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3,4-Dihydroquinolinium Salts: Preparation by Reaction of N-Arylnitrilium Salts with Alkenes

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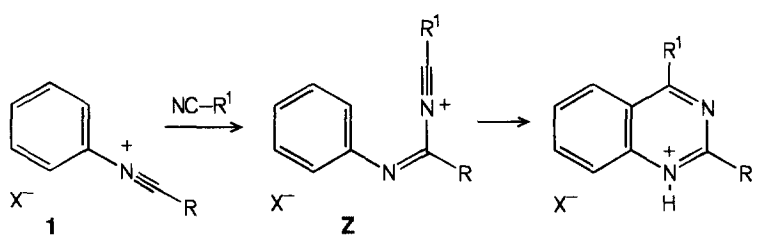
Abstract - N-Arylnitrilium salts **1** react with nucleophilic alkenes **2** to afford 3,4-dihydroquinolinium salts **3**, which can be transformed into the free bases with aqueous sodium hydroxide. Dehydrogenation of the 3,4-dihydroquinolinium salts **3** with 2,3-dichloro-5,6-dicyano-p-benzoquinone furnishes quinolinium salts **7**. If the intermediate carbenium ion **A** formed by electrophilic attack of **1** on the alkene **2** is conjugatively or hyperconjugatively stabilized, instead of 3,4-dihydroquinolinium salts **3** iminium salts **4** resulting from a Houben-Hoesch reaction, or iminium salts **5** arising from a formal ene reaction are formed. For the 3,4-dihydroquinolinium salt **3ac** X-ray structural analysis has been carried out.

Stable nitrilium salts R^1-C≡N^+-R^2 X^- were first prepared by Klages and Meerwein in 1955.[1-3] One year later Meerwein et al. described the preparation of quinazolinium salts by reaction of N-arylnitrilium salts **1** with nitriles.[4,5] Mechanistically, Meerwein's quinazoline synthesis is an intramolecular Houben-Hoesch reaction, that is, an intramolecular electrophilic aromatic substitution by an intermediate nitrilium ion **Z** .[6,7]

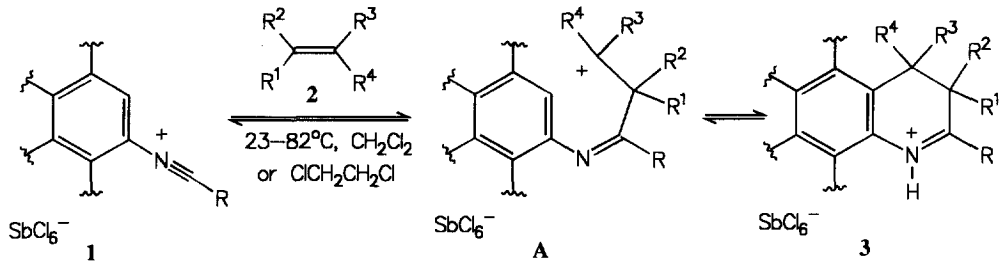


Scheme 1. Meerwein's quinazoline synthesis

Occasionally, Meerwein's quinazoline synthesis has found application.[8-16] The N-aryl group of **1** can be replaced by a heteroaryl ring,[17] by a vinyl group,[18] or by an arylamino group.[19] With acetylenes instead of nitriles R^1CN quinolinium salts are produced.[20-22] Isocyanates afford 4-oxoquinazolinium salts,[23] and azomethines furnish 4,5-dihydroquinazolinium salts.[8,24] Closely related are cyclizations, in which the C=N double bond in **Z** is replaced by other fragments. Thus, the intramolecular cyclization of N-(2-arylethyl)nitrilium salts is the well-known Bischler-Napieralski synthesis of 3,4-dihydroisoquinolinium compounds.[25,26] Isoquinolinium salts are obtained from N-(2-arylvinyl)nitrilium ions.[8,27-29] Furthermore, intramolecular additions of nitrilium ions to C=C,[8,30,31] C=N,[8,32] have been reported.

Intermolecular three-component reaction of certain nitrilium salts with nitriles and vinyl chlorides afford pyrimidinium salts.[33] Related are cycloadditions of N-arylalkylideneammonium salts with olefins to furnish 1,2,3,4-tetrahydroquinolines.[34] - Because of Meerwein's quinazoline reaction NMR spectra of N-arylnitrilium salts cannot be measured in CD_3CN as solvent.

In this study, we report cycloadditions of N-arylnitrilium salts **1** (X = $SbCl_6$) to alkenes **2** to afford 3,4-dihydroquinolinium salts **3**, which can be transformed into the neutral heterocycles with base.



