On the Reaction of 1,3-Dichloro-2-azoniaallene Salts with Isocyanates and Carbodiimides

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Received 18 January 1995; revised 1 March 1995

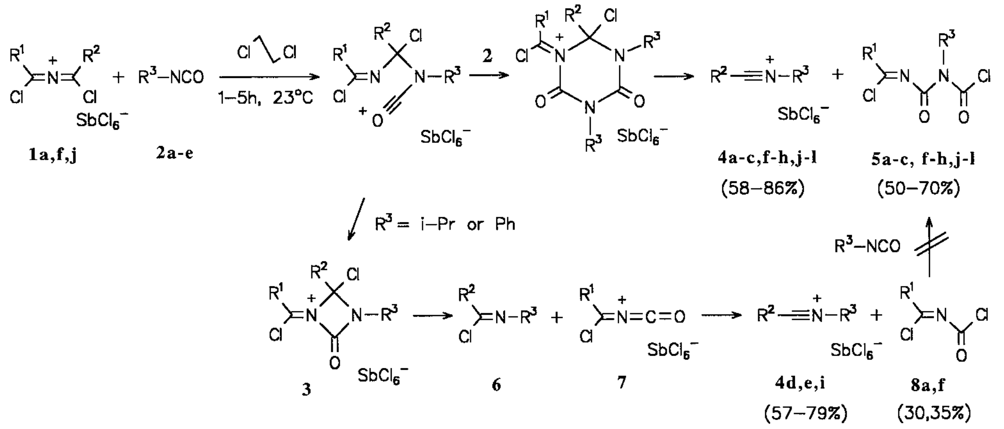
Dedicated to Professor Dr. H.-H. Brintzinger on occasion of his sixtieth birthday

1,3-Dichloro-2-azoniaallene salts **1** react with one or two equivalents of isocyanates **2** to afford nitrilium salts **4**, together with allophanoyl chlorides **5** or carbamoyl chlorides **8**. The chlorides **5** and **8** were characterized by their reactions with nitrogen nucleophiles (products **10–12**, **14**). With antimony pentachloride, the allophanoyl chlorides **5** cyclize to 2-chloro-substituted 1,3,5-oxadiazinium salts **13**. The chloro-substituted 2-azoniaallene salt **15** was obtained from the reaction of **8f** with a ketone in the presence of antimony pentachloride. The 1,3-diaryl-1,3-dichloro-2-azoniaallene salt **1f** adds to carbodiimides **16** to form labile 2,2-dichloro-1,3,5-triazinium salts **17**, which were characterized as derivatives **18–20**.

1,3-Dichloro-2-azoniaallene salts **1** without a stabilizing amino substituent[1] have only recently become available.[2,3] Compounds **1** are strong bifunctional electrophiles reacting with heteronucleophiles,[2-4] olefins, and acetylenes[5] to give heterocycles and open-chain compounds. Herein we report reactions of 2-azoniaallene salts **1** with isocyanates **2**. Although better known for their electrophilic properties,[6] isocyanates behave as *N*-nucleophiles against strong electrophiles such as α-chlorocarbenium ions.[7,8] Here we report that 2-azoniaallene salts **1** react in a quite different way with isocyanates as compared to the more conventional α-chlorocarbenium salts studied before. As far as we know, the reactions reported below are new.

The cumulenes **1a,f,j** readily reacted with two equivalents of an alkyl or aryl isocyanate **2** to furnish nitrilium salts **4** together with either allophanoyl chlorides **5** or carbamoyl chlorides **8**. Transformations of isocyanates into nitrilium salts seem to be unreported. The reaction can be recommended for the preparation of certain nitrilium salts **4**[9-11] as well as of the chlorides **5** or **8**. Only very few compounds **5** have been mentioned in the literature.[12] Thus, **5a** has been obtained from **8a** and methyl isocyanate in the presence of $SnCl_4$. On the other hand, preparations[13-18] and reactions[19-26] of carbamoyl chlorides **8** are well documented.

In a typical experiment, the allene salt **1a** was stirred at room temperature for one hour with two mol equivalents of methyl isocyanate. The analytically pure nitrilium salt **4a** precipitated from the solution and was filtered off (60%). Evaporation of the filtrate afforded **5a** as a moisture and thermally sensitive impure oil (60%), which in our hands decomposed during distillation (Lit.[12] bp 95°C/0.07 torr). Similarly, the nitrilium salts **4b,c,f–h,j–l** and the allophanoyl chlorides **5b,c,f–h,j–l** were obtained from **1a,f,j** with methyl, ethyl, and propyl isocyanate. Note that the attack of isocyanates on the allene salt **1j** with unequal substituents R^1 and R^2 proceeded with complete site selectivity (Scheme 1). Using 1 : 1 mixtures of **1** and the isocyanate, the products **4** and **5** were formed in lower yields. With excess of isocyanate (3 equiv) unreacted isocyanate was isolated besides **4** and **5**. However, even with excess (2 to 5 equiv) of isopropyl or phenyl isocyanate, the allenes **1a,f** reacted in 1 : 1 ratios to afford the nitrilium salts **4d, e, i** together with the carbamoyl chlorides **8a, f**. No reaction could be



1–15	R^1	R^2	R^3	1–15	R^1	R^2	R^3	1–15	R^1	R^2	R^3
a	Ph	Ph	Me	e	Ph	Ph	*i*-Pr	i	4-ClC_6H_4	4-ClC_6H_4	*i*-Pr
b	Ph	Ph	Et	f	4-ClC_6H_4	4-ClC_6H_4	Me	j	$Cl_2C{=}CCl$	4-MeC_6H_4	Me
c	Ph	Ph	Pr	g	4-ClC_6H_4	4-ClC_6H_4	Et	k	$Cl_2C{=}CCl$	4-MeC_6H_4	Et
d	Ph	Ph	Ph	h	4-ClC_6H_4	4-ClC_6H_4	Pr	l	$Cl_2C{=}CCl$	4-MeC_6H_4	Pr

