On the Reaction of α-Chlorocarbenium Ions with Sulfinylamines

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Dedicated to Professor Dr. R.R. Schmidt on the occasion of his 60th birthday

Aryl-, and vinyltrichloromethanes **1** are transformed with antimony pentachloride to α,α-dichlorocarbenium salts **2**, which react with sulfinylamines **3** to afford nitrilium salts **4** in good yields. In contrast to this preparatively useful reaction, the reaction of α-monochlorocarbenium ions **8** (obtained from diaryldichloromethanes **7**) with sulfinylamines **3** affords mixtures of iminium salts **10**, isoindolium salts **13**, and 2-azoniaallene salts **14**.

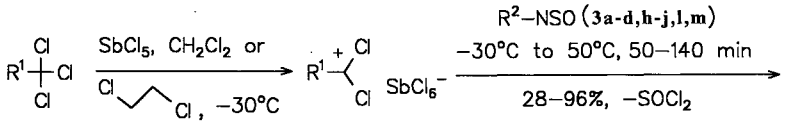
Nitrilium salts **4** are obtained by alkylation of nitriles with alkyl halides,[1-11] or with chloroformates[12-14] in the presence of Lewis acids such as antimony pentachloride or aluminum chloride, or with oxonium salts,[1,3,15-19] or with alkyl fluorosulfonates or triflates.[19-23] *N*-Arylnitrilium salts are formed from aryldiazonium salts and nitriles[1] or by treatment of imidic chlorides with Lewis acids.[1,9,24-26] Alternatively, Beckmann rearrangement of *O*-(chlorooxalyl) oximes[27,28] or of other imines with nonnucleophilic leaving groups[23,29-32] in the presence of Lewis acids affords *N*-aryl- and *N*-alkylnitrilium salts.

Recently, we described reactions of α,α-dichlorocarbenium salts with isocyanates to give 1-oxoisoindolium salts and other heterocycles.[33,34] We expected that sulfinylamines **3** would show corresponding reactions. However, it turned out that sulfinylamines react with α,α-dichlorocarbenium salts **2** to afford high yields of nitrilium salts **4**. This reaction seems to be unreported in the literature.

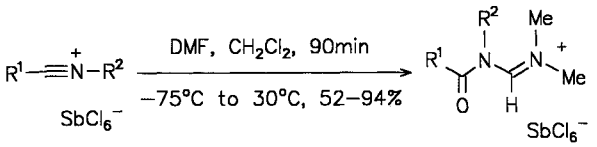
Thus, on addition of benzotrichloride **1f** to a cold (−30 °C) solution of antimony pentachloride in dichloromethane the orange-red carbenium salt **2f**[39] precipitates immediately. On addition of an equimolar amount of sulfinylaniline **3c**, the salt **2f** dissolves, and after stirring at room temperature for 30 minutes, the *N*-phenylbenzonitrilium salt **4k** was isolated in 96% yield. Correspondingly, the other nitrilium salts **4** were prepared.

Only allyl type trichloro compounds **1** (R^1 = vinyl or aryl), which form resonance stabilized α,α-dichlorocarbenium ions **2** below 20 °C, give nitrilium salts with sulfinylamines. No reactions could be achieved, for instance, with 1,1,1-trichloroethane, or hexachloroacetone, or even with 5-trichloromethyl-1,2,4-oxadiazole. The reaction can especially be recommended for the preparation of *N*-arylnitrilium salts, which are not easily obtained otherwise. There are almost no limitations with respect to the sulfinylamines, which are readily prepared from amines and thionyl chloride.[35-38]

Isolation of several carbenium salts **2** has been described in the literature.[39-41] Starting from a *cis,trans* mixture of **1a**,[42,43] a single geometric isomer **2a** was formed. The remarkably stable red salt **2a** showed a coupling of the vinyl protons of 13.3 Hz. At 295 K six ^{13}C resonances for the phenyl carbon atoms were observed (Table 1) indicating slow rotation around the phenyl-C bond. The



1a,e,f,n **2a,e,f,n**



4a-u **5c,d,f-q,s-u**

	R^1	R^2		R^1	R^2		R^1	R^2
a	PhCH=CH	C_6H_{13}	**h**	Ph	*i*-Bu	**o**	4-ClC_6H_4	*c*-C_6H_{11}
b	PhCH=CH	*c*-C_6H_{11}	**i**	Ph	CH_2CH_2Ph	**p**	4-ClC_6H_4	*i*-Bu
c	PhCH=CH	Ph	**j**	Ph	$(CH_2)_3Ph$	**q**	4-ClC_6H_4	CH_2CH_2Ph
d	PhCH=CH	4-MeC_6H_4	**k**	Ph	Ph	**r**	4-ClC_6H_4	$(CH_2)_3Ph$
e	Cl_2C=CCl	C_6H_{13}	**l**	Ph	4-$MeOC_6H_4$	**s**	4-ClC_6H_4	Ph
f	Ph	C_6H_{13}	**m**	Ph	3,5-$Cl_2C_6H_3$	**t**	4-ClC_6H_4	4-$MeOC_6H_4$
g	Ph	*c*-C_6H_{11}	**n**	4-ClC_6H_4	C_6H_{13}	**u**	4-ClC_6H_4	3,5-$Cl_2C_6H_3$

