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On the Reaction of Nitrilium Salts with Tropones

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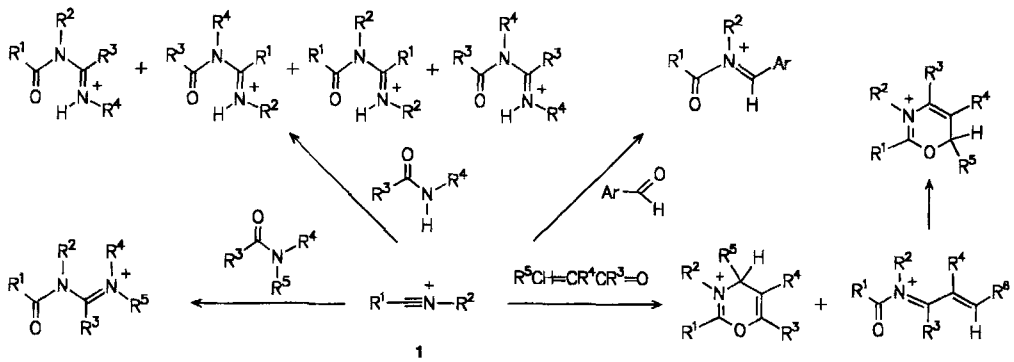
Abstract. Tropone **2a** and tropolone methyl ether **2b** react with nitrilium salts (**1a–j**) to give the bicyclic oxazolium salts **3, 5**. Cleavage of the N–C3a bond of **3, 5** followed by y Chapman rearrangement afford the stable *N*-acyliminium salts **4, 8**. A crystal structure analysis for **3a** is reported. AM1 calculations are in accord with the proposed mechanisms for the formation of **3, 5** and **4, 8**.

Recently, Luk'yanov et al. [1–4] and we [5–10] reported reactions of nitrilium salts **1** with carbonyl compounds (Scheme 1). Thus, with tertiary carboxamides *N*-acylamidinium salts were obtained [5, 6]. Mixtures of up to four different *N*-acylamidinium salts are formed by reactions of nitrilium salts with secondary amides [7, 8]. Aromatic aldehydes afford high yields of *N*-acyliminium salts [2, 9], while α,β-unsaturated carbonyl compounds give either 4*H*- or 6*H*-1,3-oxadiazinium salts, or *N*-acyl-1-azonia-1,3-butadiene salts [4, 10]. A review of the reactions of nitrilium salts with carbonyl compounds has been published by Luk'yanov [1], cp. Scheme 1.

Here we report that, differently from reactions with other α,β-unsaturated carbonyl compounds, nitrilium salts **1** react with tropones **2** to the bicyclic salts **3**. Thus, the yellow crystalline product **3a** (85%) was formed on stirring a mixture of tropone **2a** and the *N*-methylacetonitrilium salt **1a** at low temperatures (–70 to 23 °C) in dichloromethane. Compounds **3b–g** were prepared correspondingly.

The constitution of **3a** was proved by an X-ray structural analysis, see Fig. 1, Table 1. Note the planar five-membered ring and the twisted double bonds of the seven-membered ring.

In the ^{1}H NMR spectra (CD_3CN) of compounds **3** the broad signal around 4.8 ppm is assigned to H3a.



Scheme 1 Reported Reactions of Nitrilium Salts with Carbonyl Compounds (counterions omitted)

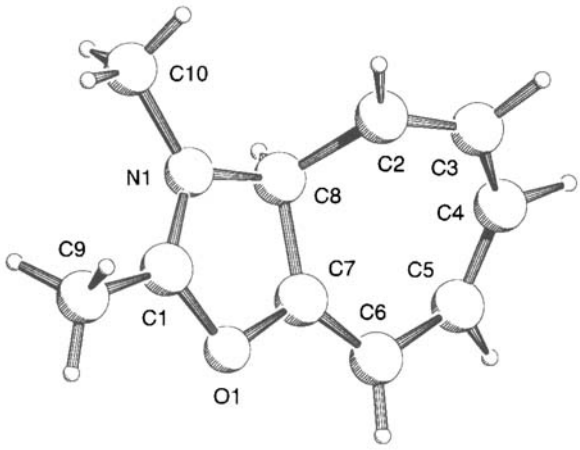


Fig.1 SCHAKAL Plot of the Cation **3a**

Table 1 Selected Bond Lengths (pm), Bond Angles (deg), and Torsional Angles (deg) of the Cation **3a** [11]