Scheme 1

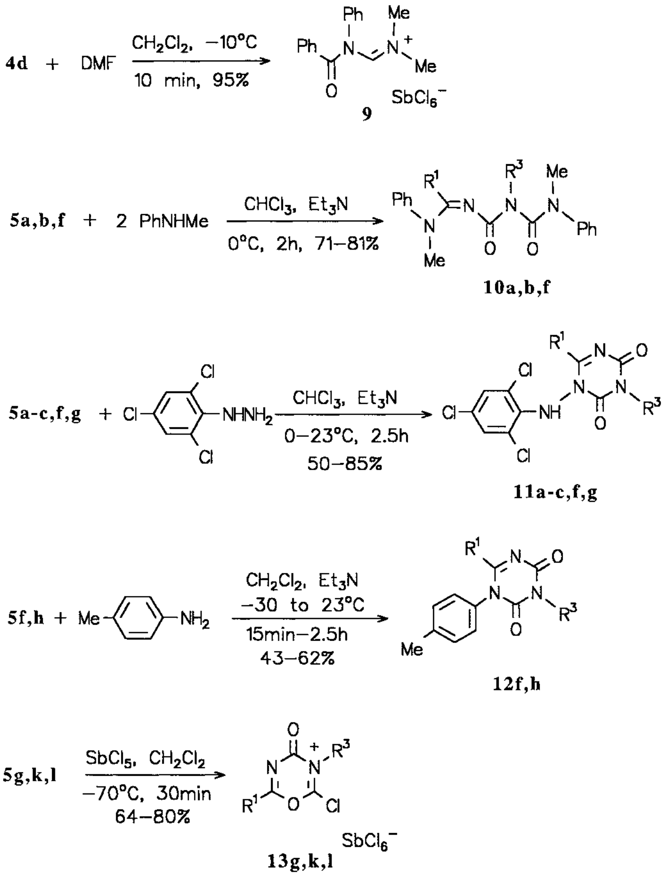
achieved between methyl isocyanate and 3-chloro-1-(dimethylamino)-3-(4-chlorophenyl)-2-azoniaallene hexachloroantimonate.

Several mechanisms for the reactions of the dichloroallenes **1** with isocyanates **2** can be envisaged. One proposal is shown in Scheme 1. The fact that with propyl isocyanate (**2c**) the chlorides **5** are formed, while with isopropyl isocyanate (**2e**) the carbamoyl chlorides **8** are produced points to steric effects. On addition of the imidoyl chloride **6a** to a solution of **7a**, prepared in situ from **8a** and antimony pentachloride, the nitrilium salt **4a** precipitated and **8a** was reformed. On the other hand, no reaction could be achieved between alkyl isocyanates and a mixture of **8a** and the nitrilium salt **4a**. It is unlikely, therefore, that compounds **5** are formed from **8**.

The carbamoyl chlorides **8** all show two very strong IR bands[14,15] for the stretching vibrations of C=N and C=O around $\nu = 1650$ and $1775\,\mathrm{cm}^{-1}$, while the allophanoyl chlorides **5** show three such bands around $\nu = 1660$, 1720 and $1770\,\mathrm{cm}^{-1}$ (CCl_4) (Table 1). Thus, the absorption at $\nu = 1720\,\mathrm{cm}^{-1}$ may be assigned to the urea carbonyl group of **5**. In the ^{13}C NMR spectra ($CDCl_3$), the C=N and C=O signals for compounds **8** were found at ca. $\delta = 148$ and 154 (Table 1). For the allophanoyl chlorides **5a–c, f–h**, three signals around $\delta = 148$, 149, and 157 were observed, while **5j–l** showed these signals at $\delta = 142$, 149, and 154 ppm. On the basis of these data, we tentatively assigned the signals at $\delta = 154$–157 to ClC=O, the resonances around $\delta = 148$, respectively at $\delta = 142$, to ClC=N, and the lines at $\delta = 149$ to NC(=O)N.

Most characteristic for the nitrilium salts **4** are IR absorptions around $\nu = 2350\,\mathrm{cm}^{-1}$ (Nujol) for C≡N. In the ^{13}C NMR spectra (CD_3CN), weak triplets around $\delta = 107$ with coupling constants of about 45 Hz are assigned to $^{13}C \equiv {}^{14}N$. Noteworthy are the rather high-field resonances for the ipso carbon atoms of the benzonitrilium salts (e.g. $\delta = 103.6$ for **4a**).[10] It is difficult to obtain NMR spectra from *N*-arylnitrilium salts such as **4d**. The solubility of **4d** in CD_2Cl_2 is low. In CD_3CN reaction with the solvent takes place. *N*-Arylnitrilium salts are known to undergo Meerwein quinazoline synthesis with nitriles.[27] Therefore, compound **4d** was characterized by its reaction with *N,N*-dimethylformamide to give the known formamidinium salt **9**.[9,28,29]

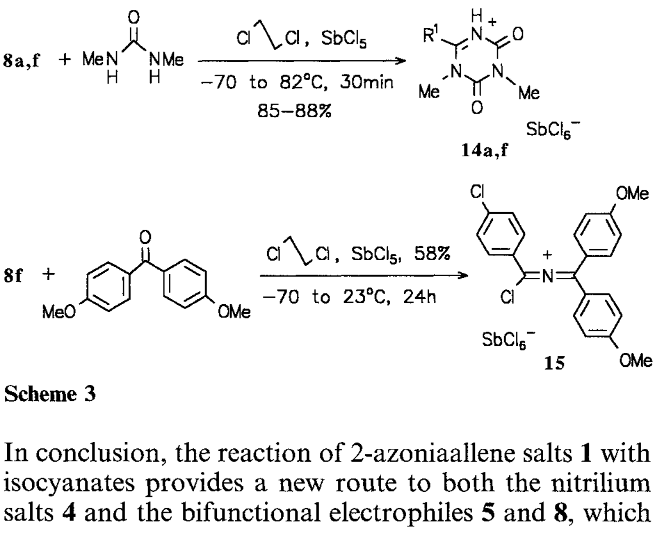
Since we were not able to obtain satisfactory elementary analyses for most of the allophanoyl chlorides **5**, these compounds were transformed into solid derivatives. With *N*-methylaniline, the biurets **10** were obtained, while 2,4,6-trichlorophenylhydrazine led to the hydrazides **11**. Reaction with *p*-toluidine afforded the triazines **12**. No crystalline derivatives could be obtained from the trichlorovinyl compounds **5j–l** with either amines, hydrazines, alcohols or water. With antimony pentachloride, the allophanoyl chlorides **5g, j–l** cyclized to the solid oxadiazinium salts **13g, j–l** (Scheme 2), although a correct elemental analysis could not be obtained for the rather unstable **13j**.



Scheme 2

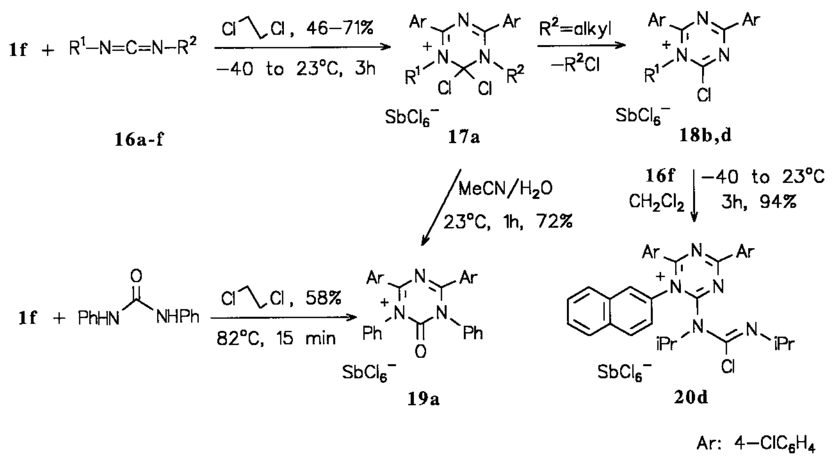
The carbamoyl chlorides **8a,f** were treated with 1,3-dimethylurea to furnish the triazinium salts **14a,f**. The site of the protonation is not known. Reaction of **8f** with antimony pentachloride and 4,4′-dimethoxybenzophenone afforded the 2-azoniaallene salt **15** (Scheme 3).[30]