Scheme 1

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

Product	Molecular Formula[a]	^{1}H NMR (CD_3CN/TMS)[b] δ, J (Hz)	^{13}C NMR (CD_3CN/TMS)[b] δ	IR (Nujol)[c] ν (cm^{-1})
1a	$C_9H_7Cl_3$ (221.5)	5.73 (d, J = 9.9), 6.31 (d, J = 9.9) (vinyl[d]), 6.71 (d, J = 15.7), 7.08 (d, J = 15.7) (vinyl[f])[g]	58.3 (CCl_3), 124.2, 126.9, 128.8, 128.9, 129.4, 138.5 (aryl, vinyl)[d,g]	1615[d,e]
2a	$C_9H_7Cl_8Sb$ (520.5)	8.37 (d, J = 13.3), 9.37 (d, J = 13.3) (vinyl), 7.99 (m, 2H), 8.39 (m, 1H), 8.52 (m, 2H) (phenyl)[h]	133.4, 133.8, 134.1, 136.5, 138.5, 150.2, 153.8, 182.3, 184.3[h,i]	1596
4a	$C_{15}H_{20}Cl_6NSb$ (548.8)	0.92 (m, CH_3), 1.30–2.02 (m, 8H), 4.27 (m, 2H, J = 7.0, ^5J = 1.8) (CH_2), 6.59 (m, J = 16.5, ^5J = 1.8), 8.33 (d, J = 16.5) (vinyl), 7.53–7.79 (phenyl)	14.3, 23.1, 26.6, 27.8, 31.5, 47.8[j] (CH_3, CH_2), 88.8, 165.5 (vinyl), 108.8 (t, J = 45, CN), 130.5, 130.7, 133.2, 135.6 (phenyl)	2340, 1610
4b	$C_{15}H_{18}Cl_6NSb$ (546.8)	1.51, 1.78, 2.14 (3m, 10H, CH_2), 4.61 (m, CH), 6.58 (m, J = 16.8, ^5J = 1.8), 8.35 (d, J = 16.8) (vinyl), 7.53–7.80 (phenyl)[k]	23.5, 25.0, 31.2 (CH_2), 59.4[j] (CH), 109.0 (t, J = 44.3, CN), 88.9, 165.5 (vinyl), 130.6, 130.7, 133.3, 135.6 (phenyl)[k]	2310, 1605
4c	$C_{15}H_{12}Cl_6NSb$ (540.7)	–[l]	–[l]	2293, 1590
4d	$C_{16}H_{14}Cl_6NSb$ (534.8)	–[l]	–[l]	2291, 1588
4e	$C_9H_{13}Cl_9NSb$ (576.0)	–[m]	–[m]	2300, 2340[m]
4f	$C_{13}H_{18}Cl_6NSb$ (522.7)	0.92 (m, CH_3), 1.38 (m, 4H), 1.55 (m, 2H), 2.06 (m, 2H), 4.39 (t, J = 6.9) (CH_2), 7.76–8.24 (m, phenyl)	14.3, 23.0, 26.6, 27.5, 31.4, 48.0[j] (CH_3, CH_2), 107.4 (t, J = 45, CN), 104.0 (*i*-C), 131.1, 136.5 (m, *o*-C), 139.6 (*p*-C)	2350
4g	$C_{13}H_{16}Cl_6NSb$ (520.7)	1.38–2.29 (m, 10H, CH_2), 4.72 (m, CH), 7.76–8.26 (m, phenyl)[k]	23.6, 25.0, 30.9 (CH_2), 59.5 (CH), 107.4 (t, J = 44, CN), 104.1 (*i*-C), 131.0, 136.6 (m, *o*-C), 139.5 (*p*-C)[k]	2320, 1600
4h	$C_{11}H_{14}Cl_6NSb$ (494.7)	1.17 (d, J = 6.7, CH_3), 2.45 (m, CH), 4.28 (d, J = 7.5, CH_2), 7.77–8.27 (phenyl)[k]	19.8 (CH_3), 28.4 (CH), 54.3[j] (CH_2), 108.0 (t, J = 45.5, CN), 103.8 (*i*-C), 131.0, 136.6 (m, *o*-C), 139.7 (*p*-C)[k]	2340[n]
4i	$C_{15}H_{14}Cl_6NSb$ (542.7)	3.36 (t, J = 6.8), 4.61 (t, J = 6.8) (CH_2), 7.33–8.09 (phenyl)[k]	33.5, 49.2[j] (CH_2), 108.0 (t, J = 47, CN), 103.6 (*i*-CCN)[k]	2350
4j	$C_{16}H_{16}Cl_6NSb$ (556.8)	2.36 (m), 2.89 (m), 4.40 (t, J = 6.7) (CH_2), 7.20–8.19 (phenyl)[k]	29.1, 32.9, 47.5[j] (CH_2), 107.5 (t, J = 45, CN), 103.8 (*i*-CCN)[k]	2330
4k	$C_{13}H_{10}Cl_6NSb$ (514.7)	–[l]	–[l]	2310, 1600
4l	$C_{14}H_{12}Cl_6NOSb$ (544.7)	–[l]	–[l]	2310
4m	$C_{13}H_8Cl_8NSb$ (583.6)	–[l]	–[l]	2315
4n	$C_{13}H_{17}Cl_7NSb$ (557.2)	0.92 (m, CH_3), 1.38 (m, 4H), 1.55 (m, 2H), 2.06 (m, 2H), 4.39 (t, J = 6.8, 2H) (CH_2), 7.80 (m), 8.19 (m, aryl)	14.2, 23.0, 26.6, 27.6, 31.4, 48.3[j] (CH_3, CH_2), 107.0 (t, J = 47, CN), 102.6 (*i*-C), 131.7, 138.1 (m, *o*-C), 146.3 (*p*-C, aryl)	2320
4o	$C_{13}H_{15}Cl_7NSb$ (555.2)	1.30–2.29 (m, 10H, CH_2), 4.72 (m, CH), 7.80 (m), 8.20 (m, aryl)	23.6, 25.0, 30.9 (CH_2), 59.9 (CH), 106.9 (t, J = 43, CN), 102.8 (*i*-C), 131.6, 138.2 (m, *o*-C), 146.2 (*p*-C)	2330
4p	$C_{11}H_{13}Cl_7NSb$ (529.2)	1.18 (d, J = 6.7, CH_3), 2.46 (m, CH), 4.29 (d, J = 6.5, CH_2), 7.68–8.26 (aryl)[k]	19.8 (CH_3), 28.4 (CH), 54.4[j] (CH_2), 107.4 (t, J = 45.3, CN), 102.5 (*i*-C), 131.5, 138.1 (m, *o*-C), 146.2 (*p*-C)[k]	2320[n]
4q	$C_{15}H_{13}Cl_7NSb$ (577.2)	3.35 (t, J = 6.8), 4.61 (t, J = 6.8) (CH_2), 7.32–8.07 (aryl)[k]	33.4, 49.3[j] (CH_2), 107.5 (t, J = 45, CN), 102.4 (*i*-CCN)[k]	2340
4r	$C_{16}H_{15}Cl_7NSb$ (591.2)	2.35 (m), 2.89 (m), 4.39 (t, J = 6.7) (CH_2), 7.19–8.15 (aryl)[k]	29.1, 33.0, 47.7[j] (CH_2), 107.0 (t, J = 47, CN), 102.7 (*i*-CCN), 127.5, 129.5, 129.7, 131.6, 138.1, 140.8, 146.3 (aryl)[k]	2340
4s	$C_{13}H_9Cl_7NSb$ (549.1)	–[l]	–[l]	2310
4t	$C_{14}H_{11}Cl_7NOSb$ (579.2)	–[l]	–[l]	2310
4u	$C_{13}H_7Cl_9NSb$ (618.0)	–[l]	–[l]	2319
5c	$C_{18}H_{19}Cl_6N_2OSb$ (613.8)	2.64 (d, J = 1), 3.58 (d, J = 0.4, CH_3), 6.33 (d, J = 15.5), 7.97 (d, J = 15.5) (vinyl), 7.35–7.72 (phenyl), 8.88[j] (CH)	41.7, 49.7 (CH_3), 115.1, 129.9, 130.0, 130.1, 131.7, 132.3, 132.8, 134.5, 135.0, 151.1, 154.8, 166.9 (sp^2-C)	1728, 1670, 1624
5d	$C_{19}H_{21}Cl_6N_2OSb$ (627.8)	2.48, 2.65 (d, J = 1), 3.55 (d, J = 0.6, CH_3), 6.35 (d, J = 15.5), 7.96 (d, J = 15.5) (vinyl), 7.38–7.50 (aryl), 8.86 (m, CH)	21.5, 41.6, 49.7 (CH_3), 115.1, 129.7, 129.8, 130.1, 132.2, 132.3, 132.8, 134.5, 143.2, 151.0, 154.8, 167.1 (sp^2-C)	1716, 1670
5f	$C_{16}H_{25}Cl_6N_2OSb$ (595.9)	0.87 (m), 3.23 (d, J = 0.9), 3.44 (d, J = 0.7) (CH_3), 1.29 (m, 6H), 1.72 (m, 2H), 3.93 (m, 2H, CH_2), 8.19[j] (CH), 7.58–7.79 (phenyl)	14.2, 23.1, 26.6, 30.0, 31.8, 43.0, 48.3, 50.7 (CH_3, CH_2), 130.5, 130.7 (*o*, *m*-C), 132.4, 135.3 (*i*, *p*-C), 160.1, 171.4 (C=N, C=O)	1730, 1660[n]

