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On the Reaction of Acylium Salts with Isocyanates

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Abstract. Alkyl isocyanates (**3**) react with acylium salts (**2**) in a 2:1 ratio to furnish 3,4-dihydro-2,4-dioxo-2*H*-1,3,5-oxadiazinium salts **4**. These cyclic N-acyliminium salts are decomposed with catalytic amounts of water to give either oxadiazinium salts **5** or pyrimidinium salts **7**. With aqueous base compounds **4** are transformed into acylureas **6**. Hetero substituted open chain N-acyliminium salts (**8a**,**11c**,**12c**,**13f**,**15g**,**16a**) are produced from **4** by treatment with heteronucleophiles such as methanol, p-anisidine, p-cresol, thiophenol, 1,3-dimethylurea, or benzohydrazide, respectively. Excess of nucleophile furnishes further degradation products of **4**, e.g. oxonium salts (**9a**) and iminium salts (**14f**).

Isocyanates are best known for their electrophilic properties. For instance, addition of amines to isocyanates affords ureas while addition of alcohols provides urethanes. The fact that isocyanates are moderately strong nucleophiles seems to have found much less recognition. In a comprehensive review on the chemistry of isocyanates [1] their nucleophilic properties have not been mentioned at all [2]. Recently, we described reactions of isocyanates with α-chlorocarbenium ions [3, 4]. In addition to the references on sulfonation, nitrosation, and nitration of isocyanates given in these papers, a report on a reaction of (chloromethylene)dimethylammonium chloride (Vilsmeier-Arnold reagent) with phenyl isocyanate should be mentioned [5].

In a patent [6, 7] Hagemann described the acylation of isocyanates with phosgene to give bis(chlorocarbonyl)amines. Correspondingly, allophanoyl chlorides have been prepared by addition of carbamoyl chlorides to isocyanates in the presence of $SnCl_4$ [8]. Chlorosulfonyl isocyanate undergoes cycloaddition with isocyanates [9]. 1,3-Oxazinediones are formed from malonyl chloride with isocyanates in the presence of Lewis acids such as $SbCl_5$ [10]. The formation of acyl isocyanates from trimethylsilyl or trialkylstannyl isocyanates and acyl chlorides in the presence of catalytic amounts of $SnCl_4$ may well start with an N-acylation of the silyl, respectively the stannyl isocyanate [11, 12].

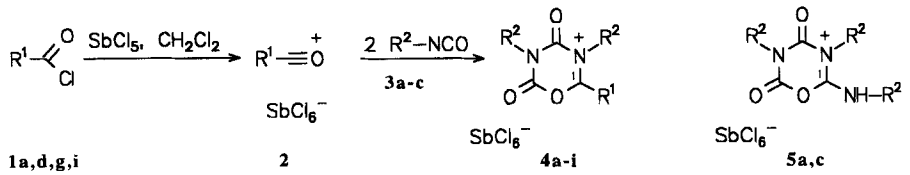
Here, we report the acylation of two molecules of an isocyanate **3** with one molecule of an acylium salt **2**, which leads to oxadiazinium salts **4** (Scheme 1). The acylium salts **2** were prepared in situ from acyl chlorides **1** and antimony pentachloride.

For example, antimony pentachloride was added to a cold (–30 °C) solution of acetyl chloride **1a** and two equivalents of methyl isocyanate **3a** in dichloromethane. After stirring for two hours at room temperature the moisture sensitive product **4a** was filtered off (90%). Correspondingly, the other heterocycles **4** were prepared.

No oxadiazinium salts could be obtained with phenyl isocyanate. All that could be isolated from reactions of the isocyanates **3a,c** with antimony pentachloride and oxalyl chloride or ethyl oxalyl chloride or methyl chloroformate, respectively, were the oxadiazinium salts **5a,c** in low yields. The mechanism for the formation of these compounds is not yet clear but traces of moisture seem to play a role.

As far as we know, cyclic N-acyliminium salts of type **4** have not been reported in the literature. Recently, Würthwein et al. described preparations and reactions of the first alkoxy substituted N-acyliminium salts [13]. Two mesoionic 1,3,5-oxadiazin-2,4-diones have been obtained by reaction of trisubstituted ureas with chlorocarbonyl isocyanate [14]. Furthermore, some heterocycles similar to **4** have been synthesized by Seng [15] and by us [4].