The NMR and IR spectra (Table 1) as well as the elemental analyses are in agreement with the constitutions of compounds **9–15**. The formation of six-membered rings by reaction of the allophanoyl chlorides **5** with 2,4,6-trichlorophenylhydrazine was confirmed by an X-ray structural analysis of **11f**.[31]



Scheme 3

In conclusion, the reaction of 2-azoniaallene salts **1** with isocyanates provides a new route to both the nitrilium salts **4** and the bifunctional electrophiles **5** and **8**, which



16–20	R^1	R^2	16–20	R^1	R^2	16–20	R^1	R^2
a	Ph	Ph	c	Ph	*i*-Pr	e	Ph_2CH	Ph_2CH
b	Ph	Ph_2CH	d	β-naphthyl	Ph_2CH	f	*i*-Pr	*i*-Pr

Scheme 4

should find application for the preparation of heterocycles and less conventional open-chain compounds.

While isocyanates react with 1,3-dichloro-2-azoniaallene salts **1** as monovalent *N*-nucleophiles, carbodiimides **16** behave as divalent *N*-nucleophiles. Here we report a few reactions of the allene **1f** with carbodiimides **16** (Scheme 4).

With diphenylcarbodiimide (**16a**), the very moisture sensitive salt **17a** was formed. Similar reactive ortho ester type compounds have been obtained from the reaction of malonyl chlorides[32] or acylium salts[33] with carbodiimides. Hydrolysis of **17a** afforded the triazinium salt **19a**, which was independently prepared by condensation of **1f**, with 1,3-diphenylurea.

Salts **18b, d** were obtained by reaction of alkylarylcarbodiimides **16b, d** with **1f** via **17** by loss of alkyl chloride (NMR). Compounds **18** are strong electrophiles. For instance, **18d** reacted with diisopropyl carbodiimide **16f** to produce the adduct **20d**. With dialkyl carbodiimides **16e, f** the cumulene **1f** afforded mixtures of compounds, from which well defined products could not be obtained.

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

Reaction of Allene Salts 1 with Isocyanates 2; General Procedure: To a solution of **1**[3] (10 mmol) in $ClCH_2CH_2Cl$ (20 mL) a solution of **2** (20 mmol) in $ClCH_2CH_2Cl$ (10 mL) was added. After stirring at 23 °C for 1 h, the solvent was evaporated and the residue was stirred in CCl_4 (40 mL) for 1 h. Filtration afforded the nitrilium salt **4**. The solvent of the filtrate was removed, and the oily residue was stirred at − 20 °C for 1 h in pentane (50 mL). Filtration and evaporation of the solvent afforded **5**, or **8**, as a colorless oil. Attempts to distil compounds **5** resulted in partial or complete decomposition.

N-Methylbenzonitrilium Hexachloroantimonate (**4a**):

From **1a** (5.98 g, 10 mmol) and **2a** (1.14 g, 20 mmol). Yield: 2.72 g (60 %) of a pale brown powder; mp 203–205 °C (dec.) [Lit.[10] mp 203–206 °C (dec.)].

N-Ethylbenzonitrilium Hexachloroantimonate (**4b**):

From **1a** (5.98 g, 10 mmol) and **2b** (1.42 g, 20 mmol). Yield: 4.01 g (86 %) of a pale yellow powder; mp 180–183 °C (dec.) [Lit.[34] 172–174 °C (dec.)].

N-Propylbenzonitrilium Hexachloroantimonate (**4c**):

From **1a** (5.98 g, 10 mmol) and **2c** (1.70 g, 20 mmol). However, the reaction mixture was stirred at 23 °C for 5 h. Reprecipitation of **4c** at − 20 °C from CH_2Cl_2 (20 mL)/Et_2O (60 mL) afforded a pale brown powder (2.79 g, 58 %); mp 150–153 °C (dec.).

N-Phenylbenzonitrilium Hexachloroantimonate (**4d**):

From **1a** (5.98 g, 10 mmol) and **2d** (5.96 g, 50 mmol), however in CH_2Cl_2 (20 mL) as solvent. The reaction mixture was stirred at 23 °C for 3 h. A pale brown powder (2.95 g, 57 %) was filtered off; mp 230–233 °C (dec.) [Lit.[9] mp 234–238 °C (dec.)].

The filtrate was evaporated under reduced pressure and the residue was dissolved in CCl_4 (50 mL). Filtration and evaporation of the solvent afforded a yellow oil, which according to the NMR spectra consisted mainly of **8a**.

N-Isopropylbenzonitrilium Hexachloroantimonate (**4e**):

From **1a** (5.98 g, 10 mmol) and **2e** (1.70 g, 20 mmol) as described for **4c**. Yield: 3.80 g (79 %) of a colorless powder; mp 135–138 °C (dec.) (Lit.[34] mp 138 °C).

4-Chloro-N-methylbenzonitrilium Hexachloroantimonate (**4f**):

From **1f** (6.67 g, 10 mmol) and **2a** (1.14 g, 20 mmol). Crystallization at − 20 °C from MeCN (10 mL)/CH_2Cl_2 (10 mL) afforded colorless cubes (3.31 g, 68 %); mp 202–205 °C (dec.) [Lit.[10] mp 216–218 °C (dec.)].

4-Chloro-N-ethylbenzonitrilium Hexachloroantimonate (**4g**):

From **1f** (6.67 g, 10 mmol) and **2b** (1.42 g, 20 mmol). Precipitation from CH_2Cl_2 (20 mL)/Et_2O (60 mL) afforded a pale-brown powder (3.46 g, 69 %); mp 148–151 °C (dec.).

4-Chloro-N-propylbenzonitrilium Hexachloroantimonate (**4h**):

From **1f** (6.67 g, 10 mmol) and **2c** (1.70 g, 20 mmol) as described for **4f**. Yield: 4.12 g (80 %) of a yellowish powder; mp 110–115 °C (dec.).