Atoms	X-ray	AM1	Atoms	X-ray	AM1
O1-C1	132.1(3)	136.6	C6-C7-O1	122.2(3)	120.6
C1-N1	129.3(3)	134.1	C7-C8-C2	109.6(2)	111.4
C1-C9	147.6(4)	148.0	C7-O1-C1	107.4(2)	108.2
N1-C8	147.3(3)	149.2	O1-C1-N1-C8	-0.6(3)	0.8
N1-C10	145.5(3)	143.6	O1-C1-N1-C10	173.9(3)	179.5
C8-C2	150.6(4)	149.2	O1-C7-C8-C2	118.9(2)	126.2
C2-C3	134.6(4)	134.2	O1-C7-C6-C5	-174.5(3)	-176.4
C3-C4	145.5(6)	144.4	O1-C7-C8-N1	0.3(2)	2.4
C4-C5	133.0(6)	134.8	C1-N1-C8-C7	0.2(3)	1.7
C5-C6	144.0(5)	144.2	C1-N1-C8-C2	-116.1(3)	-122.7
C6-C7	133.2(4)	133.9	C1-O1-C7-C6	178.8(3)	176.3
C7-O1	141.0(3)	143.4	C1-O1-C7-C8	-0.6(3)	-2.1
C7-C8	149.2(4)	151.3	N1-C8-C2-C3	169.4(3)	166.0
O1-C1-N1	113.8(2)	112.3	N1-C8-C7-C6	-179.1(3)	-175.4
O1-C1-C9	119.2(3)	117.2	N1-C1-O1-C7	0.8(3)	0.9
C9-C1-N1	127.0(3)	130.5	C8-N1-C1-C9	178.5(3)	178.9
C1-N1-C8	110.6(2)	110.3	C8-C2-C3-C4	-6.7(5)	-3.2
C1-N1-C10	127.1(2)	127.3	C8-C7-C6-C5	4.8(5)	1.3
C10-N1-C8	122.0(2)	122.4	C2-C3-C4-C5	-32.3(6)	-32.1
N1-C8-C2	112.7(2)	115.8	C2-C8-N1-C10	69.0(3)	58.5
N1-C8-C7	100.0(2)	101.4	C2-C8-C7-C6	-60.4(4)	-51.8
C8-C7-O1	108.2(2)	107.7	C3-C4-C5-C6	2.4(6)	2.3
C8-C2-C3	120.1(3)	123.1	C3-C2-C8-C7	59.0(4)	51.7
C2-C3-C4	127.4(3)	128.3	C4-C5-C6-C7	29.4(5)	28.6
C3-C4-C5	127.2(3)	127.6	C7-C8-N1-C10	-174.7(2)	-179.2
C4-C5-C6	126.2(3)	125.8	C7-O1-C1-C9	-178.4(3)	-179.4
C5-C6-C7	121.6(3)	122.1	C9-C1-N1-C10	-7.0(5)	-0.1
C6-C7-C8	129.6(3)	131.6			

An unresolved allylic coupling to H8 causes line broadening. A coupling of about 3 Hz is observed to a doublet of doublets around 5.4 ppm assigned to H4. This proton is further coupled to H5 with about 10 Hz. The signal at 5.4 ppm could alternatively arise from H8. Our assignment to H4 is based on the net atomic charges (C4: charge –0.20 e$^-$, C8: –0.02) calculated by the AM1 method [12, 13]. The ^{13}C NMR resonance of C3a appears at 62–66 ppm.