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 (Nujol)[c] ν (cm^{-1})
5g	$C_{16}H_{23}Cl_6N_2OSb$ (593.8)	1.18–2.12 (CH_2), 2.83 (d, J = 0.9), 2.47 (d, J = 0.5, CH_3), 3.90 (m, J = 12.2 and 3.8, CH), 8.17[j] (CH), 7.60–7.87 (phenyl)	25.4, 26.5, 33.1, 43.4, 47.6, 64.7 (CH_3, CH_2, CH), 130.7, 130.8 (*o*, *m*-C), 132.3, 136.1 (*i*, *p*-C), 158.6, 171.1 (C=N, C=O)	1730, 1660[n]
5h	$C_{14}H_{21}Cl_6N_2OSb$ (567.8)	0.94 (d, J = 6.7), 3.12 (d, J = 0.9), 3.45 (d, J = 0.5, CH_3), 2.01 (m, CH), 3.78 (d, J = 7.6, CH_2), 8.22 (m, CH), 7.59–7.80 (phenyl)	19.8, 29.7, 43.1, 48.3, 57.7 (CH_3, CH_2, CH), 130.5, 130.7 (*o*, *m*-C), 132.3, 135.5 (*i*, *p*-C), 159.9, 171.6 (C=N, C=O)	1730, 1660[n]
5i	$C_{18}H_{21}Cl_6N_2OSb$ (615.8)	3.10 (d, J = 0.9), 3.30 (d, J = 0.5, CH_3), 3.06 (t, J = 7.3), 4.16 (t, J = 7.3, CH_2), 8.07 (m, CH), 7.21–7.78 (phenyl)	35.9, 43.2, 48.0, 52.5 (CH_3, CH_2), 128.3, 130.0, 130.1, 130.4, 130.5, 132.4, 135.3, 137.8 (phenyl), 160.3, 171.1 (C=N, C=O)	1725, 1670[n]
5j	$C_{19}H_{23}Cl_6N_2OSb$ (629.9)	3.13 (d, J = 0.8), 3.39 (d, J = 0.4, CH_3), 2.05 (m), 2.68 (t, J = 7.6), 3.93 (m, CH_2), 8.14[j] (CH), 7.19–7.77 (phenyl)	31.5, 33.0, 42.9, 48.3, 49.8 (CH_3, CH_2), 127.3, 129.4, 129.6, 130.5, 130.7, 132.5, 135.3, 141.5 (phenyl), 160.3, 171.5 (C=N, C=O)	1730, 1670[n]
5k	$C_{16}H_{17}Cl_6N_2OSb$ (587.9)	2.75 (d, J = 1.1), 3.55 (d, J = 0.6, CH_3), 7.39–7.66 (phenyl), 8.59 (m, CH)	42.7, 49.0 (CH_3), 129.3, 129.8, 130.9, 131.1, 131.3, 131.8, 134.4, 136.8, 157.2, 170.8 (sp^2-C)	1715, 1668
5l	$C_{17}H_{19}Cl_6N_2O_2Sb$ (617.8)	2.76 (d, J = 0.8), 3.53, 3.80 (CH_3), 6.98–7.63 (aryl), 8.58[j] (CH)	42.4, 49.1, 56.6 (CH_3), 116.2, 129.0, 129.8, 130.7, 130.8, 132.0, 134.3, 157.2, 161.8, 171.1	1716, 1667
5m	$C_{16}H_{15}Cl_8N_2OSb$ (656.6)	2.87 (d, J = 0.9), 3.54 (d, J = 0.5, CH_3), 8.50[j] (CH), 7.45–7.72 (aryl)	43.5, 48.9 (CH_3), 128.0, 130.2, 131.2, 131.4, 131.5, 135.2, 137.0, 138.9 (aryl), 157.6, 170.2 (C=N, C=O)	1733, 1675[o]
5n	$C_{16}H_{24}Cl_7N_2OSb$ (630.3)	0.88 (m), 3.25 (d, J = 0.9), 3.45 (d, J = 0.5) (CH_3), 1.29 (m, 6H), 1.68 (m, 2H), 3.91 (m, 2H) (CH_2), 8.16 (m, CH), 7.60–7.75 (aryl)	14.2, 23.1, 26.6, 30.0, 31.8, 43.1, 48.4, 50.6 (CH_3, CH_2), 130.7, 131.2, 132.4, 141.1 (aryl), 160.1, 170.6 (C=N, C=O)	1730, 1670[n]
5o	$C_{16}H_{22}Cl_7N_2OSb$ (628.3)	1.15–2.11 (CH_2), 2.87 (d, J = 0.9), 3.51 (d, J = 0.5, CH_3), 3.89 (m, J = 3.9, and 12.2, CH), 8.17[j] (CH), 7.61–7.85 (aryl)	25.3, 26.4, 33.1, 43.5, 47.7, 55.3, 64.7 (CH_3, CH_2, CH), 130.8, 130.9, 132.4, 142.0 (aryl), 158.5, 170.0 (C=N, C=O)	1720, 1670[n]
5p	$C_{14}H_{20}Cl_7N_2OSb$ (602.2)	0.94 (6H, d, J = 6.7), 3.16 (d, J = 0.9), 3.48 (d, J = 0.6, CH_3), 2.01 (m, CH), 3.79 (d, J = 7.6, CH_2), 8.22 (m, CH), 7.60–7.79 (aryl)	19.7, 29.7, 43.2, 48.4, 57.6 (CH_3, CH_2, CH), 130.7, 130.9, 132.4, 141.3 (aryl), 159.8, 170.6 (C=N, C=O)	1730, 1670[n]
5q	$C_{18}H_{20}Cl_7N_2OSb$ (650.3)	3.13 (d, J = 0.9), 3.32 (d, J = 0.7, CH_3), 3.06 (t, J = 7.2), 4.16 (t, J = 7.2, CH_2), 8.06 (m, CH), 7.21–7.64 (aryl)	35.8, 43.3, 48.1, 52.5 (CH_3, CH_2), 128.3, 130.0, 130.1, 130.6, 131.0, 132.2, 137.8, 141.1 (aryl), 160.2, 170.2 (C=N, C=O)	1730, 1680[n]
5s	$C_{16}H_{16}Cl_7N_2OSb$ (622.2)	2.75 (d, J = 1.0), 3.57 (d, J = 0.7, CH_3), 7.39–7.62 (aryl), 8.59 (m, CH)	42.7, 49.1 (CH_3), 129.2, 130.0, 130.5, 131.2, 131.4, 132.5, 136.6, 140.1, 157.1, 169.9 (sp^2-C)	1710, 1668
5t	$C_{17}H_{18}Cl_7N_2O_2Sb$ (652.3)	2.78 (d, J = 0.9), 3.56 (d, J = 0.4), 3.81 (CH_3), 6.99–7.61 (aryl), 8.60[j] (CH)	42.5, 49.2, 56.5 (CH_3), 116.2, 128.6, 129.9, 130.5, 130.6, 132.4, 139.9, 156.9, 161.8, 170.1 (sp^2-C)	1713, 1667
5u	$C_{16}H_{14}Cl_9N_2OSb$ (691.1)	2.86 (d, J = 0.9), 3.54 (d, J = 0.5) (CH_3), 8.48[j] (CH), 7.45–7.69 (aryl)	43.6, 49.0 (CH_3), 128.0, 130.1, 130.4, 131.6, 132.9, 137.1, 138.7, 141.0 (aryl), 157.6, 169.3 (C=N, C=O)	1737, 1671[o]
6e	$C_9H_{14}Cl_3NO$ (258.6)	0.89 (m, CH_3), 1.31 (m, 6H), 1.58 (m, 2H), 3.33 (m, 2H) (CH_2), 6.64[j] (NH)[g]	14.0, 22.5, 26.5, 29.1, 31.4, 40.4 (CH_3, CH_2), 124.2, 125.4 (vinyl), 160.5 (CO)[g]	3270, 1655, 1552[p]
10c	$C_{19}H_{22}Cl_6NSb$ (598.9)	1.22–2.16 (m, CH_2), 3.96 (m, CH), 7.54–7.89 (phenyl), 10.66[j] (NH)	24.8, 25.2, 32.5 (CH_2), 61.8 (CH), 130.3, 130.4, 130.8, 132.7, 133.2, 134.9, 137.3 (phenyl), 182.3 (C=N)	3300, 1592, 1570
10d	$C_{19}H_{16}Cl_6NSb$ (592.8)	7.35–7.98 (phenyl), 11.19[j] (NH)[q]	124.7, 128.6, 129.4, 130.1, 130.2, 130.7, 131.7, 132.4, 132.6, 135.5, 135.6, 138.1 (phenyl), 180.8 (C=N)[q]	3245, 1595, 1561
10g	$C_{17}H_{18}Cl_8NSb$ (641.7)	0.99 (6H, d, J = 6.7, CH_3), 2.26 (m, CH), 3.70 (d, J = 7.1, CH_2), 7.53–7.73 (aryl), 10.84[j] (NH)	20.2 (CH_3), 29.4 (CH), 58.3 (CH_2), 128.6, 130.7, 130.8, 131.6, 133.3, 134.4, 141.3, 143.8 (aryl), 182.0 (C=N)	3260, 1620, 1591
11b	$C_{17}H_{19}N$ (237.3)	0.93 (d, J = 6.7, CH_3), 2.04 (m, CH), 3.20 (d, J = 6.6, CH_2), 7.10–7.65 (phenyl)[g]	20.8 (CH_3), 30.2 (CH), 61.6 (CH_2), 127.9, 128.0, 128.1, 128.3, 128.4, 129.7, 137.1, 140.1 (phenyl), 167.5 (C=N)[g]	1626[p]
11d	$C_{19}H_{15}N$ (257.3)	6.70–7.77 (phenyl)[g]	120.9, 123.1, 127.9, 128.2, 128.4, 128.5, 129.3, 129.5, 130.7, 136.2, 139.7, 151.2 (phenyl), 168.2 (C=N)[g]	1622, 1594[e]
13a	$C_{32}H_{32}Cl_6NSb$ (765.1)	0.64 (t, J = 7, CH_3), 0.61–0.89 (m, 8H), 4.18 (m, CH_2), 7.36–8.01 (aryl)[g]	13.6 (CH_3), 21.8, 26.0, 28.5, 30.2, 49.2 (CH_2), 90.6 (C), 124.5, 124.7, 127.9, 128.3, 129.1, 130.3, 130.7, 130.8, 131.0, 131.5, 133.9, 134.4, 137.9, 153.8 (aryl), 178.7 (C=N)[g]	1602, 1566
13b	$C_{30}H_{28}Cl_6NSb$ (737.0)	0.22 (6H, d, J = 6.7, CH_3), 0.79 (m, CH), 4.18 (d, J = 7.7, CH_2), 7.37–8.05 (aryl)[g]	19.6 (CH_3), 27.6 (CH), 55.4 (CH_2), 91.2 (CH), 124.5, 125.1, 128.3, 128.6, 129.3, 130.2, 130.8, 130.9, 131.0, 131.2, 134.0, 134.5, 137.9, 153.9 (aryl), 178.9 (C=N)[g]	1600, 1557