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

Product	^{1}H NMR (CD_3CN/TMS)[b] δ, *J* (Hz)	^{13}C NMR (CD_3CN/TMS)[b] δ	IR (Nujol)[c] ν (cm^{-1})
4a	4.09[d] (CH_3), 7.77–8.22 (m, phenyl)[e]	32.9 (t, $J = 7$, CH_3), 106.9 (t, $^1J_{CN} = 48.2$, $C\equiv N$), 103.6 (t, $^3J_{CH} = 9$, *i*-C), 131.0 (q, $^1J_{CH} = 168$, $^3J_{CH} = 8$, *m*-C), 136.1[d] (m, $^1J_{CH} = 170.3$, $^3J_{CH} = 7$, *o*-C), 139.5 (m, $^1J_{CH} = 167.4$, $^3J_{CH} = 8$, *p*-C)[e,f]	2354
4b	1.70 (t, $J = 7.2$, CH_3), 4.48 (q, $J = 7.2$, CH_2), 7.76–8.26 (m, phenyl)	13.0 (CH_3), 43.8[d] (CH_2), 106.9 (t, $J = 46.3$, $C\equiv N$), 103.6 (*i*-C), 130.9 (*m*-C), 136.3 (*o*-C), 139.5 (*p*-C)	2350
4c	1.17 (t, $J = 7.3$, CH_3), 2.13 (m), 4.41 (t, $J = 6.7$), CH_2), 7.77–8.27 (m, phenyl)	11.3 (CH_3), 21.4, 49.6[d], (CH_2), 107.6 (t, $J = 46.3$, $C\equiv N$), 103.6 (i-C), 130.9 (*m*-C), 136.4 (*o*-C), 139.5 (*p*-C)	2346
4d	[g]	[g]	2261
4e	1.75 (d, $J = 6.6$, CH_3), 4.90 (sept, $J = 6.6$, CH), 7.76–8.27 (phenyl)	21.2 (CH_3), 55.1 (CH), 107.0 (t, $J = 43.3$, $C\equiv N$), 103.7 (*i*-C), 130.9 (*m*-C), 136.5 (*o*-C), 139.4 (*p*-C)	2335
4f	4.05[d] (CH_3), 7.81 (m), 8.16 (m) (aryl)[e]	32.8 (t, $J = 6$, CH_3), 106.9 (t, $J = 49$, $C\equiv N$), 102,8, (*i*-C), 131.8 (*m*-C), 137.9 (*o*-C), 146.3 (*p*-C)[e]	2357
4g	1.68 (t, $J = 7.2$, CH_3), 4.45 (q, $J = 7.2$, CH_2), 7.80 (m), 8.20 (m) (aryl)	12.9 (CH_3), 43.9 (CH_2), 106.2 (t, $J = 44$, $C\equiv N$), 102.7 (*i*-C), 131.6 (*m*-C), 137.9 (*o*-C), 146.1 (*p*-C)	2338
4h	1.17 (t, $J = 7.4$, CH_3), 2.13 (m), 4.43 (t, $J = 6.7$), (CH_2), 7.81 (m), 8.23 (m) (aryl)	11.3 (CH_3), 21.4, 49.8[d] (CH_2), 107.1 (t, $J = 47$, $C\equiv N$), 102.3 (*i*-C), 131.5 (m-C), 138.0 (*o*-C), 146.2 (*p*-C)	2350
4i	1.71 (d, $J = 6.6$, CH_3), 4.86 (sept, $J = 6.6$, CH), 7.80 (m), 8.20 (m) (aryl)[e]	21.1 (CH_3), 55.1 (CH), 106.3 (t, $J = 47$, $C\equiv N$), 102.9 (*i*-C), 131.6 (*m*-C), 138.1 (*o*-C), 146.0 (*p*-C)[e]	2335
4j	2.54, 4.07[d] (CH_3), 7.61 (m), 8.07 (m) (aryl)	22.8, 32.7[d] (CH_3), 107.5 (t, $J = 47.3$, $C\equiv N$), 100.1 (*i*-C), 131.7 (*m*-C), 136.0 (*o*-C), 152.2 (*p*-C)[e]	2358
4k	1.63 (t, $J = 7.2$), 2.54 (CH_3), 4.38 (q, $J = 7.2$, CH_2), 7.60 (m), 8.07 (m) (aryl)[e]	13.0, 22.8 (CH_3), 43.6[d] (CH_2), 107.5 (t, $J = 46$, $C\equiv N$), 100.6 (*i*-C), 131.9 (*m*-C), 136.3 (*o*-C), 152.3 (*p*-C)[e]	2330
4l	1.14 (t, $J = 7.4$), 2.54 (CH_3), 2.07 (m), 4.35 (t, $J = 6.7$) (CH_2), 7.61 (m), 8.10 (m) (aryl)[e]	11.3, 21.6, 22.8, 49.4[d] (CH_3, CH_2), 108.3 (t, $J = 46.3$, $C\equiv N$), 100.4 (*i*-C), 131.9 (*m*-C), 136.4 (*o*-C), 152.4 (*p*-C)[e]	2339
5a	3.58 (CH_3), 7.45–8.08 (phenyl)[e,h]	35.6 (CH_3), 128.6 (q, $^1J_{CH} = 162$, $^3J_{CH} = 8$, *m*-C), 129.7 (sext, $^1J_{CH} = 162$, $^3J_{CH} = 6.4$, *o*-C), 132.9 (t, $^3J_{CH} = 8$, *i*-C), 133.7 (sext, $^1J_{CH} = 162$, $^3J_{CH} = 8$, *p*-C), 148.4 (q, $J = 4.3$, COCl), 149.2 (t, $J = 5.4$, ClCN), 156.6 (q, $J = 3$, NCN)[e,f,h]	1667, 1721, 1779[i]
