acyl chlorides with dialkylcyanamides, it has been observed that the substituent on the ring exerts a great influence on the rate of the reaction. Thus, electron-releasing substituent, such as a methoxy group, strongly enhances the reaction whereas electron-withdrawing substituent, such as a nitro group strongly slows it down. The above observation strongly supports the intermediacy of the acylium salt in the above reaction.

EXPERIMENTAL

Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Infrared spectra were recorded on a Pye-Unicam Sp3-300 spectrophotometer. The ^{1}H-nmr spectra were recorded on a Bruker MW-250 MHz spectrometer and are reported in δ values with tetramethylsilane as the internal standard. The ^{13}C-nmr spectra were recorded on Bruker MW-63 MHz. Elemental analysis was performed at M-H-W Laboratories, Phoenix, Arizona.

Materials.

Absolute solvents were obtained following literature procedures [7]. Acyl chlorides, diacyl chlorides and dialkylcyanamides are of guaranteed grade and are commercially available.

General Procedure for the Preparation of Compounds **4a-m** and **5a-c**.

To the diacyl chloride (5.00 mmoles) in absolute dichloromethane (10 ml) was added dropwise at -20° a solution of the Lewis acid (10.00 mmoles) in absolute dichloromethane (10 ml) followed by a solution of the dialkylcyanamide (20.00 mmoles) in absolute dichloromethane (10 ml). The reaction mixture was slowly warmed to +25°, and stirred for a few hours at this temperature. When the reaction was complete [8], the product was precipitated by the slow addition of absolute diethyl ether (50 ml). Recrystallization from hot acetonitrile afforded the crystalline product.

2,2'-bis[4,6-bis(diisopropylamino)-1,3,5-oxadiazinyl]diylium bis-Hexachloroantimonate **4a**.

Stirring at room temperature for 5 hours, provided yellow needles, yield 4.18 g (68%), mp 215-216° dec.

Anal. Calcd. for $C_{30}H_{56}N_8O_2{\cdot}2SbCl_6$ (MW, 1229.7): C, 29.30; H, 4.59; N, 9.11. Found: C, 29.42; H, 4.69; N, 9.11.

1,2-Ethylene bis[4,6-bis(diisopropylamino)-1,3,5-oxadiazene-2-yl-1-ium] bis-Hexachloroantimonate **4b**.

Stirring at room temperature for 3 hours, pale yellow needles were obtained, yield 5.66 g (90%), mp 159-161°.

Anal. Calcd. for $C_{32}H_{60}N_8O_2{\cdot}2SbCl_6$ (MW, 1257.8): C, 30.56; H, 4.81; N, 8.91. Found: C, 30.58; H, 4.87; N, 8.87.

1,2-Ethylene bis [4,6-bis morpholino-1,3,5-oxadiazene-2-yl-1-ium] bis-Hexachloroantimonate **4c**.

Stirring at room temperature for 3 hours, a yellow powder was obtained, yield 5.10 g (85%), mp 172-175°.

Anal. Calcd. for $C_{24}H_{36}N_8O_6{\cdot}2SbCl_6$ (MW, 1201.5): C, 23.99; H, 3.02; N, 9.32. Found: C, 24.45; H, 3.14; N, 9.57.

1,2-Ethylene bis[4,6-bis morpholino-1,3,5-oxadiazene-2-yl-1-ium] bis-Pentachlorostannate **4d**.

Stirring at room temperature for 4 hours, a white powder was obtained, yield 4.14 g (78%), mp 168-172° dec.

Anal. Calcd. for $C_{24}H_{36}N_8O_6{\cdot}2SnCl_5$ (MW, 1062.3): C, 27.13; H, 3.42; N, 10.55. Found: C, 27.29; H, 3.66; N, 10.78.

1,4-Butylene bis[4,6-bis(dimethylamino)-1,3,5-oxadiazene-2-yl-1-ium] bis-Hexachloroantimonate **4e**.

Stirring at room temperature for 2 hours, pale yellow needles were obtained, yield 3.98 g (75%), mp 202-204°.

Anal. Calcd. for $C_{18}H_{32}N_8O_2{\cdot}2SbCl_6$ (MW, 1061): C, 20.36; H, 3.02; N, 10.56. Found: C, 20.44; H, 3.18; N, 10.70.

1,4-Butylene bis[4,6-bis(diisopropylamino)-1,3,5-oxadiazene-2-yl-1-ium] bis-Hexachloroantimonate **4f**.

Stirring at room temperature for 3 hours, pale yellow needles were obtained, yield 5.59 g (87%), mp 205-206° dec.