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 (Nujol)[c] ν (cm^{-1})
13c	$C_{32}H_{30}Cl_6NSb$ (763.1)	0.71–1.60 (10H, m, CH_2), 4.00 (m, CH), 7.36–7.89 (aryl)[r]	24.4, 25.9, 33.8 (CH_2), 64.6 (CH), 93.0 (C), 124.0, 125.6, 127.2, 127.8, 128.5, 129.6, 130.1, 130.8, 130.9, 132.9, 133.0, 133.3, 137.8, 153.0 (aryl), 180.5 (C=N)[r]	1604, 1565
13d	$C_{32}H_{24}Cl_6NSb$ (757.0)	6.78–8.19 (aryl)[g]	93.9 (C), 124.6, 125.3, 127.3, 128.4, 129.5, 129.8, 129.9, 130.0, 130.4, 130.5, 130.8, 131.0, 131.1, 132.5, 134.9, 135.1, 138.2, 154.8 (aryl), 179.1 (C=N)[g]	1598, 1533
13e	$C_{33}H_{26}Cl_6NSb$ (771.0)	2.27 (CH_3), 6.63–8.16 (aryl)[g]	21.1 (CH_3), 93.9 (C), 124.7, 125.3, 127.1, 128.5, 129.5, 129.9, 130.2, 130.4, 130.5, 130.7, 131.0, 132.5, 132.7, 134.9, 138.2, 141.8, 154.8 (aryl), 178.9 (C=N)[q]	1595, 1539
13f	$C_{32}H_{28}Cl_8NSb$ (831.9)	0.76–1.65 (m, CH_2), 3.99 (m, CH), 7.31–7.91 (aryl)[q]	24.2, 25.6, 25.7, 33.8, 33.9 (CH_2), 64.5 (CH), 92.5 (C), 123.6, 124.0, 127.6, 128.5, 128.8, 128.9[j], 129.1, 129.9, 130.1, 130.2, 130.9, 131.1, 131.6, 132.6, 132.7, 136.9, 138.1, 139.4, 152.5 (aryl), 179.8 (C=N)[q]	1607, 1568
13g	$C_{30}H_{24}Cl_{10}NSb$ (874.8)	0.26 (6H, d, J = 6.7, CH_3), 0.92 (m, CH), 4.11 (d, J = 7.7, CH_2), 7.38–8.03 (aryl)[s]	19.6 (CH_3), 28.6 (CH), 56.2 (CH_2), 90.9 (C), 124.6, 125.8, 130.9, 131.3, 131.5, 131.7, 131.9, 132.0, 132.6, 133.5, 137.7, 141.6, 145.8, 155.6 (aryl), 179.1 (C=N)[s]	1596, 1559
14g	$C_{26}H_{16}Cl_{10}NSb$ (818.7)	7.70 (aryl)	126.8, 143.3 (*i*, *p*-C), 131.4, 134.8 (*m*, *o*-C), 155.9[j] (C=N)	1852, 1831