The constitutions of compounds **4, 5** were derived from the spectra (Table 1), the elemental analyses, and from some reactions with nucleophiles. For instance, the salt **5a** showed two singlets (3.36, 3.41 ppm in CD_3CN) and a doublet (3.16, coupled with J=4.3 Hz to NH (8.71 ppm)) for the N-methyl groups in the ^1H NMR spectrum. This rules out a symmetric 1,3,5-triazine structure. Correspondingly, in the ^{13}C NMR spectrum three lines



Schema 1

	R^1	R^2		R^1	R^2		R^1	R^2
a	Me	Me	**d**	Ph	Me	**g**	4-ClC_6H_4	Me
b	Me	Et	**e**	Ph	Et	**h**	4-ClC_6H_4	iPr
c	Me	iPr	**f**	Ph	iPr	**i**	4-MeC_6H_4	Me

Table 1. Selected NMR and IR Data for the New Compounds Prepared

Product	Molecular Formula[a)]	^1H NMR(CD_3CN/TMS)[b)] δ, J(Hz)	^{13}C NMR(CD_3CN/TMS)[b)] δ	IR(CH_2Cl_2)[c)] ν(cm^{-1})
4a	$C_6H_9Cl_6N_2O_3Sb$ (491.6)	3.03[d)], 3.48, 3.78(q,J=0.3)(CH_3)	22.3, 32.8, 36.6(CH_3), 140.7, 144.6, 182.2 (C=O,C=N)	1706,1632, 1571
4b	$C_8H_{13}Cl_6N_2O_3Sb$ (519.7)	1.32(t,J=7.2), 1.42(t,J=7.3), 3.01 (CH_3), 4.03(q,J=7.2), 4.29(q,J=7.3)	11.2, 12.0, 21.1(CH_3), 42.5, 46.7(CH_2), 140.1, 143.6, 181.2(C=O,C=N)[e)]	1698, 1617, 1567
4c	$C_{10}H_{17}Cl_6N_2O_3Sb$ (547.7)	1.48(d,J=6.9,6H), 1.63(d,J=6.8,6H), 3.02(CH_3), 4.83(sept,J=6.9), 4.91 (sept,J=6.8)(CH)[e)]	18.4, 19.3, 22.2(CH_3), 53.3, 60.8(CH), 139.9, 143.7, 181.3(C=O,C=N)[e)]	1783
4d	$C_{11}H_{11}Cl_6N_2O_3Sb$ (553.7)	3.57, 3.94(CH_3), 7.83-8.14(m, phenyl)[e)]	32.8, 39.9(CH_3), 122.6, 131.1, 132.8, 140.1 (phenyl), 141.2, 145.9, 174.6(C=O,C=N)[e)]	1846, 1777[f)]
4e	$C_{13}H_{15}Cl_6N_2O_3Sb$ (581.7)	1.39(t,J=7.3), 1.54 (t,J=7.3)(CH_3), 4.13(q,J=7.3), 4.39 (q,J=7.3)(CH_2), 7.79-8.09(m,phenyl)	11.8, 13.8(CH_3), 43.0, 49.6(CH_2), 123.0, 131.2, 131.3, 139.1(phenyl), 140.8, 144.9, 175.5(C=O,C=N)[e)]	1837, 1768