5b	1.38 (t, $J = 7.1$, CH_3), 4.10 (q, $J = 7.1$, CH_2), 7.42–8.06 (m, phenyl)[h]	13.8 (CH_3), 44.3 (CH_2), 128.5, 129.6 (*m*, *o*-C), 132.3, 133.6 (*i*, *p*-C), 148.1, 149.2, 156.1 (CN)[e,h]	1663, 1717, 1775[i]
5c	1.01 (t, $J = 7.4$, CH_3), 1.82 (m), 4.00 (m) (CH_2), 7.41–8.06 (m, phenyl)[h]	11.0 (CH_3), 22.0, 50.3 (CH_2), 128.7, 129.8 (m, *o*-C), 133.3, 133.7 (*i*, *p*-C), 148.3, 149.3, 156.4 (CN)[h]	1663, 1717, 1771[i]
5f	3.57 (CH_3), 7.45 (m), 7.97 (m) (aryl)[h]	35.6 (CH_3), 129.1, 131.1 (*m*, *o*-C), 131.7, 140.5 (*i*, *p*-C), 148.4, 148.7, 156.4 (CN)[h]	1670, 1725, 1775[i]
5g	1.39 (t, $J = 7.1$, CH_3), 4.12 (q, $J = 7.1$, CH_2), 7.43 (m), 7.97 (m) (aryl)[h]	13.8 (CH_3), 44.3 (CH_2), 129.0, 131.0 (*m*, *o*-C), 131.7, 140.4 (*i*, *p*-C), 148.1, 148.3, 156.1 (CN)[h]	1663, 1721, 1775[i]
5h	1.00 (t, $J = 7.4$, CH_3), 1.82 (m), 4.00 (m) (CH_2), 7.42 (m), 7.96 (m) (aryl)[h]	11.0 (CH_3), 22.0, 50.4 (CH_2), 129.0, 131.0 (m, *o*-C), 131.7, 140.4 (*i*, *p*-C), 148.1, 148.4, 156.2 (CN)[h]	1659, 1713, 1764[i]
5j	3.54 (CH_3)[h]	35.6 (CH_3), 123.5, 128.2 (C=C), 142.3, 148.6, 154.6 (CN)[e,h]	1679, 1725, 1779[i]
5k	1.37 (t, $J = 7.0$, CH_3), 4.09 (q, $J = 7.0$, CH_2)[h]	13.7 (CH_3), 44.4 (CH_2), 123.5, 128.0 (C=C), 142.2, 148.2, 154.3 (CN)[e,h]	1725, 1775[i]
5l	1.00 (t, $J = 7.4$, CH_3), 1.79 (m), 3.97 (m) (CH_2)[h]	10.9 (CH_3), 21.9, 50.3 (CH_2), 123.5, 128.0 (C=C), 142.2, 148.5, 154.6 (CN)[e,h]	1679, 1725, 1771[i]
8a	7.46–8.07 (m, phenyl)[h]	129.0, 129.9 (*m*, *o*-C), 132.0, 134.6 (*i*, *p*-C), 149.3, 153.8 (C=N, C=O)[h]	1648, 1774[i]
8f	7.46 (m), 7.98 (m) (aryl)[h]	129.3, 131.1 (*m*, *o*-C), 130.5, 141.4 (*i*, *p*-C), 148.2, 153.6 (C=N, C=O)[h]	1648, 1776[i]
10a	2.80, 3.41, 3.51 (CH_3), 6.97–7.40 (m, 15H, phenyl)[h]	32.8, 38.6, 40.5 (CH_3), 125.4, 126.2, 126.5, 127.2, 127.8, 128.6, 128.9, 129.1, 129.2, 133.9, 143.8, 144.8 (phenyl), 158.5, 161.4, 164.4 (CN)[h]	1675[j]
10b	1.05 (t, $J = 7.1$), 3.42, 3.50 (CH_3), 3.27[d] (q, $J = 7.1$, CH_2), 7.01–7.37 (m, phenyl)[h]	13.7, 38.7, 40.4, 40.8 (CH_3, CH_2), 125.5, 126.2, 126.6, 127.3, 127.8, 128.7, 128.9, 129.1, 129.2, 134.0, 143.8, 144.9 (phenyl), 158.0, 161.2, 164.3 (CN)[h]	1644[k], 1675[j]
10f	2.79, 3.41, 3.50 (CH_3), 6.95–7.41 (m, aryl)[h]	32.1, 38.6, 40.5 (CH_3), 125.3, 126.5, 126.6, 127.1, 128.2, 129.1, 129.2, 130.0, 132.4, 135.1, 143.7, 144.5 (aryl), 158.4, 161.3, 163.3 (CN)[h]	1555, 1644[k], 1675[j]
11a	3.32 (CH_3), 7.23 (aryl), 7.34 (NH), 7.42–7.90 (m, phenyl)[h]	29.4 (CH_3), 124.3, 128.0, 128.6, 129.3, 130.2, 131.5, 132.0, 136.1 (aryl), 150.2, 153.4, 165.3 (C=N, C=O)[h]	1690, 1744[j]
11b	1.24 (t, $J = 7.3$, CH_3), 3.94 (q, $J = 7.3$, CH_2), 7.24 (aryl), 7.26 (NH), 7.42–7.88 (m, phenyl)[h]	12.4 (CH_3), 38.3 (CH_2), 124.1, 127.9, 128.5, 129.2, 130.1, 131.2, 132.0, 135.8 (aryl), 149.6, 153.0, 165.4 (C=N, C=O)[e,h]	1690, 1744[j]