[a] Satisfactory microanalyses obtained: C ± 0.55, H ± 0.49, N ± 0.37, with exception of **4l** (C − 0.98) and **5l** (C + 0.91).
[b] Bruker AC 250 spectrometer; internal standard TMS; δ-scale; 295 K.
[c] Perkin-Elmer FTIR 1650.
[d] (*Z*)-Form.
[e] In CCl_4.
[f] (*E*)-Form.
[g] In $CDCl_3$.
[h] In $CD_2Cl_2/CF_3SO_3H/SO_2Cl_2/SbCl_5$ (4 : 4 : 3 : 3); $CHDCl_2$ assigned at δ = 273 K.
[i] CD_2Cl_2 assigned at δ = 53.8.
[j] Broad.
[k] At 273 K.
[l] Unstable in CD_3CN, almost insoluble in CD_2Cl_2.
[m] Not isolated. The IR spectrum of the crude reaction mixture was recorded in CH_2Cl_2.
[n] In KBr.
[o] In CH_2Cl_2.
[p] Film.
[q] In $CDCl_3/SOCl_2$ (1 : 1).
[r] In $CDCl_3/SOCl_2$ (4 : 1).
[s] At 313 K.

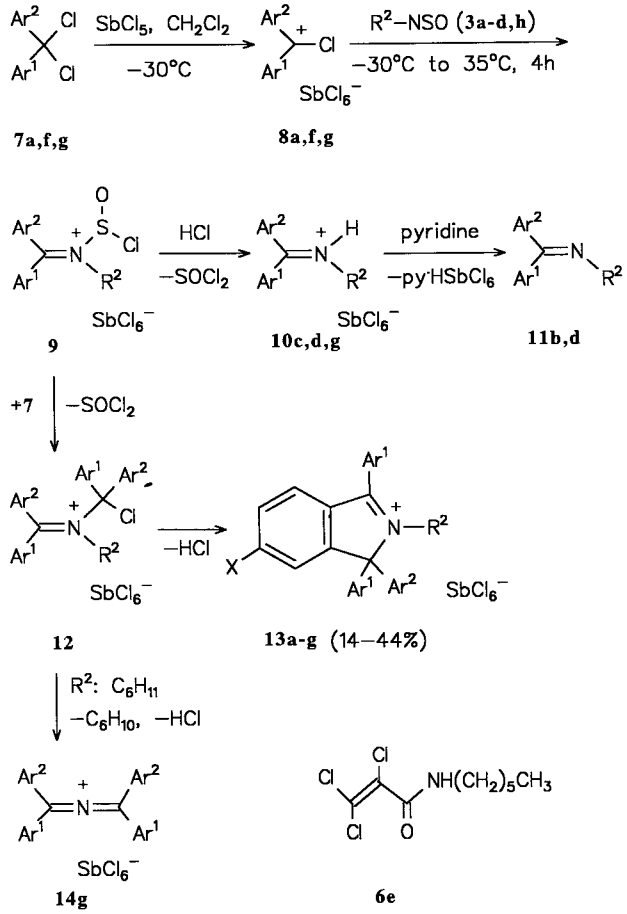
nitrilium salts **4a,b** obtained from **2a** were stereochemically homogeneous showing couplings of the vinylic protons of 16 to 17 Hz (Table 1).