4f	$C_{15}H_{19}Cl_6N_2O_3Sb$ (609.8)	1.56(d,J=6.9), 1.69 (d,J=6.7)(CH_3), 4.95(sept,J=6.7), 5.01(sept,J=6.9) (CH), 7.80-8.07 (phenyl)	18.6, 20.4(CH_3), 53.7, 63.4(CH), 123.7, 130.9, 131.3, 138.7(phenyl), 140.2, 144.5, 175.9(C=O,C=N)	1856, 1775
4g	$C_{11}H_{10}Cl_7N_2O_3Sb$ (588.1)	3.57, 3.93(CH_3), 7.86(m), 8.10(m) (aryl)	32.9, 39.8(CH_3), 121.1, 131.6, 134.4, 146.6(aryl), 140.9, 145.7, 174.0(C=O,C=N)	1783, 1694, 1590
4h	$C_{15}H_{18}Cl_7N_2O_3Sb$ (644.2)	1.55(d,J=6.8), 1.69(d,J=6.7)(CH_3), 4.92(sept,J=6.7), 5.01(sept,J=6.8) (CH), 7.82-7.94(m, aryl)	18.6, 20.4(CH_3), 53.8, 63.6(CH), 122.2, 145.1 (i,p-C), 131.7, 132.8(m,o-C), 140.1, 144.4, 175.1(C=O,C=N)	1856, 1775
4i	$C_{12}H_{13}Cl_6N_2O_3Sb$ (567.7)	2.59, 3.55, 3.95(CH_3), 7.68(m), 8.04(m)(aryl)	22.7, 32.7, 39.9(CH_3), 119.5, 131.9, 133.3, 153.7(aryl), 141.2, 146.1, 174.1(C=O,C=N)	1856, 1779, 1682
5a	$C_6H_{10}Cl_6N_3O_3Sb$ (506.6)	3.16(d,J=4.3), 3.36, 3.41(CH_3), 8.71[d)](NH)	30.3, 31.9, 32.0(CH_3), 141.4, 146.5, 155.3 (C=O,C=N)	1856, 1771, 1679
5c	$C_{12}H_{22}Cl_6N_3O_3Sb$ (590.8)	1.39(d,J=6.6), 1.44(d,J=6.9), 1.54(d, J=6.7)(CH_3), 4.27(m), 4.33(sept,J= 6.7), 4.86(sept,J=6.9)(CH), 8.35[d)](NH)	18.9, 19.3, 21.6(CH_3), 50.2, 51.6, 54.7(CH), 140.4, 145.7, 153.9(C=O,C=N)	1852, 1837[g)], 1760, 1648
6a	$C_5H_{10}N_2O_2$ (130.2)	2.31, 2.86(d,J=4.6), 3.30(CH_3), 9.09[d)](NH)[h)]	25.5, 26.9, 32.4(CH_3), 155.5, 174.5(C=O)[h)]	3303, 1713, 1667[i)]
6g	$C_{10}H_{11}ClN_2O_2$ (226.7)	2.93(d,J=4.5), 3.20 (CH_3), 7.39-7.46(m, aryl), 8.97[d)](NH)h)	27.1, 35.8(CH_3), 128.2, 129.0, 134.4, 137.0(aryl), 155.8, 173.4(C=O)[h)]	3319, 1713, 1652[i)]
6h	$C_{14}H_{19}ClN_2O_2$ (282.8)	0.99(d,J=6.5), 1.42 (d,J=6.8)(CH_3), 3.84(m), 4.40(sept, J=6.8)(CH), 6.59[d)] (d,J=5.4,NH), 7.38–7.50(m,aryl)[h)]	20.8, 22.2(CH_3), 42.8, 50.2(CH), 128.0, 128.9, 135.4, 136.9, (aryl), 153.9, 171.0 (C=O)[h)]	1710, 1652[i)]