Anal. Calcd. for $C_{34}H_{64}N_8O_2{\cdot}2SbCl_6$ (MW, 1285): C, 31.75; H, 4.98; N, 8.72. Found: C, 31.66; H, 5.04; N, 8.62.

1,4-Butylene bis[4,6-bis(diisopropylamino)-1,3,5-oxadiazene-2-yl-1-ium] bis-Tetrachloroferrate **4g**.

Stirring at room temperature for 3 hours, yellow needles were obtained, yield 4.25 g (84%), mp 166-169° dec.

Anal. Calcd. for $C_{34}H_{64}N_8O_2 \cdot 2FeCl_4$ (MW, 1011.4): C, 40.34; H, 6.33; N, 11.07. Found: C, 40.53; H, 6.44; N, 11.11.

1,4-Butylene bis[4,6-bis morpholino-1,3,5-oxadiazene-2-yl-1-ium] bis-Hexachloroantimonate **4h**.

Stirring at room temperature for 2 hours, yellow needles were obtained, yield 5.10 g (83%), mp 166-168°.

Anal. Calcd. for $C_{26}H_{40}N_8O_6 \cdot 2SbCl_6$ (MW, 1229.6): C, 25.40; H, 3.28; N, 9.11. Found: C, 25.45; H, 3.52; N, 9.29.

1,8-Octylene bis[4,6-bis(dimethylamino)-1,3,5-oxadiazene-2-yl-1-ium] bis-Hexachloroantimonate **4i**.

Stirring at room temperature for 3 hours, a pale yellow powder was obtained, yield 4.36 g (78%), mp 179-181°.

Anal. Calcd. for $C_{22}H_{40}N_8O_2 \cdot 2SbCl_6$ (MW, 1117.5): C, 23.64; H, 3.61; N, 10.03. Found: C, 23.77; H, 3.48; N, 9.97.

1,8-Octylene bis[4,6-bis(diisopropylamino)-1,3,5-oxadiazene-2-yl-1-ium] bis-Hexachloroantimonate **4j**.

Stirring at room temperature for 3 hours, a pale yellow powder was obtained, yield 5.90 g (88%), mp 202-203° dec.

Anal. Calcd. for $C_{38}H_{72}N_8O_2 \cdot 2SbCl_6$ (MW, 1341): C, 34.00; H, 5.37; N, 8.35. Found: C, 34.02; H, 5.46; N, 8.36.

1,8-Octylene bis[4,6-bis(diisopropylamino)-1,3,5-oxadiazene-2-yl-1-ium] bis-Tetrachloroferrate **4k**.

Stirring at room temperature for 4 hours, yellow needles were obtained, yield 4.91 g (92%), mp 193-195° dec.

Anal. Calcd. for $C_{38}H_{72}N_8O_2 \cdot 2FeCl_4$ (MW, 1067.4): C, 42.72; H, 6.74; N, 10.49. Found: C, 42.93; H, 6.81; N, 10.63.

1,8-Octylene bis[4,6-bis(diisopropylamino)-1,3,5-oxadiazene-2-yl-1-ium] bis-Pentachlorostannate **4l**.

Stirring at room temperature for 4 hours, a white powder was obtained, yield 5.0 g (83%), mp 202-205° dec.

Anal. Calcd. for $C_{38}H_{72}N_8O_2 \cdot 2SnCl_5$ (MW, 1202.8): C, 37.95; H, 6.03; N, 9.32. Found: C, 37.64; H, 6.21; N, 9.61.

1,8-Octylene bis[4,6-bismorpholino-1,3,5-oxadiazene-2-yl-1-ium] bis-Hexachloroantimonate **4m**.

Stirring at room temperature for 3 hours, yellow prisms were obtained, yield 4.50 g (70%), mp 180-184° dec.

Anal. Calcd. for $C_{30}H_{48}N_8O_6 \cdot 2SbCl_6$ (MW, 1285.7): C, 28.03; H, 3.87; N, 8.71. Found: C, 28.29; H, 3.76; N, 8.83.

1,2-Phenylene bis[4,6-bis(dimethylamino)-1,3,5-oxadiazene-2-yl-1-ium] bis-Hexachloroantimonate **5a**.

Stirring at room temperature for 22 hours, an orange powder was obtained, yield 2.49 g (46%), mp 145-147° dec.

Anal. Calcd. for $C_{20}H_{28}N_8O_2 \cdot 2SbCl_6$ (MW, 1081.5): C, 22.21; H, 2.61; N, 10.37. Found: C, 22.25; H, 2.81; N, 10.31.