Table 1. (continued)

Product	^{1}H NMR (CD_3CN/TMS)[b] δ, J (Hz)	^{13}C NMR (CD_3CN/TMS)[b] δ	IR (Nujol)[c] ν (cm^{-1})
11c	0.90 (t, J = 7.5, CH_3), 1.67 (m), 3.83 (m) (CH_2), 7.23 (aryl), 7.30 (NH), 7.41–7.89 (m, phenyl)[h]	11.0 (CH_3), 20.5, 44.7 (CH_2), 124.2, 128.1, 128.6, 129.3, 130.3, 131.5, 132.2, 136.1 (aryl), 150.0, 153.3, 165.5 (C=N, C=O)[h]	1690, 1744[j]
11f	3.29 (CH_3), 7.25 (*N*-aryl), 7.44 (NH), 7.45 (m), 7.86 (m) (*C*-aryl)[h]	29.4 (CH_3), 124.4, 128.3, 128.8, 129.2, 129.6, 131.7, 135.8, 138.6 (aryl), 149.8, 153.5, 164.6 (C=N, C=O)[e,h]	1694, 1744[l]
11g	1.22 (t, J = 7.1, CH_3), 3.92 (q, J = 7.1, CH_2), 7.26 (*N*-aryl), 7.34 (NH), 7.43 (m), 7.85 (m) (*C*-aryl)[h]	12.4 (CH_3), 38.5 (CH_2), 124.2, 128.5, 128.9, 129.4, 129.8, 131.8, 135.9, 138.8 (aryl), 149.7, 153.0, 164.5 (C=N, C=O)[h]	1690, 1744[j]
12f	2.35, 3.46 (CH_3), 7.03–7.34 (m, aryl)[h]	21.2, 29.3 (CH_3), 128.2, 128.3, 130.1, 130.7, 130.8, 133.1, 137.6, 139.7 (aryl), 151.0, 154.5, 162.9 (C=N, C=O)[e,h]	1598, 1694, 1740[i]
12h	0.99 (t, J = 7.6), 2.34 (CH_3), 1.78 (m), 3.96 (m) (CH_2), 7.00–7.34 (m, aryl)[h]	11.3, 20.5, 21.2, 44.4 (CH_3, CH_2), 128.1, 128.2, 130.0, 130.5, 130.6, 132.9, 137.4, 139.5 (aryl), 150.7, 154.2, 162.8 (C=O, C=N)[e,h]	1598, 1679, 1737[j]
13g	1.54 (t, J = 7.0, CH_3), 4.51 (q, J = 7.0, CH_2), 7.77 (m), 8.69 (m) (aryl)	13.2 (CH_3), 48.9 (CH_2), 129.8, 131.6, 136.1, 147.6, 148.5, 161.9, 177.6 (aryl, C=N, C=O)[e]	1648, 1764
13k	1.47 (t, J = 7.1, CH_3), 4.44 (q, J = 7.1, CH_2)[e]	12.7 (CH_3), 50.8 (CH_2) 126.2, 147.8, 157.6, 164.6, 179.7 (C=C, C=O, C=N)[e]	1773, 1582
13l	1.04 (t, J = 7.4, CH_3), 1.90 (m), 4.33 (m) (CH_2)[e]	11.0 (CH_3), 21.4, 55.9 (CH_2), 126.2, 148.0, 157.7, 164.6, 179.5 (C=C, C=N, C=O)[e]	1775, 1579
14a	3.33, 3.47 (CH_3), 7.64–8.29 (m, phenyl), 8.80 (NH)	30.2, 31.2 (CH_3), 126.0, 130.6, 131.0, 137.9 (phenyl), 148.1, 157.1, 161.9 (C=N, C=O)	1636, 1682, 1744[m]
14f	3.31, 3.45 (CH_3), 7.69 (m), 8.22 (m) (aryl), 8.73 (NH)	30.2, 31.2 (CH_3), 124.9, 131.1, 132.7, 144.3 (aryl), 148.1, 157.2, 161.4 (C=N, C=O)	1594, 1636, 1682, 1767[m]
15	4.07 (OCH_3), 7.31 (m, 4 H), 7.70 (m, 2 H), 8.03 (m, 4 H), 8.21 (m, 2 H), (aryl)	58.1 (OCH_3), 118.0, 122.3, 130.6, 130.7, 133.2, 140.8, 142.9, 149.0, 171.7, 182.6 (aryl, C=N)	1690[d], 1810[k,l]
17a	1.97 (CH_3CN), 7.40–7.71 (m, aryl)	n	1450, 1470[k], 1590
18b	7.46–7.80 (m, 11 H), 8.74 (m, 2 H) (aryl)	128.2, 129.1, 130.3, 130.7, 131.6, 131.9, 133.5, 133.6, 135.1, 137.6, 141.7, 146.4 (aryl), 165.8, 170.5, 174.1 (C=N)	1580, 1600[l]
18d	7.38–8.47 (m, 13 H), 8.76 (m, 2 H) (aryl), 5.44 (CH_2Cl_2)	55.3 (CH_2Cl_2), 124.1, 128.2, 129.2, 129.5, 129.9, 130.3, 130.5, 130.8, 131.5, 131.7, 132.3, 133.6, 133.7, 134.9, 135.0, 135.2, 141.6, 146.5 (aryl), 166.1, 170.7, 174.1 (C=N)	1550, 1570[k,l]
19a	7.48–7.75 (m, aryl), 1.14 (t, J = 7.0, CH_3), 3.44 (q, J = 7.0, CH_2) (Et_2O)	15.7, 66.3 (Et_2O), 128.8, 129.7, 130.4, 131.4, 132.4, 134.2, 135.9, 142.5 (aryl), 149.0, 170.8 (C=O, C=N)	1565, 1589, 1778[l]
20d	0.62 (d, J = 6.3), 1.55 (d, J = 6.7) (CH_3), 3.01 (sept, (J = 6.3), 5.30 (sept, J = 6.7) (CH), 7.27–8.03 (m, 13 H), 8.67 (m, 2 H) (aryl)	20.8, 22.0 (CH_3), 55.9, 59.8 (CH), 126.1, 127.0, 129.0, 129.2, 129.5, 129.6, 130.3, 130.6, 130.8, 131.1, 131.3, 132.0, 132.2, 132.5, 133.3, 134.0, 134.6, 139.1 (aryl), 144.3, 159.8, 170.5, 172.6 (C=N)	1565, 1590

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[a] Satisfactory microanalyses obtained: C ± 0.53, H ± 0.49, N ± 0.58. With the exceptions of **5a,k**, satisfactory analyses could not be obained for compounds **5**.

[b] Bruker AC 250 spectrometer; internal standard TMS; δ-scale; 295 K.

[c] Perkin-Elmer FTIR 1600.

[d] Broad.

[e] At 273 K.

[f] Gated decoupling experiment.

[g] The nitrilium salt reacted with CD_3CN.

[h] In $CDCl_3$.

[i] In CCl_4.

[j] In $CHCl_3$.

[k] Shoulder.

[l] In CH_2Cl_2.

[m] In KBr.

[n] Poor solubility in CD_2Cl_2 or CD_3CN, fast hydrolysis.

4-Chloro-N-isopropylbenzonitrilium Hexachloroantimonate (**4i**):

From **1f** (6.67 g, 10 mmol) and **2e** (1.70 g, 20 mmol). Precipitation from CH_2Cl_2 (15 mL)/Et_2O (60 mL) afforded a yellow powder (3.76 g, 73 %); mp 117–120 °C (dec.).

4,N-Dimethylbenzonitrilium Hexachloroantimonate (**4j**):

From **1j** (6.65 g, 10 mmol) and **2a** (1.14 g, 20 mmol), however in CH_2Cl_2 (30 mL) as solvent. After stirring at 23 °C for 3 h, the solvent was evaporated. The residue was suspended in CCl_4 (30 mL). After stirring for 10 min, the liquid was decanted and the residue was stirred again in CCl_4 (30 mL) for 10 min. Filtration afforded a brown solid, which was precipitated from CH_2Cl_2 (20 mL)/Et_2O (60 mL) to furnish a pale brown powder (3.45 g, 74 %); mp 176–180 °C (dec.).

N-Ethyl-4-methylbenzonitrilium Hexachloroantimonate (**4k**):

From **1j** (6.65 g, 10 mmol) and **2b** (1.42 g, 20 mmol) as described for **4j**. Yield after reprecipitation at − 20 °C from CH_2Cl_2 (10 mL)/Et_2O (40 mL): 3.46 g (72 %) of a pale green powder, mp 90–93 °C (dec.).

4-Methyl-N-propylbenzonitrilium Hexachloroantimonate (**4l**):

From **1j** (6.65 g, 10 mmol) and **2c** (1.70 g, 20 mmol) as described for **4j**. Yield after reprecipitation from CH_2Cl_2 (10 mL)/Et_2O (50 mL): 3.77 g (76 %) of a pale green powder; mp 101–106 °C (dec.).

4-[Chloro(phenyl)methylene]-2-methylallophanoyl Chloride (**5a**):

Yield: 1.56 g (60 %) of a colorless oil (Lit.[12] colorless oil, bp 95 °C/0.07 Torr).

After stirring **5a** with 2 equiv of **2a** in CH_2Cl_2 at 25 °C for 16 h, with or without catalytic amounts of $SbCl_5$, the starting material **5a** was isolated unchanged.

4-[Chloro(phenyl)methylene]-2-ethylallophanoyl Chloride (**5b**):

Yield: 1.64 g (60 %) of a colorless oil.

4-[Chloro(phenyl)methylene]-2-propylallophanoyl Chloride (**5c**):

Yield: 1.81 g (63 %) of a yellow oil. An impurity was identified by ^{13}C NMR as **8a**.