Table 1 Continued.

Product	Molecular Formula[a)]	^{1}H NMR(CD_3CN/TMS)[b)] δ, J(Hz)	^{13}C NMR(CD_3CN/TMS)[b)] δ	IR(CH_2Cl_2)[c)] ν(cm^{-1})
7a	$C_{10}H_{17}Cl_6N_4O_2Sb$ (559.8)	2.58, 2.79(d,J=4.6), 3.35, 3.44, 3.60(CH_3), 6.31[d)] (NH), 6.64(CH)	22.3, 28.0, 35.3, 37.3, 38.7(CH_3), 101.5 (CH), 150.3, 154.7, 163.1, 167.9 (C=O,C=N)	1733, 1609
8a	$C_6H_{13}Cl_6N_2O_2Sb$ (479.7)	2.60(d,J=0.8), 2.87 (d,J=4.8), 3.35(d, J=0.8), 4.34(CH_3), 6.91[d)](NH)[j)]	17.8, 28.5, 36.5, 62.9(CH_3), 151.4, 180.2(C=O,C=N)[j)]	3371, 1769, 1625
9a	$C_4H_9Cl_6O_2Sb$ (423.6)	2.79, 4.39[d)], 4.64[d)](CH_3)[e)]	20.6, 63.1[d)], 66.4[d)] (CH_3)[e)], 192.2(C)[e)]	1587[f)]
11c	$C_{16}H_{26}Cl_6N_3O_2Sb$ (626.9)	1.24(d,J=6.6), 1.45 (d,J=6.6), 2.18, 3.84 (CH_3), 3.88(m), 4.27(sept,J=6.6)(CH), 6.96[d)](d,J=6.9), 9.03[d)](NH), 7.04–7.27(m,aryl)	18.6, 20.4, 21.8, 45.3, 51.5[d)], 56.4, (CH_3,CH_2), 116.0, 128.0, 129.4, 149.4, 161.1, 164.0(aryl,C=O, C=N)	3368, 1743, 1617
12c	$C_{16}H_{25}Cl_6N_2O_2Sb$ (611.9)	1.27(d,J=6.6), 1.49 (d,J=6.7), 2.36, 2.41(CH_3), 3.96(m), 4.87(sept,J=6.7) (CH), 7.07[d)](NH), 7.19–7.42(m,aryl)	19.8, 20.3, 21.0, 21.7(CH_3), 45.9, 54.8 (CH), 121.3, 132.2, 140.1, 147.0, 149.9, 176.7(aryl,C=O,C=N)[e)]	3361, 1760, 1617
13f	$C_{20}H_{25}Cl_6N_2OSSb$ (676.0)	0.69[d)](d,J=6.5), 1.68(d,J=6.5)(CH_3), 3.46(m), 4.86(sept, J=6.5)(CH), 6.90[d)] (d,J=6.8,NH), 7.23–7.47(m,phenyl)	20.2, 21.2(CH_3), 45.5, 59.9(CH), 125.0, 129.4, 129.5, 130.2, 131.0, 132.8, 133.4, 137.0(phenyl), 147.3, 193.6(C=O,C=N)	3365, 1764
14f	$C_{16}H_{18}Cl_6NSSb$ (590.9)	1.55(d,J=6.5,CH_3), 4.54(m), 10.98[d)] (NH), 7.25–7.48 (phenyl)	21.0(CH_3), 54.7(CH), 125.7, 129.6, 130.3, 130.9, 131.0, 132.3, 134.3, 136.4(phenyl), 191.4(C=N)	3268, 1567[k)]
15g	$C_{13}H_{18}Cl_7N_4O_2Sb$ (632.2)	2.63(d,J=4.7,6H), 3.37(6H)(CH_3), 6.75[d)](NH), 7.70 (aryl)	28.1, 41.2(CH_3), 127.7, 131.1, 132.9, 142.3, 152.9, 170.2 (aryl,C=O,C=N)[e)]	3369, 1713[f)]
16a	$C_{12}H_{17}Cl_6N_4O_2Sb$ (583.7)	2.53, 2.84(d,J=4.2), 3.39(CH_3), 6.87[d)], 9.59[d)](NH), 7.53–7.91(phenyl)	17.4, 28.1, 37.5(CH_3), 128.8, 130.0, 131.5, 134.3(phenyl), 156.8, 167.3, 173.0(C=O,C=N)	3438, 1721, 1663, 1613[f)]

[a)] Satisfactory microanalyses obtained: C ±0.55, H ±0.71, N ±0.45%. [b)] Bruker AC 250 spectrometer; internal standard TMS; δ-scale; 295 K. [c)] Perkin-Elmer FTIR 1600. [d)] Broad. [e)] At 273 K. [f)] In nujol. [g)] Shoulder. [h)] In $CDCl_3$. [i)] In CCl_4. [j)] Contains a minor amount of a second isomer. [k)] In KBr.

for N-methyl (30.3, 31.9, 32.0 ppm in CD_3CN) and three signals for sp^2 hybridized carbon atoms (141.4, 146.5, 155.3 ppm) were found. Hydrolysis of compounds **4a,g,h** in the presence of a base afforded the acyl ureas **6a,g,h**.

No reaction could be achieved between **4a** and N,N-dimethylformamide or dimethylcyanamide or 1,3-dimethylurea, respectively. Instead, in all cases the pyrimidinium salt **7a** was isolated. The formation of **7a** can be understood assuming a water catalyzed decomposition of **4a** (Scheme 2). No reactions took place between **4a** and methyl thiocyanate, acetophenone, phenylacetylene, or 2,3-dimethyl-2-butene, respectively.