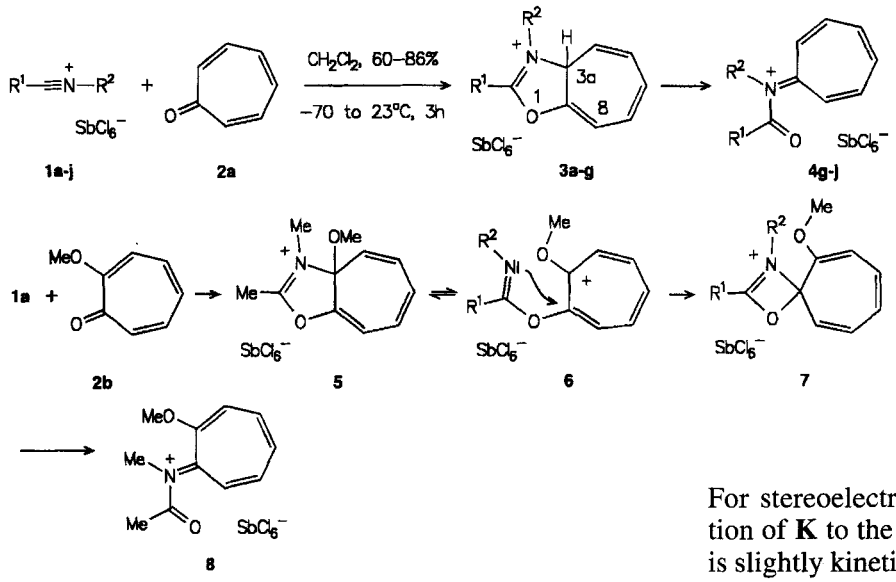
3a*H*-Cycloheptoxadiazolium salts **3** seem to be not reported in the literature. However, a few hexahydro-3a*H*-cycloheptoxadiazoles have been prepared [14, 15], and a patent covers the synthesis of 2-aryloxazolotropylium salts [16].

In solution the salts **3** undergo rearrangement to the *N*-acyliminium salts **4**. Thus, reaction of **1g** with tropone at room temperature for twenty minutes afforded the bicyclus **3g** (85%). When a solution of this compound was stirred at room temperature for twelve hours the rearranged salt **4g** was isolated (90%). Similarly, at low temperatures compounds **3h,j** could be observed in the ^{1}H NMR spectra. At room temperature rearrangement occurred to the iminium salts **4h,j**. For R^1,R^2 = phenyl the ring opening of **3** is especially fast. *N*-Acylamidinium salts are known to be moisture sensitive compounds, which usually cannot be isolated [9, 17, 18]. However, compounds **4** are well crystallizing stable salts.

The structural assignments are based on the NMR spectra. At 263 K the ^{1}H NMR spectrum (CD_3CN) of **4j** showed five doublets for the isopropyl methyl groups, while at 351 K a sharp doublet for one isopropyl group and one broad signal for the two other isopropyl groups were observed. At 263 K six methyl signals and seven resonances for the ring carbons were found in the ^{13}C NMR spectrum, while at 351 K one sharp and one very broad CH_3 signal and only four signals for the ring carbon atoms were observed. This is indicative for hindered rotation around the C=N double bond in **4j**.

For the transformation **3**→**4** either cleavage of the C8a–O or the C3a–N bond of **3** can be envisaged. It was found that the reaction of the tropolone methyl ether **2b** with **1a** affords the temperature sensitive compound **5**, which on warming rearranges to **8**. The constitution of **8** requires cleavage of the C3a–N bond of **5** to give **6** which undergoes a Chapman type rearrangement [19] via **7** to **8**. Most likely, compounds **3** rearrange correspondingly.

In the ^{1}H NMR spectrum (CD_3CN, 263 K) of **5** the OCH_3 signal appears at unusual high field (2.85 ppm). No signal for an sp^3-CH proton was found between 4 and 6 ppm. A sharp doublet at 5.99 ppm is assigned to H4. In the gated decoupled ^{13}C NMR spectrum the resonance at 94.8 ppm assigned to C3a shows no $^1J_{CH}$ coupling. The constitution of **8** follows from the 600 MHz ^{1}H NMR spectrum of the vinylic protons, which consists of three well separated triplets and two doublets with coupling constants of 10 to 11 Hz. No signal for a saturated ring carbon atom was found in the ^{13}C NMR spectrum.