4-[Chloro(4-chlorophenyl)methylene]-2-methylallophanoyl Chloride (**5f**):

Yield: 2.05 g (70 %) of a yellow oil.

4-[Chloro(4-chlorophenyl)methylene]-2-ethylallophanoyl Chloride (**5g**):

Yield: 1.54 g (50 %) of a colorless oil.

4-[Chloro(4-chlorophenyl)methylene]-2-propylallophanoyl Chloride (**5h**):

Yield: 1.87 g (58 %) of a yellow oil.

2-Methyl-4-(tetrachloroprop-2-en-1-ylidene)allophanoyl Chloride (**5j**):

Yield: 1.87 g (60 %) of a pale yellow oil.

2-Ethyl-4-(tetrachloroprop-2-en-1-ylidene)allophanoyl Chloride (**5k**):

Yield: 2.27 g (70 %) of a pale yellow oil.

2-Propyl-4-(tetrachloroprop-2-en-1-ylidene)allophanoyl Chloride (**5l**):

Yield: 2.28 g (67 %) of a pale yellow oil.

(Chlorophenylmethylene)carbamoyl Chloride (**8a**):

From the mother liquor of the preparation of **4e**. Yield: 0.71 g (35 %) of a pale yellow oil; bp 123–126 °C/13 Torr (Lit.[35] bp 85–90 °C/1 Torr).

[Chloro(4-chlorophenyl)methylene]carbamoyl Chloride (**8f**):

From the mother liquor of the preparation of **4i**. Yield: 0.71 g (30 %) of a pale yellow oil; bp 66–69 °C/0.2 Torr.

1,3-Dimethyl-5-[(methylphenylamino)phenylmethylene]-1-phenylbiuret (10a); Typical Procedure:

A solution of PhNHMe (2.15 g, 20 mmol) and Et_3N (2.02 g, 20 mmol) in $CHCl_3$ (30 mL) was added at 0 °C to a solution of **5a** (2.59 g, 10 mmol) in $CHCl_3$ (30 mL). After stirring at 0 °C for 2 h, the mixture was twice extracted with water and dried (Na_2SO_4). Evaporation of the solvent and stirring of the oily residue under Et_2O (15 mL) afforded a colorless powder (3.24 g, 81 %); mp 139–141 °C.

2-Ethyl-1-methyl-5-[(methylphenylamino)phenylmethylene]-1-phenylbiuret (**10b**):

From **5b** (2.73 g, 10 mmol) as described for **10a**. Yield: 2.94 g (71 %) of a colorless powder; mp 92–94 °C.

5-[(4-Chlorophenyl)(methylphenylamino)methylene]-1,3-dimethyl-1-phenylbiuret (**10f**):

From **5f** (2.94 g, 10 mmol) as described for **10a**. Yield: 3.18 g (73 %) of a colorless powder; mp 120–123 °C.

1,2,3,4-Tetrahydro-3-methyl-6-phenyl-1-(2,4,6-trichlorophenylamino)-1,3,5-triazine-2,4-dione (11a); Typical Procedure:

A solution of **5a** (2.59 g, 10 mmol) in $CHCl_3$ (30 mL) was added at 0 °C to a suspension of 2,4,6-trichlorophenylhydrazine (2.12 g, 10 mmol) and Et_3N (2.02 g, 20 mmol) in $CHCl_3$ (30 mL). After stirring at 0 °C for 30 min and then at 23 °C for 2 h, the mixture was twice extracted with water and dried (Na_2SO_4). Evaporation of the solvent and stirring of the oily residue under pentane (100 mL) afforded a colorless powder (2.19 g, 55 %); mp 228–230 °C (dec.).

3-Ethyl-1,2,3,4-tetrahydro-6-phenyl-1-(2,4,6-trichlorophenylamino)-1,3,5-triazine-2,4-dione (**11b**):

From **5b** (2.73 g, 10 mmol) as described for **11a**. Yield: 2.70 g (50 %) of a colorless powder; mp 148–149 °C (dec.).

1,2,3,4-Tetrahydro-6-phenyl-3-propyl-1-(2,4,6-trichlorophenylamino)-1,3,5-triazine-2,4-dione (**11c**):

From **5c** (2.87 g, 10 mmol) as described for **11a**. Yield: 2.21 g (52 %) of a colorless powder; mp 195–196 °C (dec.).

6-(4-Chlorophenyl)-1,2,3,4-tetrahydro-3-methyl-1-(2,4,6-trichlorophenylamino)-1,3,5-triazine-2,4-dione (**11f**):

From **5f** (2.94 g, 10 mmol) as described for **11a**. However, the crude product was stirred under pentane (60 mL)/$CHCl_3$ (15 mL) to give a colorless powder. Yield: 3.12 g (70 %); mp 215–217 °C (dec.).

6-(4-Chlorophenyl)-3-ethyl-1,2,3,4-tetrahydro-1-(2,4,6-trichlorophenylamino)-1,3,5-triazine-2,4-dione (**11g**):

From **5g** (2.94 g, 10 mmol) as described for **11a**. Yield: 3.67 g (85 %) of a colorless powder; mp 170–172 °C (dec.).

6-(4-Chlorophenyl)-1,2,3,4-tetrahydro-3-methyl-1-(4-methylphenyl)-1,3,5-triazine-2,4-dione (12f); Typical Procedure:

p-Toluidine (1.07 g, 10 mmol) and Et_3N (2.02 g, 20 mmol) were added to a cold (0 °C) solution of **5f** (2.94 g, 10 mmol) in CH_2Cl_2 (40 mL). After stirring at 0 °C for 15 min and filtration, the filtrate was extracted with H_2O (2 × 20 mL) and dried (Na_2SO_4). The solvent was evaporated and the residue was crystallized at −20 °C from $CHCl_3$ (10 mL)/pentane (20 mL) to furnish a colorless powder (1.41 g, 43 %); mp 176–178 °C (dec.).

6-(4-Chlorophenyl)-1,2,3,4-tetrahydro-1-(4-methylphenyl)-3-propyl-1,3,5-triazine-2,4-dione (**12h**):

From **5h** (3.22 g, 10 mmol), *p*-toluidine (1.07 g, 10 mmol), andEt$_3$N (2.02, 20 mmol) as described for **12f**. However, the solution of **5h** was added dropwise at −30 °C to the solution of *p*-toluidine and Et_3N. Stirring was continued at −30 °C for 30 min and then at 23 °C for 2 h. Workup afforded a colorless powder (2.21 g, 62 %), which was crystallized at −20 °C from MeOH to give a colorless powder; mp 170–173 °C (dec).

2-Chloro-6-(4-chlorophenyl)-3-ethyl-4-oxo-4*H*-1,3,5-oxadiazinium Hexachloroantimonate (13g); Typical Procedure:

A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (20 mL) was added dropwise at −70 °C to a solution of **5g** (3.08 g, 10 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at −70 °C for 30 min. Warming to 23 °C and filtration afforded a moisture sensitive pale yellow powder (4.84 g, 80 %); dec. above 105 °C.