With one equivalent of methanol **4a** reacted to give the oxy substituted N-acyliminium salt **8a** [13]. With two equivalents of methanol the carbenium salt **9a** [16, 17] was formed. In the mother liquor 1,3-dimethylurea **10a** was identified (^{1}H NMR).

From the reaction of **4c** and p-anisidine the N-acylamidinium salt **11c** was isolated almost quantitatively. Similarly, with p-cresol the oxy substituted N-acyliminium salt **12c** was produced.

Compound **4f** was characterized by its reaction with thiophenol. At low temperature the thio substituted N-acyliminium salt **13f** was isolated, while in boiling (83 °C) 1,2-dichloroethane the iminium salt **14f** was formed.

With 1,3-dimethylurea the oxadiazinium salt **4g** afforded the diacylated amidinium salt **15g**. Finally, **4a** reacted with benzohydrazide to furnish the amidrazonium salt **16a**.

In conclusion, the reaction of alkyl isocyanates with acylium salts gives access to diverse types of N-acyliminium salts. Many interesting applications of N-acyliminium salts in natural product synthesis and preparative organic chemistry have been reported [18–22].

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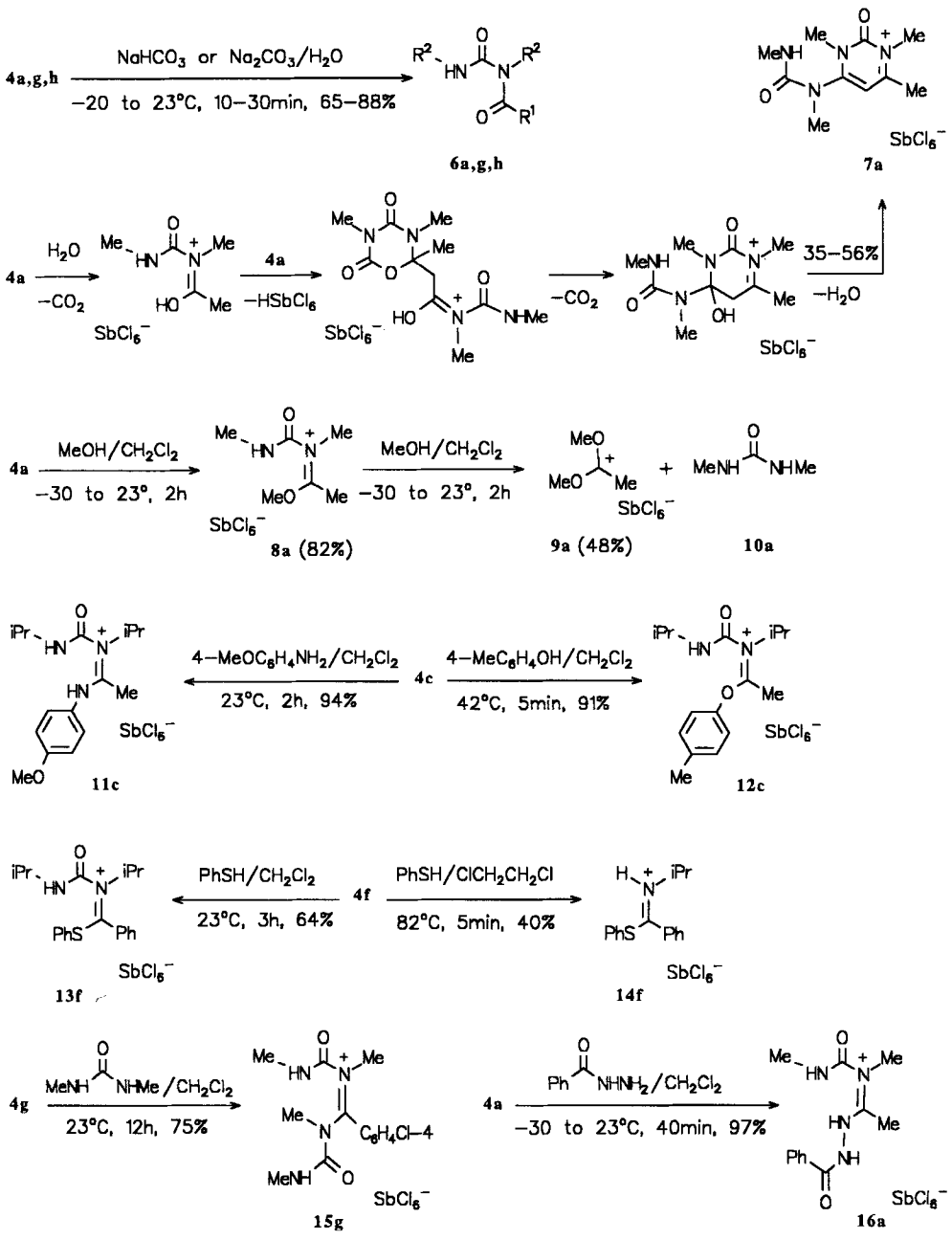
Experimental