Scheme 2

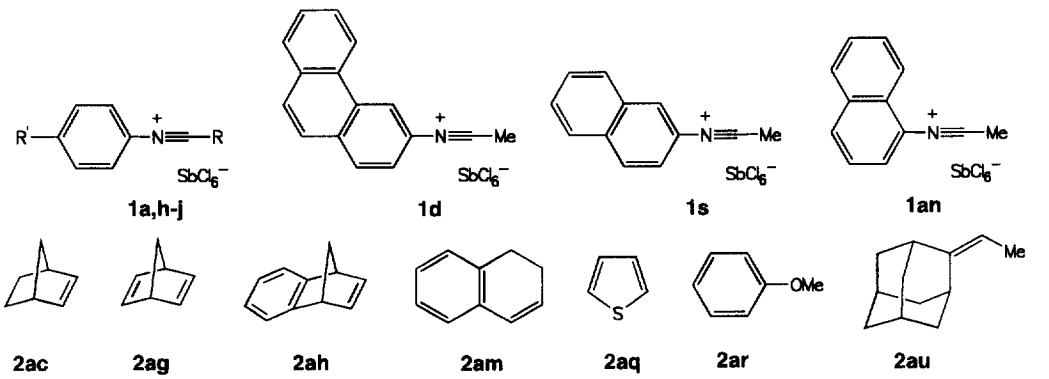
While 1,2-dihydro- and 1,2,3,4-tetrahydroquinolines are well established classes of compounds, little seems to be known about 3,4-dihydroquinolines.[35] Dehydration of oximes of ß-arylketones under acidic conditions furnishes quinolines via 3,4-dihydroquinolines as intermediates.[36] Alkylation of 1,2,3,4-tetrahydroquinoline-2-thiones gives 3,4-dihydro-2-alkylthioxyquinolines.[37,38] Such compounds were also obtained by reaction of 1-alkyl-1-hydroxyindanes with hydrazoic acid,[39] or can be prepared by palladium-catalyzed Michael addition of 2-(N-acylamino)arylmercury compounds to α,ß-unsaturated ketones followed by cyclization under the influence of acid.[40] A recent paper describes partial oxidation of 1,2,3,4-tetrahydroquinolines to 3,4-dihydroquinolines.[41] One report describes screening of some 3,4-dihydro-quinolines for their biological activities.[38]

After stirring a mixture of N-phenylacetonitrilium hexachloroantimonate (**1a**) and propene (**2b**) at room temperature in dichloromethane for fifty minutes the quinolinium salt **3b** was isolated in 74% yield. Correspondingly, the other compounds **3-6** were obtained (Table 1; Schemes 3-5).

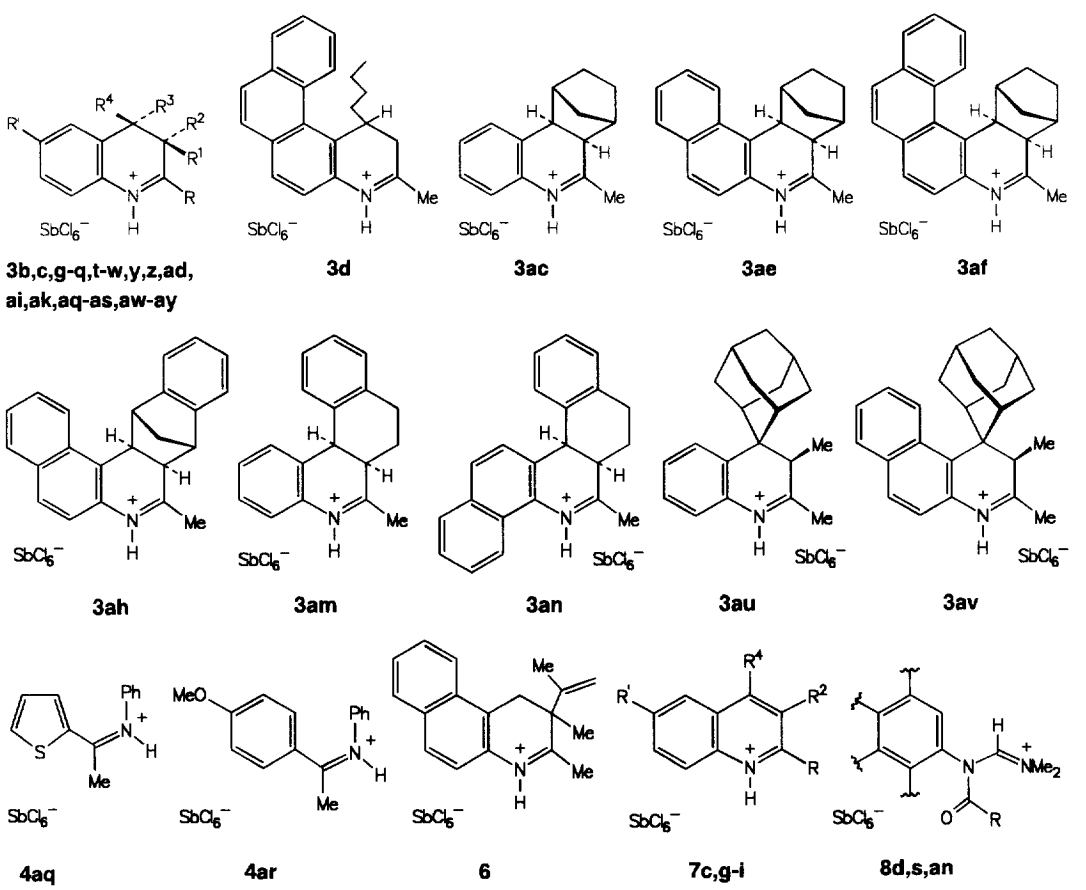
In order to check scope and limitations of this cycloaddition we studied reactions of seven N-arylnitrilium salts **1**[1,3,42] with ethene and with twenty-five mono to tetrasubstituted alkenes **2**. No well defined products were obtained with ethene. For example, while **1a** underwent smooth reactions with the monosubstituted alkenes propene (**2b**) and 1-hexene (**2c**), with ethene even after prolonged reaction time (24 hours) only mixtures of unreacted **1a**, protonated acetanilide, and unidentified products were obtained. No reactions could be achieved with less nucleophilic alkenes, such as vinyl chloride (**2e**), allyl chloride (**2f**), or allyl bromide. On the other hand, styrene (**2g**) and 1,3-butadiene (**2k**, reacting across only one double bond) afforded high yields of products (**3g-k**).