2-Chloro-3-ethyl-4-oxo-6-trichlorovinyl-4H-1,3,5-oxadiazinium Hexachloroantimonate (**13k**):

From **5k** (3.26 g, 10 mmol) as described for **13g**. Yield: 4.44 g (71 %) of a yellow powder; mp 174–176 °C (dec.).

2-Chloro-4-oxo-3-propyl-6-trichlorovinyl-4H-1,3,5-oxadiazinium Hexachloroantimonate (**13l**):

From **5l** (3.40 g, 10 mmol) as described for **13g**. However, after stirring at −70 °C for 30 min, CCl_4 (100 mL) was added and the product was filtered off. Yield: 4.09 g (64 %) of a yellow powder; mp 172–174 °C (dec.).

2,3,4,5-Tetrahydro-3,5-dimethyl-2-oxo-6-phenyl-1,3,5-triazinium Hexachloroantimonate (14a); Typical Procedure:

A solution of $SbCl_5$ (2.99 g, 10 mmol) in $ClCH_2CH_2Cl$ (10 mL) was added dropwise at −70 °C to a solution of **8a** (2.02 g, 10 mmol) in $ClCH_2CH_2Cl$ (50 mL). After warming to 23 °C, a solution of 1,3-dimethylurea (0.88 g, 10 mmol) in $ClCH_2CH_2Cl$ (10 mL) was added. The mixture was boiled under reflux for 30 min. Evaporation of the solvent and crystallization of the oily residue from MeCN (10 mL)/Et_2O (20 mL) afforded a yellowish powder (4.86 g, 88 %); mp 172–174 °C (dec.).

6-(4-Chlorophenyl)-2,3,4,5-tetrahydro-3,5-dimethyl-2-oxo-1,3,5-triazinium Hexachloroantimonate (**14f**):

From **8f** (2.37 g, 10 mmol) as described for **14a**. Yield: 5.02 g (85%) of a pale yellow powder; mp 137–141 °C (dec.).

1-Chloro-1-(4-chlorophenyl)-3,3-bis(4-methoxyphenyl)-2-azonia-allene Hexachloroantimonate (15):
A solution of $SbCl_5$ (2.99 g, 10 mmol) in $ClCH_2CH_2Cl$ (10 mL) was added dropwise at −70 °C to a solution of **8f** (2.37 g, 10 mmol) and 4,4′-dimethoxybenzophenone (2.42 g, 10 mmol) in $ClCH_2CH_2Cl$ (50 mL). The mixture was stirred at −70 °C for 10 min, then at 23 °C for 24 h. The solvent was evaporated. The oily residue solidified on stirring under $CHCl_3$ (20 mL)/pentane (5 mL). Yield: 4.28 g (58%) of an orange powder, which was crystallized at −15 °C from MeCN (10 mL) to give orange prisms; mp 165–168 °C (dec.).

Reaction of 1f with Carbodiimides 16; General Procedure:
To a cold (−40 °C) solution of **1f** (6.67 g, 10 mmol) in $ClCH_2CH_2Cl$ (60 mL), a solution of **16** (10 mmol) in $ClCH_2CH_2Cl$ (10 mL) was added. After stirring between −40 and 23 °C for 1 h and then at 23 °C for 2 h, Et_2O (50 mL) was added dropwise and the precipitate was isolated by filtration.

2,2-Dichloro-4,6-bis(4-chlorophenyl)-2,3-dihydro-1,3-diphenyl-1,3,5-triazinium Hexachloroantimonate (**17a**):

From **16a** (1.94 g, 10 mmol). However, after stirring the reaction mixture at 0 °C for 2 h, the product was filtered off. Recrystallization at −20 °C from hot MeCN (70 mL) afforded a moisture sensitive yellow powder (4.15 g, 46%) containing 1 molecule of crystal MeCN; 216–219 °C (dec.).

2-Chloro-4,6-bis(4-chlorophenyl)-1-phenyl-1,3,5-triazinium Hexachloroantimonate (**18b**):
(a) From **16b** (2.84 g, 10 mmol). Yield: 4.66 g (62%) of a yellow powder, which was reprecipitated from CH_2Cl_2 (20 mL)/MeCN (2 mL)/Et_2O (100 mL) to afford a yellow powder (3.59 g, 48%); mp 220–223 °C.
(b) From **16c** (1.60 g, 10 mmol). Yield after reprecipitation: 4.41 g (59%); mp 218–223 °C.

2-Chloro-4,6-bis(4-chlorophenyl)-1-(β-naphthyl)-1,3,5-triazinium Hexachloroantimonate (**18d**):
(a) From **16d** (2.72 g, 10 mmol), however, in CH_2Cl_2 as solvent. Yield: 6.36 g (72%) of an orange powder containing 1 molecule of crystal CH_2Cl_2; mp 265–270 °C (dec.).

4,6-Bis(4-chlorophenyl)-2,3-dihydro-1,3-diphenyl-2-oxo-1,3,5-triazinium Hexachloroantimonate (19a):
(a) A suspension of **17a** (9.02 g, 10 mmol) in MeCN (50 mL)/H_2O (0.90 g, 50 mmol) was stirred at 23 °C for 1 h. The solvent was evaporated. Precipitation of the residue from MeCN (40 mL)/Et_2O (250 mL) afforded a yellow powder (5.94 g, 72%) containing 0.25 mol of crystal Et_2O; mp 305–309 °C (dec.).

(b) 1,3-Diphenylurea (2.12 g, 10 mmol) was added to a solution of **1f** (6.67 g, 10 mmol) in $ClCH_2CH_2Cl$ (60 mL). After boiling under reflux for 15 min and cooling to 23 °C, Et_2O (60 mL) was added. The precipitate was isolated and reprecipitated from MeCN (50 mL)/Et_2O (150 mL) to afford a yellow powder (4.76 g, 58%); mp 302–307 °C (dec.).

4,6-Bis(4-chlorophenyl)-2-(*N,N′*-diisopropylchloroformimidoylamino)-1-(β-naphthyl)-1,3,5-triazinium Hexachloroantimonate (20d):
To a cold (−40 °C) suspension of **18d** (8.83 g, 10 mmol) in CH_2Cl_2 (60 mL), a solution of **16f** (1.26 g, 10 mmol) in CH_2Cl_2 (10 mL) was added. After stirring between −40 and 23 °C for 1 h and at 23 °C for 2 h the solvent was evaporated. The residue was twice precipitated from CH_2Cl_2 (30 mL)/Et_2O (100 mL) to give a yellow powder (8.70 g, 94%); mp 151–155 °C (dec.).

We would like to thank Prof. Dr. H. Fischer for valuable discussions and Mr. S. Herzberger for technical assistance.

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