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



Schema 2

3,4-Dihydro-2,4-dioxo-2*H*-1,3,5-oxadiazinium Hexachloroantimonates (4):
General Procedure

A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 ml) was added to a cold (–30 °C) solution of **1** (10 mmol) and **3** (20-22 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at –30 °C for 15 min and then at 23 °C for 2h. The moisture sensitive colorless product was filtered off.

3,4-Dihydro-3,5,6-trimethyl-2,4-dioxo-2H-1,3,5-oxadiazinium Hexachloroantimonate (**4a**)

From **1a** (0.79 g, 10 mmol) and **3a** (1.26 g, 22 mmol). Yield: 4.42 g (90%) of a moisture sensitive colorless powder; mp 175–178 °C (dec).

3,5-Diethyl-3,4-dihydro-6-methyl-2,4-dioxo-2H-1,3,5-oxadiazinium Hexachloroantimonate (**4b**)

From **1a** (0.79 g, 10 mmol) and **3b** (1.42 g, 20 mmol). Yield: 4.46 g (86%) of a moisture sensitive colorless powder; mp 133–137 °C (dec).

3,4-Dihydro-3,5-diisopropyl-6-methyl-2,4-dioxo-2H-1,3,5-oxadiazinium Hexachloroantimonate (**4c**)

From **1a** (0.79 g, 10 mmol) and **3c** (1.70 g, 20 mmol). Yield: 4.10 g (75%) of a moisture sensitive colorless powder; mp 90–93 °C (dec).

3,4-Dihydro-3,5-dimethyl-2,4-dioxo-6-phenyl-2H-1,3,5-oxadiazinium Hexachloroantimonate (**4d**)

From **1d** (1.41 g, 10 mmol) and **3a** (1.26 g, 22 mmol). Yield: 4.37 g (79%) of a very moisture sensitive pale yellow powder; mp 218–220 °C (dec).

3,5-Diethyl-3,4-dihydro-2,4-dioxo-6-phenyl-2H-1,3,5-oxadiazinium Hexachloroantimonate (**4e**)

From **1d** (1.41 g, 10 mmol) and **3b** (1.56 g, 22 mmol). Yield: 2.91 g (50%) of a very moisture sensitive colorless powder; mp 176–180 °C (dec).

3,4-Dihydro-3,5-diisopropyl-2,4-dioxo-6-phenyl-2H-1,3,5-oxadiazinium Hexachloroantimonate (**4f**)

From **1d** (1.41 g, 10 mmol) and **3c** (1.70 g, 20 mmol). Yield: 5.84 g (96%) of a moisture sensitive colorless powder; mp 180–183 °C (dec).

6-(4-Chlorophenyl)-3,4-dihydro-3,5-dimethyl-2,4-dioxo-2H-1,3,5-oxadiazinium Hexachloroantimonate (**4g**)

From **1g** (1.75 g, 10 mmol) and **3a** (1.26 g, 22 mmol). Yield: 5.35 g (81%) of a moisture sensitive colorless powder; mp 198–204 °C (dec).

6-(4-Chlorophenyl)-3,4-dihydro-3,5-diisopropyl-2,4-dioxo-2H-1,3,5-oxadiazinium Hexachloroantimonate (**4h**)

From **1g** (1.75 g, 10 mmol) and **3c** (1.70 g, 20 mmol). Yield: 3.97 g (62%) of a very moisture sensitive colorless powder; mp 111–113 °C (dec).