Most of the nitrilium salts **4** have been isolated. An exception is the unstable salt **4e**, which was characterized as the amide **6e**. No NMR spectra could be obtained for *N*-arylnitrilium salts. These salts are almost insoluble in CD_2Cl_2. In CD_3CN a fast reaction with the solvent takes place leading to intermediates of the Meerwein quinazoline synthesis.[44] The ^{13}C NMR spectra (CD_3CN) of the *N*-alkylnitrilium salts all show characteristic triplets for C≡N at δ = ~ 108 with couplings to ^{14}N of 44–47 Hz. Another interesting feature of the ^{13}C NMR spectra of benzonitrilium salts is the high-field position of the signal for the aromatic ipso-carbon atoms at δ = ~ 103 (Table 1). The long-range proton–proton couplings across the CN triple bond have been discussed elsewhere.[14]

Since decomposition points of the moisture sensitive nitrilium salts **4** are not very characteristic and NMR spectra could not be obtained for *N*-aryl salts **4**, we transformed compounds **4** with dimethylformamide into the stable and well crystallizing *N*-acylamidinium salts **5**.[45,46] In the case of the extremely moisture sensitive salt **4e** hydrolysis was faster than reaction with dimethylformamide.

Next, we studied reactions of α-monochlorocarbenium ions **8** with sulfinylamines **3**. Salts **8** are readily obtained from diaryldichloromethanes with Lewis acids.[39–41] On addition of sulfinylamines **3** the orange-red precipitates of **2** dissolved with formation of mixtures of iminium salts **10**, isoindolium salts **13**, and 2-azoniaallene salts **14** (in the case of R^2 = secondary alkyl). A mechanism for the formation of these products is proposed in Scheme 2. Using molar ratios of 3 : 2 : 2 of the dichloromethane **7**, antimony pentachloride and sulfinylamine **3** approximately equal amounts of the iminium salts **10** and the isoindolium salts **13** were produced. On addition of pyridine to the reaction mixtures the iminium salts **10** were transformed into the free azomethines **11** and pyridinium hexachloroantimonate, which precipitated from the reaction mixtures. Slow addition of diethyl ether to the filtrates resulted in precipitation of the isoindolium salts **13**. With cyclohexylsulfinylamine (**3b**) mixtures of 2-azoniaallene salts **14**, iminium salts **10**, and isoindolium salts **13** were obtained. If the Friedel–Crafts alkylation **12** → **13** was slow (X = Cl) the mixtures contained only

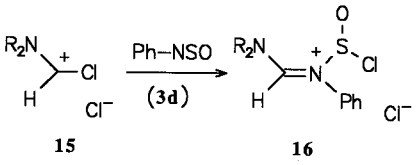
iminium salts **10** and 2-azoniaallene salts **14**. A hint for an intermediate **12** came from the finding that two equivalents of the azomethine **11d** react with one equivalent each of antimony pentachloride and the diphenylcarbenium salt **8a** to give a mixture of the isoindolium salts **13d** and the iminium salt **10d** (^{1}H NMR). Intermediates **9** seem likely because it is known that Vilsmeier–Arnold reagents **15** react with the sulfinylamine **3d** to give stable adducts **16**.[38,47,48]



7–14	Ar^1	Ar^2	R^2	X
a	Ph	Ph	C_6H_{13}	H
b	Ph	Ph	*i*-Bu	H
c	Ph	Ph	*c*-C_6H_{11}	H
d	Ph	Ph	Ph	H

7–14	Ar^1	Ar^2	R^2	X
e	Ph	Ph	4-MeC_6H_4	H
f	4-ClC_6H_4	Ph	*c*-C_6H_{11}	H
g	4-ClC_6H_4	4-ClC_6H_4	*i*-Bu	Cl

Scheme 2



Constitutional proof for the new compounds was straightforward [^{1}H, ^{13}C NMR spectra, IR spectra, elemental analyses (Table 1)]. Noteworthy are the high-field shifts of the ^{1}H NMR resonances for the isobutyl protons of **13b,g** (Table 1). The ^{13}C NMR spectrum of **13f** indicates slow rotation around the cyclohexyl-*N* bond at 293 K. Only in a few cases has the separation of the components from the mixtures of **10** to **14** been carried out.

In conclusion, while the reaction of α,α-dichlorocarbenium ions **2** with sulfinylamines **3** is preparatively valuable giving nitrilium salts **4** in good yields, the corresponding reaction of α-monochlorocarbenium ions **8** furnishing mixtures of compounds **10, 13, 14** is synthetically less useful.

The melting points are uncorrected. All experiments were carried out with exclusion of moisture in solvents dried by standard methods. The sulfinylamines **3a**,[49] **3b**[50] (prepared in Et_2O as solvent), **3c**,[50] **3d**,[35] **3h**,[51] **3i**,[52] **3j**,[53] **3**,[54] **3m**[55] as well as the diaryldichloromethanes **7a**,[56] **7f**,[57], **7g**,[58] were prepared according to literature procedures.

3,3,3-Trichloro-1-phenylpropene (1a):

Styrene (52.07 g, 0.50 mol) and $BrCCl_3$ (495.8 g, 2.50 mol) were transformed[42] in the presence of didodecanoyl peroxide (35.87 g, 0.09 mol) to 3-bromo-3-phenyl-1,1,1-trichloropropane (121.90 g, 81%); bp 90–115°C/0.1 Torr (Lit.[42] 92°C/0.2 Torr). The product was crystallized from MeOH (500 mL). The crystals were melted. On cooling to room temperature a first crop of the forming crystals was collected by decanting the supernatant melt (from which impure crystals with mp below 40°C were obtained). This melting process was repeated to afford a colorless powder (46.14 g, 31%); mp 49–52°C (Lit.[42] 54.5–55°C). Treatment with Et_3N as described[42] furnished after two distillations a colorless oil (19.42 g, 18% based on styrene) of a *E*/*Z* mixture of **1a** [major component: (*Z*)-form]; bp 61–74°C/0.01 Torr (Lit.[42] 93–95°C/0.3 Torr).