Most 1,1-disubstituted alkenes tested so far underwent cyclization. From methylene cyclopentane (**2m**) the spiro compounds **3m,n** were prepared. Small differences in the stabilities of the nitrilium salts decide in favour of or against the formation of heterocycles **3**. Thus, while α-methylstyrene (**2o**) reacted with the acetonitrilium salts **1a,h,i** to give the 3,4-dihydroquinolinium salts **3o-q** decomposition (hydrolysis) of the benzonitrilium salt **1j** and the ß-naphthylacetonitrilium salt **1s** was faster than reaction with **2o**. The N-(p-tolyl)acetonitrilium salt **1h** reacted with 1,1-diphenylethene (**2t**) to give **3t**. However, the unsubsti-

tuted nitrilium salts **1a** and the N-(p-chlorophenyl)acetonitrilium salt **1i** furnished the open-chain iminium salts **4u,v** (Scheme 5). This is consistent with the mechanism shown in Scheme 2. For R^1 = H



Scheme 3. Some starting materials

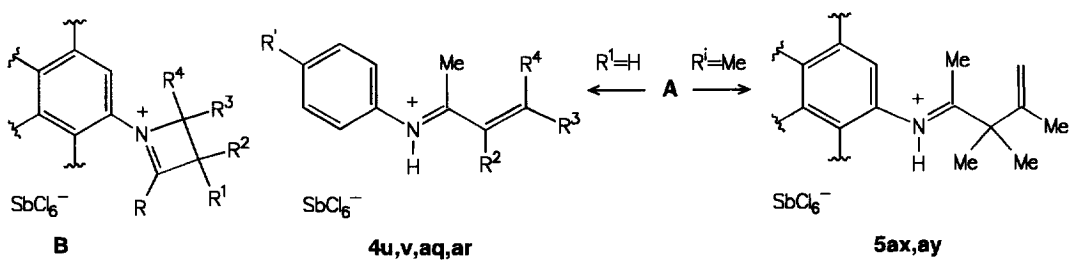


Scheme 4. Some products

Table 1. Products obtained by the reaction of N-arylnitrilium salts **1** with alkenes **2**