3,4-Dihydro-3,5-dimethyl-6-(4-methylphenyl)-2,4-dioxo-2H-1,3,5-oxadiazinium Hexachloroantimonate (**4i**)

From **1i** (1.55 g, 10 mmol) and **3a** (1.26 g, 22 mmol). Yield: 3.38 g (60%) of a moisture sensitive colorless powder; mp 174–176 °C (dec).

3,4-Dihydro-3,5-dimethyl-6-(methylamino)-2,4-dioxo-2H-1,3,5-oxadiazinium Hexachloroantimonate (**5a**)

From methyl chloroformate (0.95 g, 10 mmol) or oxalyl chloride (1.27 g, 10 mmol) and **3a** (1.26 g, 22 mmol). After stirring for 6h at 23 °C a colorless powder (0.58 g, 16%) was filtered off; mp 229–231 °C (dec). Evaporation of the mother liquor afforded a mixture of compounds containing **5a** (^{1}H NMR).

3,4-Dihydro-3,5-diisopropyl-6-(isopropylamino)-2,4-dioxo-2H-1,3,5-oxadiazinium Hexachloroantimonate (**5c**)

From ethyl oxalyl chloride (1.37 g, 10 mmol) and **3c** (1.70 g, 20 mmol). However, after stirring for 3h at 23 °C the solvent was evaporated and the residue (3.36 g) was crystallized at –15 °C from CH_2Cl_2(10 ml)/Et_2O(10 ml) to afford a colorless powder (1.39 g, 35%); mp 187–189 °C (dec).

1-Acetyl-1,3-dimethylurea (**6a**)

At –20 °C a solution of $NaHCO_3$ (5.88 g, 70 mmol) in H_2O (50 ml) was added to a suspension of **4a** (4.92 g, 10 mmol) in CH_2Cl_2 (50 ml). After stirring at 23 °C for 30 min the organic phase was separated and the aqueous phase was repeatedly extracted with CH_2Cl_2. Workup afforded a colorless oil (1.04 g, 80%)([23] colorless oil, [24] mp 51–52 °C).

1-(4-Chlorobenzoyl)-1,3-dimethylurea (**6g**)

From **4g** (5.88g, 10 mmol) as described for **6a**. Yield: 2.00 g (88%) of a colorless powder; mp 67–69 °C.

1-(4-Chlorobenzoyl)-1,3-diisopropylurea (**6h**)

A mixture of **4h** (3.22 g, 5 mmol) and Na_2CO_3 (2.12 g, 20 mmol) in H_2O (20 ml) was stirred for 10 min. A colorless precipitate was filtered off. Recrystallization from MeOH (10 ml) afforded colorless needles (0.92 g, 65%); mp 134–137 °C.

2,3-Dihydro-1,3,6-trimethyl-2-oxo-4-(1,3-dimethylureido)pyrimidinium Hexachloroantimonate (**7a**)

A solution of DMF (0.73 g, 10 mmol) or Me_2NCN (0.71 g, 10 mmol) or 1,3-dimethylurea (0.88 g, 10 mmol) in CH_2Cl_2 (25 ml) was added to a cold (–20 °C) suspension of **4a** (4.92 g, 10 mmol) in CH_2Cl_2 (25 ml). The resulting clear solution was stirred at 23 °C for 2h. Evaporation of the solvent and stirring the oily residue with $CHCl_3$ (25 ml) afforded a colorless powder (1.96–3.14 g, 35–56%); mp 167–169 °C (dec).

(1-Methoxyethylidene)methyl(methylcarbamoyl)ammonium Hexachloroantimonate (**8a**)

A solution of MeOH (0.32 g, 10 mmol) in CH_2Cl_2 (10 ml) was added to a cold (–30 °C) suspension of **4a** (4.92 g, 10 mmol) in CH_2Cl_2 (25 ml). After stirring at 23 °C for 2h the solvent was evaporated. The pale yellow residue was precipitated from CH_2Cl_2(10 ml)/MeCN(4 ml)/Et_2O(25 ml) to afford a colorless powder (2.94 g, 62%); mp 118–120 °C (dec).