1,1-Dichloro-3-phenylpropenylium Hexachloroantimonate (2a):

A solution of **1a** (2.22 g, 10 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a cold (−50°C) solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (20 mL). Stirring at −50°C for 10 min and then at 23°C for 20 min afforded a red powder which was washed with CH_2Cl_2; yield: 5.06 g (97%); decomposition above 80°C without melting.

Nitrilium Salts 4 from α,α-Dichlorocarbenium Salts 2 and Sulfinylamines 3; General Procedure:

A solution of **1** (11 mmol) in CH_2Cl_2 (5 mL) was added dropwise at −30°C to $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 mL). After stirring for 5 min a solution of the sulfinylamine **3** (11 mmol) in CH_2Cl_2 (5 m) was added dropwise. Stirring at −30°C for 20 min, then at +23°C for 30 min and precipitation at 23°C with Et_2O (50 mL) or the solvent specified in Table 2 afforded the nitrilium salt **4** (Tables 1 and 2).

***N*^{1}-Acyl-*N*^{2},*N*^{2}-dimethylformamidinium Salts 5; General Procedure:**

A solution of DMF (0.81 g, 11 mmol) in CH_2Cl_2 (10 mL) was added dropwise at −75°C to a suspension of the nitrilium salt **4** (10 mmol) in CH_2Cl_2 (20 mL). Stirring was continued at 23°C for 1 h and then at 30°C for 30 min. Et_2O (100 mL) was added dropwise and the precipitate was filtered off (Tables 1 and 2).

Table 2. Yields, Mps, and Appearances of the Compounds Prepared

Product	Yield (%)	mp (°C)	Appearance
4a	53[a]	127–128[b]	brownish needles
4b	61[c]	124–125[b]	pale yellow powder
4c	85[d]	194–195[b]	yellow powder[e]
4d	67[f]	187–188[b]	orange-yellow powder[g]
4f	84	142–143[b]	colorless powder
4g	89	126–127[b]	colorless powder
4h	71	142–146[b]	colorless powder
4i	28	135–140[b]	pale yellow prisms
4j	68	145–155[b]	yellow powder[g]
4k	96[h]	239–242[b]	yellow powder
4l	89[i]	126–128[b]	dark brown powder
4m	83[j]	221–222[b]	yellow powder
4n	83[k]	82–85	colorless powder
4o	89[l]	91–93[b]	grey powder
4p	85	113–117[b]	pale yellow powder
4q	87	130–135[b]	pale yellow powder[g]
4r	81[j]	120–125[b]	colorless powder
4s	92[m]	216–218[b]	pink powder[g]
4u	87[j]	227–229[b]	pale yellow powder
5c	59[n]	156–158	yellow prisms
5d	86[o]	176–178[b]	yellow powder
5f	78	100–103	colorless powder
5g	61[p]	114–118	colorless powder
5h	85[q]	130–135	pale yellow powder
5i	84	80–85	colorless powder
5j	52[r]	125–127	colorless powder
5k	84[s]	154–156	pale yellow needles
5l	77[t]	168–169	orange-yellow powder
5m	90	174–176[b]	colorless powder
5n	74	95–98	colorless powder
5o	75[u]	120–125	yellow prisms
5p	94	125–130	colorless powder
5q	80[u]	100–105	yellow prisms
5s	83[s]	166–167	pale yellow powder
5t	78[v]	166–168	yellow powder
5u	90	191–193[b]	colorless powder
11b	28[w]	–	colorless oil[59]
11d	49[x]	105–108	pale brown leaflets
13a	44[y]	141–143	pale yellow powder
13b	43[z]	236–238[b]	pale yellow needles
13c	35[aa]	249–250[b]	pale yellow prisms
13d	40[ab]	197–202	pale yellow needles
13e	39[ac]	215–217	yellow prisms
13f	27[ad]	259–260[b]	pale yellow prisms
13g	14[ae]	272–274[b]	pale yellow powder

[a] The solution of **3a** was added at 23 °C. After stirring at 23 °C for 10 min the reaction mixture was cooled to −20 °C. The product was precipitated at −20 °C by slow addition of Et_2O (100 mL).
[b] Melts with decomposition.
[c] After stirring at 23 °C for 90 min, then at 30 °C for 30 min and cooling to 23 °C the product was precipitated by slow addition of Et_2O (60 mL).
[d] In $ClCH_2CH_2Cl$ instead of CH_2Cl_2. The solution of **3c** was added at 40 °C. After stirring at 40 °C for 1 h and then at 50 °C for 15 min the mixture was cooled to 23 °C. The product was filtered off and washed with CH_2Cl_2.
[e] Unstable in solution.
[f] The solution of **3d** was added at +40 °C. After stirring at 40 °C for 1 h and cooling to −20 °C the product was filtered off and washed with cold CH_2Cl_2.
[g] Decomposes quickly.
[h] The product was precipitated by slow addition of CCl_4 (30 mL) [Lit.[24] mp 236–237 °C (dec)].
[i] The product was precipitated by slow addition of pentane (80 mL) [Lit.[26] mp 173–176 °C (dec)].
[j] The product crystallized at 23 °C from the reaction mixture.
[k] The product was precipitated by slow addition of Et_2O (80 mL).
[l] The product was precipitated by slow addition of pentane (90 mL).
[m] The product was precipitated by slow addition of CCl_4 (30 mL).
[n] After crystallization at −20 °C from CH_2Cl_2 (8 mL)/Et_2O (4 mL).
[o] After reprecipitation from CH_2Cl_2 (30 mL)/Et_2O (90 mL).
[p] After crystallization at −20 °C from CH_2Cl_2.
[q] After reprecipitation from CH_2Cl_2/Et_2O.
[r] The solvent was evaporated. The oily residue solidified after drying, and was crystallized at −20 °C from CH_2Cl_2 (20 mL).
[s] The product was precipitated with CCl_4 (75 mL) and crystallized at −20 °C from CH_2Cl_2 (25 mL).
[t] After reprecipitation at −30 °C from CH_2Cl_2 (75 mL)/Et_2O (50 mL).
[u] After crystallization from CH_2Cl_2.
[v] After reprecipitation from CH_2Cl_2 (100 mL)/Et_2O (150 mL). The nitrilium salt **4t** was prepared without isolation and transformed directly to **5t**.
[w] The crude oily **11b** contained solid impurities, which were removed by filtration.
[x] Crystallization at −20 °C from CCl_4/pentane (Lit.[60] mp 112 °C).
[y] Stirring at 35 °C was not required. The product was precipitated by slow addition of pentane (150 mL), and reprecipitated from CH_2Cl_2/Et_2O/pentane.
[z] The product was precipitated by slow addition of Et_2O (100 mL) and crystallized at −20 °C from MeCN (3 mL)/Et_2O (20 mL).
[aa] After crystallization at −20 °C from MeCN (15 mL).
[ab] The stirring period at 35 °C was extended to 3 h. The precipitate was crystallized at −20 °C from CH_2Cl_2 (35 mL)/Et_2O (70 mL) (Lit.[61] mp 213–214 °C).
[ac] The reaction mixture was stirred at 35 °C for 3 h. The crude product was crystallized at −20 °C from CH_2Cl_2 (20 mL)/Et_2O (80 mL).
[ad] Crystallization at −20 °C from MeCN.
[ae] Evaporation of the solvent afforded an oily residue consisting of **13g** and **10g** (2 : 3), which was stirred in CH_2Cl_2 (30 mL) for 2 h. Filtration and slow addition at −20 °C of Et_2O (50 mL)/pentane (50 mL) to the filtrate afforded a pale yellow powder, which was recrystallized at −20 °C from MeCN/Et_2O.