	R^1	R^2		R^1	R^2
a	Me	Me	**f**	Ph	Me
b	Me	*i*-Pr	**g**	Ph	*i*-Pr
c	Et	*i*-Pr	**h**	Me	Ph
d	$PhCH_2$	*i*-Pr	**i**	Ph	Ph
e	iPr	*i*-Pr	**j**	$(iPr)_2N$	*i*-Pr

Scheme 2 Reactions of Nitrilium Salts with Tropones

The mechanism outlined in Scheme 2 implies a reversible cleavage of the C3a-N bond suggesting that the cycloaddition of **1** to **2** is a non concerted process starting with an attack of the nitrilium salt **1** on the carbonyl oxygen atom of **2b** [cf. 7]. In agreement with this proposal are AM1 calculations for the cycloaddition of **1a** to **2a** (Figure 2). According to these calculations the first enthalpy minimum is a complex **K** of **1a** and **2a**. For stereoelectronic reasons [20–23] the transformation of **K** to the cation (*Z*)-**9** with *trans* methyl groups is slightly kinetically favoured over the transformation to (*E*)-**9**. From **9** either compound **3a** is formed or – a little slower – the intermediate **10**, which opens the four-membered ring with a low activation enthalpy to give the stable end product (*E*)-**4a** with *cis* methyl groups (torsional angle H_3C–C–N–CH_3: 9°). For the rotation around the OC–N bond of (*E*)-**4a** no transition structure could be located. The formation of **3a** and **4a** from nitrilium salts **1a** and tropone is exothermic. Cleavage of the C8a–O bond in **3a** was calculated to be at least 100 kJ mol^{-1} less favourable than cleavage of the C3a–N bond.

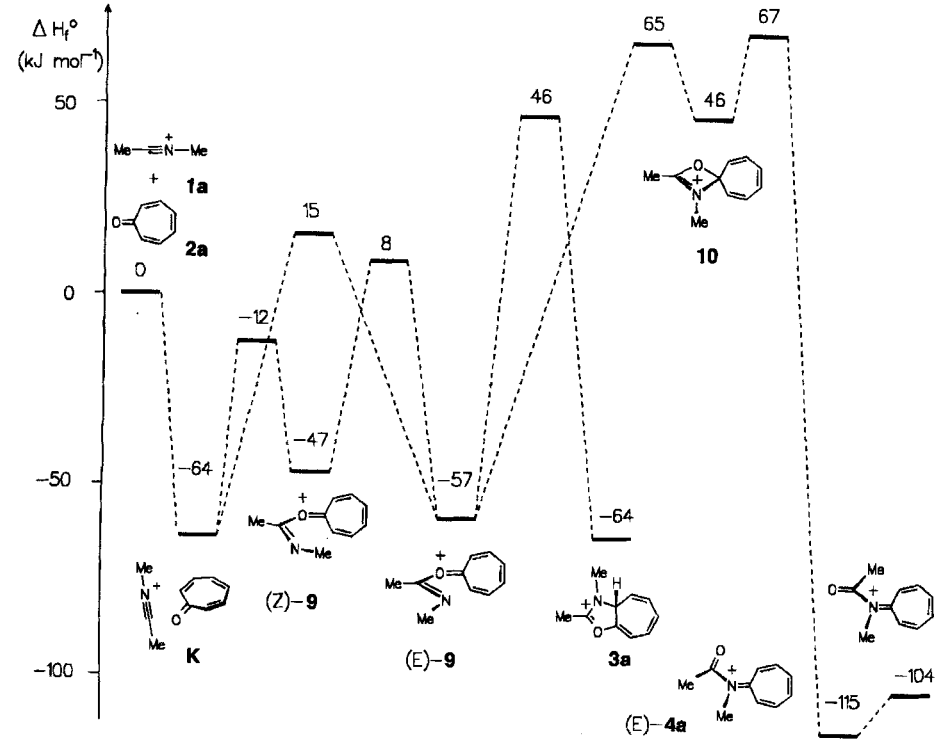


Fig. 2 AM1 calculations for the reaction of **1a** with tropone; enthalpies of formation relative to the sum of H(cation **1a**) = 798 kJ mol^{-1} and H(**2a**) = 59 kJ mol^{-1}