	R	R'	R^1	R^2	R^3	R^4	p[a]	y[b]		R	R'	R^1	R^2	R^3	R^4	p[a]	y[b]
a	Me	H	H	H	H	H	-	-	**aa**	Me	Cl	Et	H	Et	H	-	-
b	Me	H	H	H	Me	H	**3**	74	**ab**	**1s**		Et	H	Et	H	-	-
c	Me	H	H	H	Bu	H	**3**	83	**ac**	Me	H	**2ac**				**3**	83
d	**1d**		H	H	Bu	H	**3**	69	**ad**	Me	Me	**2ac**				**3**	81
e	Me	H	H	H	Cl	H	-	-	**ae**	**1s**		**2ac**				**3**	81
f	Me	H	H	H	$ClCH_2$	H	-	-	**af**	**1d**		**2ac**				**3**	82
g	Me	H	H	H	Ph	H	**3**	82	**ag**	Me	H	**2ag**				-	-
h	Me	Me	H	H	Ph	H	**3**	83	**ah**	**1s**		**2ah**				**3**	63
i	Me	Cl	H	H	Ph	H	**3**	63	**ai**	Me	H	H	$(CH_2)_3$		H	**3**	77
j	Ph	H	H	H	Ph	H	**3**	96	**aj**	Me	H	H	$(CH_2)_4$		H	-	-
k	Me	H	H	H	$H_2C=CH$	H	**3**	93	**ak**	Me	H	Me	H	Ph	H	**3**	77
l	Me	H	H	H	Me	Me	**3**	88	**al**	Me	Me	Me	H	Ph	H	-	-
m	Me	H	H	H	$(CH_2)_4$		**3**	80	**am**	Me	H	**2am**				**3**	75
n	Me	Me	H	H	$(CH_2)_4$		**3**	89	**an**	**1an**		**2am**				**3**	75
o	Me	H	H	H	Me	Ph	**3**	84	**ao**	**1s**		**2am**				-	-
p	Me	Me	H	H	Me	Ph	**3**	80	**ap**	**1d**		**2am**				-	-
q	Me	Cl	H	H	Me	Ph	**3**	55	**aq**	Me	H	**2aq**				**4**	86
r	Ph	H	H	H	Me	Ph	-	-	**ar**	Me	H	**2ar**				**4**	61
s	**1s**		H	H	Me	Ph	-	-	**as**	Me	H	H	Me	Me	Me	**3**	62
t	Me	Me	H	H	Ph	Ph	**3**	42	**at**	Ph	H	H	Me	Me	Me	-	-
u	Me	H	H	H	Ph	Ph	**4**	69	**au**	Me	H	**2au**				**3**	95
v	Me	Cl	H	H	Ph	Ph	**4**	52	**av**	**1s**		**2au**				**3**	91
w	Me	Me	H	H	$H_2C=CMe$	Me	**3**	69	**aw**	Me	H	H	$(CH_2)_4$		Me	**3**	59
x	Me	H	Me	H	Me	H	-	-	**ax**	Me	H	Me	Me	Me	Me	**5**	57
y	Me	Me	Me	H	Me	H	**3**	74	**ay**	Me	Cl	Me	Me	Me	Me	**5**	69
z	Ph	H	Et	H	Et	H	**3**	50	**az**	**1s**		Me	Me	Me	Me	**6**	75

[a] Type of product. [b] Yield (%) of isolated compound after recrystallization or reprecipitation.



Scheme 5

elimination of a proton from the intermediate **A** giving a salt **4** competes with electrophilic substitution of the aryl ring. The formation of compounds **4** can be classified as Houben-Hoesch reaction of the alkene **2**.

At time it cannot be excluded that cylization of **A** to the dihydroquinolinium salt **3** occurs via a second intermediate **B** (Scheme 5), since we found that N-*alkyl*nitrilium salts react with certain olefins to furnish stable azetinium salts.[43]

1,2-Disubstituted alkenes are less reactive than 1,1-disubstituted olefins. For instance, with (E)-2-butene (**2x**) cyclization could be achieved with the N-(p-tolyl)acetonitrilium salts **1h** but not with the N-phenyl-acetonitrilium salt **1a**. On the other hand, **1j** reacted with (E)-3-hexene (**2z**) to give **3z**, while for N-(p-chlorophenyl)nitrilium salt **1i** (and also for **1s**) decomposition was faster than reaction with **2z**. Smooth cyclizations occurred with the strained olefin norbornene (**2ac**) and with its benzo derivative **2ah**. However, no reaction could be induced between **1a** and norbornadiene (**2ag**). While cyclopentene reacted with **1a** cyclohexene gave mixtures of compounds. Similarly, 1-phenylpropene (**2ak**) underwent cycloaddition with **1a** to afford **3ak** but gave mixtures of compounds with **1h**. The closely related 1,2-dihydronaphthalene (**2am**) reacted with **1a** and the α-naphthylnitrilium salt **1an** to afford **3am,an**. However, no products were obtained with the ß-naphthylnitrilium salt **1s** or the phenanthrylnitrilium salt **1d**. Thus, while many new heterocyclic ring systems, such as **3af** or **3an** could be prepared, the hope to synthesize simple aza helicenes was not borne out. Not unexpectedly, thiophene and anisole did not react as 1,2-disubstituted alkenes but underwent Houben-Hoesch reaction to afford **4aq,ar** (Schemes 4,5).

In solution (CD_3CN) the 3,4-dihydroquinolinium salt **3ak** underwent equilibration to a second compound (ca. 5:1). If the interpretation as isomerization at C-4 is correct it would prove the reversibility of the cyclization **A** ⇌ **3**.