1,4-Phenylene bis[4,6-bis(diisopropylamino)-1,3,5-oxadiazene-2-yl-1-ium] bis-Hexachloroantimonate **5b**.

Stirring at room temperature for 8 hours, a pale yellow powder was obtained, yield 4.90 g (75%), mp 232-235° dec.

Anal. Calcd. for $C_{36}H_{60}N_8O_2 \cdot 2SbCl_6$ (MW, 1305.8): C, 33.11; H, 4.63; N, 8.58. Found: C, 33.40; H, 4.39; N, 8.52.

1,4-Phenylene bis[4,6-bismorpholino-1,3,5-oxadiazene-2-yl-1-ium] bis-Hexachloroantimonate **5c**.

Stirring at room temperature for 3 hours, a yellow powder was obtained, yield 4.69 g (75%), mp 193-195° dec.

Anal. Calcd. for $C_{28}H_{38}N_8O_6 \cdot 2SbCl_6$ (MW, 1249.5): C, 26.91; H, 2.90; N, 8.97. Found: C, 26.69; H, 3.21; N, 9.21.

General Procedure for the Preparation of Compounds **6a-g**.

The same procedure as in compounds **4a-m**, except that 5.00 mmoles of the Lewis acid and 10.00 mmoles of cyanamide were added.

2,4-bis(dimethylamino)-6-methyl-1,3,5-oxadiazinium Hexachloroantimonate **6a**.

Stirring at room temperature for 3 hours, yellow prisms were obtained, yield 2.35 g (91%), mp 123-126° dec.

Anal. Calcd. for $C_7H_{12}N_4O \cdot SbCl_6$ (MW, 517.5): C, 18.55; H, 2.90; N, 10.83. Found: C, 18.79; H, 3.09; N, 10.97.

2,4-Bis(dimethylamino)-6-phenyl-1,3,5-oxadizinium Hexachloroantimonate **6b**.

Stirring at room temperature for 3 hours, yellow prisms were obtained, yield 3.46 g (85%), mp 254-258° dec, lit [9] 255-261° dec.

2,4-Bis(dimethylamino)-6-(*p*-nitrophenyl)-1,3,5-oxadiazinium Hexachloroantimonate **6c**.

Stirring at room temperature for 6 hours, pale yellow needles were obtained, yield 1.81 g (58%), mp 245-247°.

Anal. Calcd. for $C_{13}H_{16}N_5O_3 \cdot SbCl_6$ (MW, 624.7): C, 24.99; H, 2.58; N, 11.21. Found: C, 25.03; H, 2.60; N, 11.30.

2,4-Bis(dimethylamino)-6-(*m*-methoxyphenyl)-1,3,5-oxadiazinium Hexachloroantimonate **6d**.

Stirring at room temperature for 2 hours, orange needles were obtained, yield 2.59 g (85%), mp 230-232°.

Anal. Calcd. for $C_{14}H_{19}N_4O_2 \cdot SbCl_6$ (MW, 609.8): C, 27.57; H, 3.21; N, 9.19. Found: C, 27.38; H, 3.30; N, 9.36.

2,4-Morpholino-6-(*p*-methoxyphenyl)-1,3,5-oxadiazinium Hexachloroantimonate **6e**.

Stirring at room temperature for 2 hours, yellow prisms were obtained, yield 3.02 g (87%), mp 219-221° dec.

Anal. Calcd. for $C_{18}H_{23}N_4O_4 \cdot SbCl_6$ (MW, 693.9): C, 31.16; H, 3.34; N, 8.08. Found: C, 31.27; H, 3.41; N, 8.14.

2,4-Bis(diisopropylamino)-6-(α-naphthyl)-1,3,5-oxadiazinium Hexachloroantimonate **6f**.

Stirring at room temperature for 4 hours, orange needles were obtained, yield 3.12 g (84%), mp 235-237° dec.

Anal. Calcd. for $C_{25}H_{35}N_4O \cdot SbCl_6$ (MW, 742.1): C, 40.47; H, 4.75; N, 7.55. Found: C, 40.57; H, 4.84; N, 7.58.

2,4-Bis(dimethylamino)-6-(α-naphthyl)-1,3,5-oxadiazinium Hexachloroantimonate **6g**.

Stirring at room temperature for 5 hours, orange needles were obtained, yield 2.45 g (78%), mp 163-164°.

Anal. Calcd. for $C_{17}H_{19}N_4O \cdot SbCl_6$ (MW, 629.9): C, 32.42; H, 3.04; N, 8.90. Found: C, 32.77; H, 3.16; N, 9.10.

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