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Experimental

All solvents were dried by standard methods. The experiments were carried out with exclusion of moisture. The melting points are uncorrected. Satisfactory microanalyses were obtained: C±0.20%, H±0.22%, N±0.31%. – ^{1}H, ^{13}C NMR: Bruker AC-250 and WM-250 spectrometers; CD_3CN; internal standard TMS; δ in ppm. – IR spectra: Perkin-Elmer FTIR 1600 spectrometer; CH_2Cl_2; cm^{-1}. – X-ray structural analysis: Enraf-Nonius CAD4 diffractometer (graphite monochromator, $\lambda_{Mo\text{-}K\alpha}$ = 71.069 pm).
b: broad; d: doublet; dd: doublet of doublets; dt: doublet of triplets; sept: septet; m: multiplet; sh: shoulder.

2,3-Dimethyl-3aH-cycloheptoxazol-3-ium Hexachloroantimonate (**3a**)

A solution of **2a** [23, 24] (1.06 g 10 mmol) in CH_2Cl_2 (10 ml) was added dropwise at –78 °C to a suspension of **1a** [25] (3.91 g, 10 mmol) in CH_2Cl_2 (20 ml). After stirring at –78 °C for 20 min and at 0–10 °C for 2h the product was precipitated at –20 °C by slow addition of Et_2O (80 ml) to afford a yellow powder (4.07 g, 82%). Crystallization at –15 °C from CH_2Cl_2 gave yellow prisms; *m.p.* 135–137 °C (dec). – IR: 1694, 1659, 1607. – ^{1}H NMR (295 K): 2.59, 3.53 (CH_3), 4.74 (b, H3a), 5.32 (dd, *J*=10.1 and 2.7, coupl. to 4.74, H4), 6.37–6.73 (m, 4H). – ^{13}C NMR(295 K; gated decoupling): 14.2 (q, *J*=133.9), 34.1(q, *J*=145.7) (CH_3), 64.6 (d, *J*=163, C3a), 104.7 (dd, *J*=165.4 and 11.8, C4?), 113.4 (d, *J*=169.3), 126.9 (dd, *J*=165.4 and 7.9), 127.3 (dd, *J*=161.5 and 9.8) (C5,7,8?), 131.1 (dt, *J*=162.4 and 9.8,C6), 141.3 (C-8a), 176.9(C2). $C_{10}H_{12}Cl_6NOSb$ (496.7).
Monoclinic space group $P2_1/c$; *a* = 791.5(4) pm, *b* = 1387.7(2) pm, *c* = 1562.9(6) pm; ß = 95.39(2)°; volume 1709(1)·10^6 pm^3; *Z* = 4; *T*= 153(2) K; 5898 independent reflections; 5341 observed reflections (I>2σ(I)); solution by the Patterson method; full-matrix least-squares refinement; positions of three hydrogen atoms of the methyl groups calculated; the other hydrogen atoms were located by difference fourier synthesis; R = 3.65% (I>2σ(I)); wR = 9.54% [11].

3-Isopropyl-2-methyl-3aH-cycloheptoxazol-3-ium Hexachloroantimonate (**3b**)

From **1b** [26] (4.19 g, 10 mmol) as described for **3a**. Washing the product with CH_2Cl_2 (7 ml) afforded a yellow-orange powder (3.99 g, 76%); *m.p.* 121–124 °C (dec.). – IR: 1680, 1625, 1605(sh). – ^{1}H NMR (263 K): 1.46 (d, *J*=6.7), 1.60 (d, *J*=7.0), 2.65 (CH_3), 4.56 (sept, *J*=6.7, CH), 4.76 (b, H-3a), 5.35 (dd, *J*=10.4 and 2.7, H4), 6.35–6.76 (m,4H). – ^{13}C NMR (263 K): 14.7, 19.8, 21.4 (CH_3), 53.8 (CH), 61.6 (C3a), 103.7, 113.3, 126.4, 126.9, 130.9, 141.0 (C8a), 176.7(C2). $C_{12}H_{16}Cl_6NOSb$ (524.8).