Sterical hindrance could be responsible for the sluggish cyclizations of trisubstituted alkenes. 2-Methyl-2-butene (**2as**) and **1a** afforded the 2,3,4,4-tetramethylquinoline **3as** in 62% yield, while the less stable benzonitrilium salt **1j** gave a mixture of compounds. From **1a** and 1-methylcyclohexene (**2aw**) a moderate yield of one stereoisomer (probably the cis form) of **3aw** was isolated. On the other hand, ethylidene-adamantane (**2au**) reacted especially smooth to afford high yields of the multicyclic compounds **3au,av**.

A tetraalkyl substituted olefin should form a rather stable cation **A**. For 2,3-dimethyl-2-butene (**2ax**) elimination of a proton from a methyl group turned out to be faster than electrophilic substitution of the aromatic ring. Hence, the nitrilium salts **1a,i** undergo formal ene reactions with **2ax** to afford the iminium salts **5ax,ay**. However, the reaction of the N-(ß-naphthyl)nitrilium salt **1s** with **2ax** gave the dehydro product **6** instead of the expected iminium salt **5az**.

In conclusion, N-arylnitrilium salts **1** react with many mono to tetra substituted alkenes to furnish 3,4-dihydroquinolinium salts **3** via intermediates **A**, which either cyclize directly or via second intermediates **B**. Effective conjugative or hyperconjugative stabilization of the carbenium ion **A** prevents cyclization to **3** affording instead iminium salts **4** (Houben-Hoesch reaction) or **5** (formal ene reaction). The formation of **3** is sensitive to sterical hindrance, requires nucleophilic olefins and a nucleophilic N-aryl moiety of **1**.

The 3,4-dihydroquinolinium salts can be transformed into the free bases by aqueous sodium hydroxide. Exemplary, the free base of the 3,4-dihydroquinoline **3ac** was prepared. The oily compound was characterized as the picrate **3ac'**.

For $R^1 = R^3 = H$ compounds **3** can be dehydrogenated to quinolinium salts **7** with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ). As examples, the salts **7c,g-i** were prepared (Scheme 4).

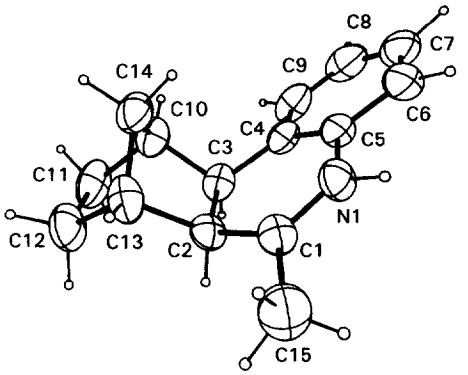


Figure 1. ORTEP-plot of the cation **3ac**

Finally, it should be mentioned that analytical data for the sensitive nitrilium salts **1d,s,an** could not be obtained. Therefore, these salts were characterized as their reaction products **8d,s,an** with N,N-dimethylformamide (Scheme 4).[44]

The structural assignments of the new compounds based on the NMR spectra, and the elemental analyses are straightforward (Experimental Section). The constitution of **3ac** was secured by X-ray crystallographic analysis (Figure 1, Table 2).[45]

Table 2. Selected bond lengths [pm], bond angles, and torsional angles [°] for the cation **3ac**[45]

C1-N1	128.6(6)	C12-C11	154(1)	C3-C4-C9	121.7(5)	C3-C4-C5-N1	5.8(7)
N1-C5	141.2(7)	C11-C10	153.8(9)	C4-C3-C10	110.0(5)	C3-C4-C9-C8	177.3(5)
C5-C4	138.5(7)	C10-C3	155.2(7)	C1-C2-C13	109.8(4)	C3-C4-C5-C6	-177.5(5)
C4-C3	152.4(8)	C10-C14	151.3(8)	N1-C1-C2-C3	10.5(7)	C3-C2-C1-C15	-170.5(5)
C3-C2	156.0(8)	C14-C13	152.2(9)	N1-C1-C2-C13	-106.4(5)	C3-C2-C13-C12	74.7(5)
C2-C1	148.0(7)	C1-C15	149.3(8)	C1-C2-C3-C4	-5.5(6)	C4-C5-N1-C1	-1.0(8)
C5-C6	140.1(7)	N1-C1-C2	121.0(5)	C1-C2-C3-C10	-124.2(5)	C4-C3-C10-C14	-82.8(5)
C6-C7	138.0(9)	C1-C2-C3	117.3(4)	C1-C2-C13-C12	-159.7(5)	C4-C3-C2-C13	115.0(4)
C7-C8	136(1)	C2-C3-C4	114.1(4)	C1-C2-C13-C14	93.3(5)	C5-N1-C1-C2	-7.5(8)
C8-C9	139(1)	C3-C4-C5	120.8(5)	C2-C3-C4-C5	- 2.2(7)	C5-N1-C1-C15	173.4(5)
C9-C4	137.9(8)	C4-C5-N1	120.2(4)	C2-C3-C4-C9	178.7(5)	C5-C4-C3-C10	111.8(5)
C2-C13	157.2(7)	N1-C1-C15	119.1(5)	C2-C3-C10-C11	- 68.4(5)	C13-C2-C1-C15	72.7(6)
C13-C12	151.9(8)	N1-C5-C6	117.3(5)	C2-C3-C10-C14	38.6(5)	C13-C2-C3-C10	-3.6(5)