N-Hexyl-2,3,3-trichloro-2-propenamide (6e):

A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (5 mL) was added at −50 °C to a solution of **1e** (2.74 g, 11 mmol) and **3a** (1.52 g, 11 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at −40 °C for 10 min and then at 23 °C for 1 h [IR: ν = 2340, 2300 (sh) cm^{-1}]. The solution was poured into a cold (0 °C) solution of NaOH (4.00 g, 100 mmol) in H_2O (80 mL). After stirring for 10 min and filtration, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and evaporated in vacuo. The brown oily residue was purified by flash chromatography (silica gel, eluent: CH_2Cl_2). Workup furnished a pale yellow oil which crystallized at 20–23 °C; yield: 1.27 g (49%).

Cyclohexyl(diphenylmethylene)ammonium Hexachloroantimonate (10c):

The mixture of compounds obtained from the reaction of **7a**, $SbCl_5$ and **3c** by precipitation with Et_2O (general procedure) was crystallized at −20 °C from MeCN (15 mL). The mother liquor of this crystallization was evaporated in vacuo, and the residue was precipitated from CH_2Cl_2 (10 mL)/Et_2O (20 mL) to give a colorless powder, which was crystallized at −20 °C from CH_2Cl_2 (5 mL); yield: 1.82 g (30%); colorless prisms; mp 196–198 °C.

(Diphenylmethylene)anilinium Hexachloroantimonate (10d):
A solution of **7a** (2.37 g, 10 mmol) in CH_2Cl_2 (5 mL) was added to a cold (−30 °C) solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 mL). An orange-red precipitate was formed. After 5 min a solution of **3a** (2.78 g, 20 mmol) in CH_2Cl_2 (10 mL) was added. The mixture was stirred at −30 °C for 30 min, then at 23 °C for 1 h, and finally at 35 °C for 5 min. Precipitation with Et_2O (100 mL) afforded an ochreous powder (3.08 g, 52%), which was reprecipitated from CH_2Cl_2 (20 mL)/Et_2O (60 mL) and then from $SOCl_2$ (5 mL)/$CHCl_3$ (100 mL) to give yellow needles; yield: 0.95 g (16%); mp 180–192 °C (dec).

[Bis(4-chlorophenyl)methylene]isobutylammonium Hexachloroantimonate (10g):
A solution of **7g** (3.06 g, 10 mmol) in CH_2Cl_2 (5 mL) was added to a cold (−30 °C) solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 mL). After 5 min a solution of **3h** (1.31 g, 11 mmol) in CH_2Cl_2 (10 mL) was added. The mixture was stirred at −30 °C for 30 min, then at 23 °C for 24 h. After addition of CH_2Cl_2 (45 mL), the suspension was refluxed for 2 h and then left at −20 °C for 2 h. Filtration afforded a colorless powder; yield: 4.25 g (66%); mp 222–223 °C.

Azomethines 11 and the Isoindolium Salts 13; General Procedure:
A solution of the diaryldichloromethane **7** (15 mmol) in CH_2Cl_2 (5 mL) was added to a cold (−30 °C) solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (5 mL). An orange-red precipitate was formed. After 5 min a solution of the sulfinylamine **3** (10 mmol) in CH_2Cl_2 (5 mL) was added. The mixture was stirred at −30 °C for 30 min, then at 23 °C for 3 h, and finally at 35 °C for 30 min. Precipitation with Et_2O (50 mL) afforded mixtures of **10** and **13** (ca. 1:1), which were dissolved in CH_2Cl_2 (20–40 mL). After cooling to −20 °C pyridine (2.37 g, 30 mmol) in CH_2Cl_2 (5 mL) was added. After stirring for 30 min pyridinium hexachloroantimonate was filtered off (40–60%) and washed with a few drops of CH_2Cl_2. Slow addition of Et_2O (20 mL)/pentane (60 mL) to the filtrate afforded a precipitate of **13**, which was filtered off. Evaporation of the filtrate gave crude **11** (Tables 1 and 2).

Tetrakis(4-chlorophenyl)-2-azoniaallene Hexachloroantimonate (14g):
From **7g** (4.59 g, 15 mmol) and **3b** (1.46 g, 10 mmol) according to the general procedure for the preparation of the isoindolium salts **13**. The solvent from the reaction mixture was evaporated. The residue consisted of **10h/14g** (1:1) without any trace of **13h**. Crystallization at −20 °C from warm CH_2Cl_2 (100 mL) afforded a pale yellow powder (5.06 g), which was recrystallized at −20 °C from MeCN (20 mL) to afford pale yellow needles of **14g**; yield: 3.14 g (38%); mp 248–251 °C (dec) [Lit.[62] mp 224–227 °C (dec)].

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