2-Ethyl-3-isopropyl-3aH-cycloheptoxazol-3-ium Hexachloroantimonate (**3c**)

From **1c** [27] (4.33 g, 10 mmol) as described for **3b**. Yield: 4.74 g (88%) of a yellow powder; *m.p.* 93–95 °C (dec.). The compound decomposed in boiling MeCN. – IR: 1680, 1620, 1600. – ^{1}H NMR (263 K): 1.33 (t, *J*=7.3), 1.44 (d, *J*=7.0), 1.58 (d, *J*=6.7) (CH_3), 2.98 (m, CH_2), 4.54 (sept, *J*=6.8, CH), 4.76 (b, H-3a), 5.35 (dd, *J*=10.1 and 3.0, H4), 6.35–6.76 (m, 4H). – ^{13}C NMR (263 K): 8.3, 19.8, 21.6, 22.1, 53.4 (CH_3, CH_2, CH), 61.8 (C3a), 103.7, 113.5, 126.3, 127.0, 130.9, 141.3 (C8a), 179.3 (C2).– $C_{13}H_{18}Cl_6NOSb$ (538.8).

2-Benzyl-3-isopropyl-3aH-cycloheptoxazol-3-ium Hexachloroantimonate (3d)

From **1d** [5] (4.95 g, 10 mmol) as described for **3a**. Yield: 5.05 g (84%) of an orange powder; *m.p.* 116–118 °C (dec.). – IR: 1680, 1620, 1590. – ^{1}H NMR (263 K): 1.46 (d, *J*=6.7), 1.64 (d, *J*=6.7) (CH_3), 4.31(d, *J*=17.7), 4.42 (d, *J*=17.7) (CH_2), 4.73 (sept, *J*=6.7, CH), 4.79 (b, H3a), 5.39 (dd, *J*=9.8 and 2.8, H4), 6.30–6.75 (m, 4H), 7.45 (m, phenyl). – ^{13}C NMR (263 K): 19.8, 21.6, 33.9, 53.8 (CH_3, CH_2, CH), 62.0 (C3a), 103.9, 113.5, 126.3, 126.9, 129.5, 129.8, 130.0, 131.1, 141.2(C8a), 176.6(C-2). – $C_{18}H_{20}Cl_6NOSb$ (600.8).

2,3-Diisopropyl-3aH-cycloheptoxazol-3-ium Hexachloroantimonate (**3e**)

From **1e** [26] (4.47 g, 10 mmol) as described for **3a**. Yield after reprecipitation at –50 °C from CH_2Cl_2 (15 ml)/Et_2O (120 ml): 4.86 g (88%) of a yellow powder; *m.p.* 150–153 °C (dec.). The compound rearranged at 23 °C in CH_2Cl_2 within 14d to **4e**. – IR: 1680, 1620, 1595. – ^{1}H NMR (263 K): 1.39 (d, *J*=6.7), 1.40 (d, *J*=7.0), 1.47 (d, *J*=6.8), 1.61 (d, *J*=6.7) (CH_3), 3.39 (sept, *J*=6.9), 4.63 (sept, *J*=6.7) (CH), 4.78(b, H3a), 5.38 (dd, *J*=10.1 and 3.0,H4), 6.34–6.76 (m, 4H). – ^{13}C NMR (263 K): 18.6, 19.0, 20.2, 22.1, 28.2, 53.6 (CH_3, CH), 62.1 (C3a), 103.7, 113.7, 126.2, 127.0, 130.9, 141.3 (C8a), 181.4 (C2). – $C_{14}H_{20}Cl_6NOSb$ (552.8).

3-Methyl-2-phenyl-3aH-cycloheptoxazol-3-ium Hexachloroantimonate (**3f**)

From **1f** [25] (4.53 g, 10 mmol) as described for **3a**. After stirring at –78 °C for 20 min and at 23 °C for 1h the product crystallized at 0 °C. Washing at 0 °C with CH_2Cl_2 (20 ml) afforded a yellow powder (5.14 g, 92%); *m.p.* 130–135 °C (dec.). – IR: 1680, 1625, 1600. – ^{1}H NMR (263 K): 3.76 (CH_3), 4.96 (b, H3a), 5.48 (dd, *J*=10.1 and 3.0, H4), 6.44–6.77 (m, 4H), 7.78 (*m*-H), 7.95 (*p*-H), 8.03(*o*-H). – ^{13}C NMR (263 K): 36.1 (CH_3), 66.4 (C3a), 104.6, 113.8, 120.1, 126.9, 127.0, 130.6, 130.9, 131.8, 137.6, 141.0(C8), 171.3(C2). – $C_{15}H_{14}Cl_6NOSb$ (558.8).