Experimental Section

X-Ray diffraction analysis of **3ac**:[45] The cell constants and the reflections were measured with a Syntex P3 diffractometer (graphite monochromator, $\lambda_{Mo\text{-}K\alpha}$ = 71.073 pm). The structure was solved by direct methods with subsequent difference-Fourier synthesis using the programs SHELXS-86 and SHELXL-93, respectively. Four hydrogen atoms were included in calculated positions. The other hydrogen atoms were found by difference Fourier synthesis. All hydrogen atoms were fixed during refinement. **3ac**, $[C_{15}H_{18}N]^+SbCl_6^-\cdot CH_3CN$; MW = 587.81; crystal size [mm]: 0.5 x 0.5 x 0.5; space group C2/c; Z = 8; monoclinic; a = 2051.9(5), b = 1729.9(5), c = 1563.6(4) pm, β = 124.19(2)°; $V = 4591 \cdot 10^6$ pm^3; d_{calcd} = 1.70 Mg m^{-3}; $F(000)$ = 2320; $\mu(Mo\text{-}K_\alpha)$ = 1.906 mm^{-1}; T = 244 K; Wyckoff scan; $\Delta\omega$ = 1.4°; scan speed variable 2 to 29.3° min^{-1} in ω; $4 \le 2\Theta \le 54°$; 5146 reflections collected; 5009 independent reflections; 4336 observed reflections ($I > 2\sigma(I)$). The anisotropic refinement converged to $R_1(F_{obs.})$ = 4.88% and $R_1(F_{all})$ = 5.71%.

All experiments were carried out with exclusion of moisture in solvents dried by standard methods. Melting points: uncorrected. IR: Perkin-Elmer FTIR 1600; absorptions in cm^{-1}. ^{1}H and ^{13}C NMR spectra: Bruker AC-250 spectrometer; internal reference TMS; δ-scale; coupling constants J in Hz; solvent: CD_3CN; 295 K.

N-(3-Phenanthryl)acetonitrilium Hexachloroantimonate (**1d**)[42] and N^1-Acetyl-N^2,N^2-dimethyl-N^1-(3-phenanthryl)formamidinium Hexachloroantimonate (**8d**):[44] A solution of 3-acetylphenanthrene oxime[46] (5.88 g, 25 mmol) in Et_2O (25 ml) was added dropwise to a cold (-50°C) solution of oxalyl chloride (4.74 g, 37.3 mmol) in Et_2O (25 ml). The mixture was stirred at -50°C for 1 h. At -20°C the solvent was evaporated and the residue was dissolved in cold (-40°C) CH_2Cl_2 (25 ml). A solution of $SbCl_5$ (7.50 g, 25 mmol) in CH_2Cl_2 (25 ml) was added dropwise. Stirring at -40°C for 1 h followed by slow addition of pentane (75 ml) afforded an orange powder (**1d**, 11.25 g, 81%), for which NMR spectra could not be obtained. IR(nujol): 2362, 2342. (MW = 552.7). - A solution of DMF (0.73 g, 10 mmol) in CH_2Cl_2 (40 ml) was added dropwise to a cold (-30°C) suspension of **1d** (5.53 g, 10 mmol) in CH_2Cl_2 (40 ml). After stirring at -30°C for 20 min, then at 23°C for 2 h, the mixture was cooled to -20°C and pentane (80 ml) was added dropwise. The oily precipitate was reprecipitated first from CH_2Cl_2 (20 ml)/Et_2O (80 ml) and then from CH_2Cl_2 (30 ml)/MeCN (5 ml)/CCl_4 (30 ml) to afford a yellow powder (**8d**, 5.38 g, 83%); mp 160-164°C (dec). IR(CH_2Cl_2): 1678, 1764. ^{1}H NMR: 2.18, 2.55(d,J=0.9), 3.57(d,J=0.6)(CH_3), 8.91 (CH). ^{13}C NMR: 23.9, 41.7, 49.8(CH_3), 154.4, 172.7(C=O,C=N). (Found: C, 36.37; H, 3.12; N, 4.30. Calcd for $C_{19}H_{19}Cl_6N_2OSb$ (MW = 625.8): C, 36.46; H, 3.06; N, 4.48%).