1,1-Dimethoxyethylium Hexachloroantimonate (**9a**)

A solution of MeOH (0.65 g, 20 mmol) in CH_2Cl_2 (25 ml) was added at –30 °C to a cold (–30 °C) suspension of **4a** (4.92 g, 10 mmol) in CH_2Cl_2 (25 ml). The resulting clear solution was stirred at 23 °C for 2h. A very moisture sensitive colorless powder (2.03 g, 48%) was filtered off, for which a correct elemental analysis could not be obtained; mp 134–136 °C (dec). Evaporation of the solvent afforded a mixture of compounds consisting mainly of 1,3-dimethylurea **10a** (^{1}H NMR).

Isopropyl(isopropylcarbamoyl)[1-(4-methoxyanilino)ethylidene]ammonium Hexachloroantimonate (**11c**)

A solution of p-anisidine (1.23 g, 10 mmol) in CH_2Cl_2 (25 ml) was added at –30 °C to a suspension of **4c** (5.48 g, 10 mmol) in CH_2Cl_2 (25 ml). The clear blue solution was stirred at 23 °C for 2h. Evaporation of the solvent afforded a pink powder, which was precipitated from CH_2Cl_2/Et_2O to furnish a pink powder (5.14 g, 82%); mp 167–171 °C (dec).

Isopropyl(isopropylcarbamoyl)[1-(4-methylphenoxy)ethylidene]ammonium Hexachloroantimonate (**12c**)

A solution of p-cresol (1.08 g, 10 mmol) in CH_2Cl_2 (25 ml) was added to a suspension of **4c** (5.48 g, 10 mmol) in CH_2Cl_2 (25 ml). After boiling under reflux for 5 min the mixture became a clear reddish solution. Slow addition of Et_2O (20 ml) at –10 °C afforded a pale orange powder (5.56 g, 91%); mp 156–159 °C (dec).

Isopropyl(isopropylcarbamoyl)[phenyl(phenylthio)methylene]-ammonium Hexachloroantimonate (**13f**)

A solution of thiophenol (1.10 g, 10 mmol) in CH_2Cl_2 (25 ml) was added to a suspension of **4f** (6.10 g, 10 mmol) in CH_2Cl_2 (25 ml). After stirring at 23 °C for 3h the product was precipitated from the clear yellow solution by slow addition of Et_2O (100 ml). A colorless powder (4.33 g, 64%) was filtered off. Reprecipitation from MeCN (20 ml)/Et_2O(100 ml) afforded colorless crystals; mp 168–170 °C (dec).

Isopropyl[phenyl(phenylthio)methylene]ammonium Hexachloroantimonate (**14f**)

A solution of thiophenol (1.10 g, 10 mmol) in $ClCH_2CH_2Cl$ (25 ml) was added to a suspension of **4f** (6.10 g, 10 mmol) in $ClCH_2CH_2Cl$ (25 ml). After boiling under reflux for 5 min and cooling the solvent was evaporated and the residue was stirred in CH_2Cl_2 (10 ml) to afford a faint yellow powder (2.36 g, 40%); mp 167–169 °C (dec).

Methyl(methylcarbamoyl)[(1,3-dimethylureido)(4-chlorophenyl)methylene]ammonium Hexachloroantimonate (**15g**)

A solution of 1,3-dimethylurea (8.81 g, 10 mmol) in CH_2Cl_2 (25 ml) was added to a suspension of **4g** (5.88 g, 10 mmol) in CH_2Cl_2 (5.88 g, 10 mmol). Stirring at 23 °C for 12h, evaporation of the solvent, and stirring the residue under pentane (20 ml) afforded a colorless powder (4.74 g, 75%), which was reprecipitated from MeCN (20 ml)/Et_2O (60 ml) to give colorless fine crystals (3.54 g, 53%); mp 141–144 °C (dec).

[1-(2-Benzoylhydrazino)ethylidene]methyl(methylcarbamoyl)-ammonium Hexachloroantionate (**16a**)

A solution of benzhydrazide (1.36 g, 10 mmol) in CH_2Cl_2 (20 ml) was added to a cold (–30 °C) suspension of **4a** (4.92 g, 10 mmol) in CH_2Cl_2 (40 ml). After a few min **4a** dissolved and a colorless powder started to precipitate. Stirring was continued at –30 °C for 5 min and then at 23 °C for 30 min. Filtration afforded a colorless powder (5.66 g, 97%); mp 133–135 °C (dec).

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