3-Isopropyl-2-phenyl-3aH-cycloheptoxazol-3-ium Hexachloroantimonate (**3g**)

From **1g** [28] (4.81 g, 10 mmol) in CH_2Cl_2 (20 ml). After stirring at –78 °C for 20 min and at 23 °C for 1h the product was precipitated at –50 °C by slow addition of Et_2O (80 ml). Washing with CH_2Cl_2 (7 ml) afforded a yellow-orange powder

(4.99 g, 85%); *m.p.* 135–140 °C (dec.). – IR: 1680, 1615 (sh), 1585, 1570 (sh). – ^{1}H NMR (263 K): 1.39 (d, J=6.7), 1.79 (d, J=7.0) (CH_3), 4.81 (sept, J=6.8,CH), 4.96 (b, H3a), 5.49 (dd, J=10.3,coupl. to 6.43, J=3.1,coupl. to 4.96, H4), 6.43 (m, coupl. to 5.49, H7), 6.56 (m, 1H), 6.70–6.82 (m, 2H), 7.78 (*m*-H), 7.98 (*o,p*-H). – ^{13}C NMR (263 K): 20.4, 22.0 (CH_3), 55.4 (CH), 62.0 (C3a), 104.0, 113.9, 120.6, 126.3, 127.2, 130.7, 131.1, 131.6, 137.3, 141.0 (C8a), 172.5(C2). – $C_{17}H_{18}Cl_6NOSb$ (586.8).

Benzoylcycloheptatrienylideneisopropylammonium Hexachloroantimonate (**4g**)

A solution of **3g** (5.87 g, 10 mmol) in CH_2Cl_2 (100 ml) was stirred at 23 °C for 12h. Evaporation of the solvent and precipitation of the residue at –50 °C from CH_2Cl_2 (180 ml)/Et_2O (500 ml) afforded a yellow-orange powder (5.28 g, 90%); *m.p.* 133–136 °C. – IR: 1720, 1620, 1590. – ^{1}H NMR(300 K): 1.49 (d, J=6.7, CH_3), 4.90 (sept, J=6.7, CH), 7.54–8.23 (m, 11H). – ^{13}C NMR (300 K): 20.6 (CH_3), 54.6 (CH), 130.7, 131.7, 132.0, 136.1, 135.9, 144.8, 148.1, 165.5, 172.4 (C=O, C=N). – $C_{17}H_{18}Cl_6NOSb$ (586.8).

Acetylcycloheptatrienylideneanilinium Hexachloroantimonate (**4h**)

A solution of **2a** (1.06 g 10 mmol) in CH_2Cl_2 (10 ml) was added dropwise at 23 °C to a suspension of **1h** [29] (4.53 g, 10 mmol). The clear yellow solution was boiled under reflux for 1h. Cooling to 23 °C and slow addition of Et_2O (80 ml) afforded a pale green-yellow powder (4.58 g, 82%) which was reprecipitated at –15 °C from CH_2Cl_2 (12 ml)/Et_2O (80 ml) to give a yellow powder (4.53 g, 81%); *m.p.* 157–159 °C. – IR: 1732, 1612. – ^{1}H NMR (295 K): 2.16 (CH_3), 7.53–7.76 (m, phenyl), 8.64–8.83 (m, 6H). – ^{13}C NMR (295 K): 26.1 (CH_3), 129.8, 131.5, 132.4, 140.5, 142.0, 145.9, 150.5, 151.4, 166.9, 173.6. – $C_{15}H_{14}Cl_6NOSb$ (558.7).
When the reaction was carried out as decribed for **3a** the NMR spectra of the crude product showed mixtures of **3h** and **4h**.