N-(2-Naphthyl)acetonitrilium Hexachloroantimonate (**1s**)[42] and N^1-Acetyl-N^2,N^2-dimethyl-N^1-(2-naphthyl)formamidinium Hexachloroantimonate (**8s**): From 2-acetylnaphthalene oxime[47] (4.63 g, 25 mmol) in Et_2O (25 ml) as described for **1d**. Yield of **1s**: 11.98 g (95%) of a yellow powder, for which NMR spectra could not be obtained. IR(nujol): 2360. (MW = 502.7). Yield of **8s**: 4.48 g (78%) of a yellow powder; mp 173-175°C (dec). IR(CH_2Cl_2): 1678, 1768. ^{1}H NMR: 2.17, 2.58, 3.59(CH_3), 8.88(CH). ^{13}C NMR: 23.7, 41.6, 49.7(CH_3), 154.4, 172.4(C=O,C=N). (Found: C, 31.38; H, 2.95; N, 4.95. Calcd for $C_{15}H_{17}Cl_6N_2OSb$ (MW = 575.8): C, 31.29; H, 2.98; N, 4.87%).

N-(1-Naphthyl)acetonitrilium Hexachloroantimonate (**1an**)[42] and N^1-Acetyl-N^2,N^2-dimethyl-N^1-(1-naphthyl)formamidinium Hexachloroantimonate (**8an**): From 1-acetylnaphthalene oxime[48] (4.63 g, 25 mmol) as described for **1d**. Yield of **1an**: 11.85 g (94%) of a yellow powder, for which NMR spectra could not be obtained. IR(nujol): 2358; (MW = 502.7). Yield of **8an**: 4.80 g (83%) of a yellow powder; mp 176-178°C (dec). IR(CH_2Cl_2): 1679, 1765. ^{1}H NMR: 2.03, 2.36, 3.56(CH_3), 9.04(CH). ^{13}C NMR: 22.8, 40.6, 49.9(CH_3), 154.9, 172.4(C=O,C=N). (Found: C, 31.10; H, 2.94; N, 4.69. Calcd for $C_{15}H_{17}Cl_6N_2OSb$ (MW = 575.8): C, 31.29; H, 2.98; N, 4.87%).

Preparation of 3,4-Dihydroquinolinium Hexachloroantimonates: General Procedures: a) A solution of liquid **2** (10 mmol) in CH_2Cl_2 (20 ml) was added dropwise to the suspension of **1** (10 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at 23°C for the reaction time (rt) specified until a clear solution resulted. Evaporation of the solvent and crystallization of the residue at -15°C from the solvent specified afforded the pure product. b) An excess of gaseous **2** was bubbled at -20°C into a suspension of **1** (10 mmol) in CH_2Cl_2 (40 ml). Stirring at -20°C for 30 min, then at 23°C until a clear solution resulted and workup as described afforded the pure product.

3,4-Dihydro-2,4-dimethylquinolinium Hexachloroantimonate (**3b**): From **1a**[42] (4.53 g, 10 mmol) and **2b** (excess); rt 50 min; from CH_2Cl_2 (10 ml); pale yellow leaflets (3.66 g, 74%); mp 133-135°C (dec). IR(CH_2Cl_2): 1616, 1668, 3216. ^{1}N NMR: 1.30(d,J=7.0), 2.68(d,J=1.3)(CH_3), 12.29(br,t,J≈56,NH). ^{13}C NMR(gated decoupling): 20.0(q,J=127), 25.7(q,J=132)(CH_3), 27.2(d,J=135,CH), 38.0(t,J=131, CH_2), 121.1(dd,J=7.6 and 164.1,C5), 128.6(m,J≈6 and 161), 129.3(dd,J=8 and 165), 132.4(dd,J=8 and 163)(C5-8), 132.1(br), 132.9(br)(C8a,4a), 189.1(br,C=N). (Found: C, 26.69; H, 2.89; N, 2.87. Calcd for $C_{11}H_{14}Cl_6NSb$ (MW = 494.7): C, 26.71; H, 2.85; N, 2.83%).

4-Butyl-3,4-dihydro-2-methylquinolinium Hexachloroantimonate (**3c**): From **1a** (4.53 g, 10 mmol) and **2c** (0.84 g, 10 mmol); rt 10 h; from CH_2Cl_2 (6 ml)/CCl_4 (4 ml); yellow powder (4.46 g, 83%); mp 123-125°C (dec). IR(nujol): 1665, 3275. ^{1}H NMR: 0.88(t,J=7.0), 2.68(d,J=1.2)(CH_3), 12.26(br,t,J≈48, NH). ^{13}C NMR: 14.2, 23.1, 25.8, 28.9, 32.5, 34.7, 36.0(CH_3,CH_2,CH), 121.2, 129.3, 129.8, 131.9, 132.1, 132.3(aryl), 189.3(C=N). (Found: C, 31.34; H, 3.81; N, 2.66. Calcd for $C_{14}H_{20}Cl_6NSb$ (MW = 536.8): C, 31.33; H, 3.76; N, 2.61%).