Benzoylcycloheptatrienylideneanilinium Hexachloroantimonate (**4i**)

From **1i** [29] (5.15 g, 10 mmol) as described for **4h**. Yield: 5.09 g (82%) of a yellow powder which was analytically pure without reprecipitation; *m.p.* 175–180 °C (dec). – IR: 1720 (sh), 1704, 1583. – ^{1}H NMR (295 K): 7.37–7.75 (m, 10H), 8.60 (6H). – ^{13}C NMR (295 K): 129.4, 129.8, 131.0, 131.2, 132.1, 133.4, 134.4, 141.2, 145.5, 150.2, 151.4, 168.8, 172.7. $C_{20}H_{16}Cl_6NOSb$ (620.8).

(Diisopropylcarbamoyl)cycloheptatrienylidene(isopropyl) ammonium Hexachloroantimonate (**4j**)

From **1j** [30] (5.04 g, 10 mmol) as described for **3a**. Yield after reprecipitation at –20 °C from CH_2Cl_2 (30 ml)/Et_2O (240 ml): 3.96 g (65%) of a yellow leaflets; *m.p.* 157–160 °C (dec.). – IR: 1700, 1630. – ^{1}H NMR (263 K): 1.08 (d, J=6.4), 1.25 (d, J=6.4), 1.46 (d, J=6.4), 1.47 (d, J=6.7,6H), 1.59 (d, J=6.7) (CH_3), 3.75 (sept, J=6.7), 3.93 (sept, J=6.4), 4.59 (sept, J=6.7) (CH), 7.53 (m, 1H), 7.88–8.20 (m, 5H). – ^{13}C NMR (263 K): 19.5, 19.6, 19.7, 20.5, 21.2, 21.5 (CH_3), 48.3, 52.4, 53.8 (CH), 132.0, 133.0, 142.6, 143.1, 147.1, 147.8, 150.1, 164.0. – $C_{17}H_{27}Cl_6N_2OSb$ (609.9).

2,3-Dimethyl-3a-methoxycycloheptoxazol-3-ium Hexachloroantimonate (**5**)

From **2b** [31,32] and **1a** (3.91 g, 10 mmol) as described for **3a**. Precipitation at 0 °C with Et_2O (100 ml) afforded a temperature sensitive pale yellow powder (4.64 g, 88%); *m.p.* 166–168 °C (dec). – IR(nujol): 1645. – ^{1}H NMR (263 K): 2.74, 2.84, 3.55 (CH_3), 5.99 (d, J=10.5,H8), 6.82–7.02 (m, 3H), 7.19 (d, J=7.2,1H). – ^{13}C NMR (263 K;gated decoupling): 14.8 (q, J=135), 30.6 (J=145), 50.7 (J=145) (CH_3), 94.8 (b, C3a), 111.4 (dd, J=166.4 and 11.8,C4?), 116.2 (dd, J=169.3 and 7.9), 125.2 (dd, J=163.4 and 7.9), 129.5 (dd, J=160.5 and 10.8) (C5,7,8), 131.5 (dt, J=162.4 and 9.8, C6), 139.6 (C8a), 175.8 (b,C2). – $C_{11}H_{14}Cl_6NO_2Sb$ (526.7).

Acetyl(2-methoxycycloheptatrienylidene)methylammonium Hexachloroantimonate (**8**)

A solution of **5** (5.27 g, 10 mmol) in MeCN (10 ml) was stirred at 23 °C for 12h. Slow addition of Et_2O (150 ml) afforded a yellow powder (3.85 g, 73%); *m.p.* 165–167 °C (dec). – IR(nujol): 1609. – ^{1}H NMR (323 K; 250 and 600 MHz): 1.96, 3.26, 3.32 (CH_3), 7.59 (d, J=11.1), 7.69 (t, J=9.9), 7.74 (d, J=9.9), 7.95 (t, J=10.2), 8.20 (t, J=10.1) (CH). – ^{13}C NMR (323 K): 24.4, 30.2, 51.6 (CH_3), 122.1, 122.7, 123.3, 135.5, 144.4, 148.5, 157.0, 163.5(C=). – $C_{11}H_{14}Cl_6NO_2Sb$ (526.7).

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