1-Butyl-1,2-dihydro-3-methylnaphtho[1,2-f]quinolinium Hexachloroantimonate (**3d**): From **1d** (5.53 g, 10 mmol) in $ClCH_2CH_2Cl$ (50 ml) and **2c** (0.84 g, 10 mmol) in CH_2Cl_2 (25 ml); rt 48 h. Filtration and workup afforded a red powder. Precipitation at 23°C from CH_2Cl_2 (10 ml)/CCl_4 (15 ml), then from CH_2Cl_2 (15 ml)/MeCN (2 ml)/CCl_4 (25 ml) gave a red powder (4.40 g, 69%); mp 145-147°C (dec). IR(CH_2Cl_2): 1672, 3220. ^{1}H NMR(CD_3CN/CD_2Cl_2(7:1)): 0.92(t,J=7.2), 2.79(CH_3), 3.00(m,1H), 3.39 (d,J=9.2,1H)(CH_2), 4.27(m,CH), 12.55(br,NH). ^{13}C NMR(CD_3CN/CD_2Cl_2(7:1)): 14.3, 23.1, 25.8, 29.0, 31.6, 31.9, 34.7(CH_3,CH_2,CH), 119.9-136.3(14 lines,aryl), 188.6(C=N). (Found: C, 39.73; H, 3.76; N, 2.18. Calcd for $C_{22}H_{24}Cl_6NSb \cdot 1/2CH_2Cl_2$ (MW = 679.4): C, 39.78; H, 3.71; N, 2.06%).

3,4-Dihydro-2-methyl-4-phenylquinolinium Hexachloroantimonate (**3g**): From **1a** (4.53 g, 10 mmol) and freshly dist. **2g** (1.04 g, 10 mmol); rt 10 min; from CH_2Cl_2 (6 ml); pale yellow powder (4.56 g, 82%); mp 128-130°C (dec). IR(CH_2Cl_2): 1610, 1674, 3216. ^{1}H NMR: 2.67(d,J=1.2)(CH_3), 3.42(m,CH_2), 4.51(m,CH), 12.43(br,NH). ^{13}C NMR: 25.5, 38.3, 38.4(CH_3,CH_2,CH), 188.5(C=N). (Found: C, 34.88; H, 2.94; N, 2.52. Calcd for $C_{16}H_{16}Cl_6NSb$ (MW = 556.8): C, 34.52; H, 2.90; N, 2.52%).

3,4-Dihydro-2,6-dimethyl-4-phenylquinolinium Hexachloroantimonate (**3h**): From **1h**[42] (4.67 g, 10 mmol) and freshly dist. **2g** (1.04 g, 10 mmol); rt 1 h; from CH_2Cl_2 (10 ml)/MeCN (1 ml); yellow powder (4.76 g, 83%); mp 148-150°C (dec). IR(CH_2Cl_2): 1616, 1669, 3216. ^{1}H NMR: 2.24, 2.69(d,J=1.0)(CH_3), 4.49(m,CH), 12.49(br,NH). ^{13}C NMR: 21.5, 25.3, 38.2, 38.3(CH_3,CH_2,CH), 186.4(C=N). (Found: C, 35.70; H, 3.14; N, 2.52. Calcd for $C_{17}H_{18}Cl_6NSb$ (MW = 570.8): C, 35.77; H, 3.18; N, 2.45%).

6-Chloro-3,4-dihydro-2-methyl-4-phenylquinolinium Hexachloroantimonate (**3i**): From **1i**[23] (4.87 g, 10 mmol) and freshly dist. **2g** (1.04 g, 10 mmol); rt 20 min; from CH_2Cl_2 (10 ml)/CCl_4 (6 ml); pale yellow powder (3.72 g, 63%); mp 124-126°C (dec). IR(CH_2Cl_2): 1605, 1673, 3205. ^{1}H NMR: 2.75(d,J=1.0, CH_3), 3.47(m,CH_2), 4.55(m,CH), 12.69(br,NH). ^{13}C NMR: 25.6, 38.0, 38.1(CH_3,CH_2,CH), 188.5 (C=N). (Found: C, 32.67; H, 2.44; N, 2.32. Calcd for $C_{16}H_{15}Cl_7NSb$ (MW = 591.3): C, 32.50; H, 2.56; N, 2.37%).

3,4-Dihydro-2,4-diphenylquinolinium Hexachloroantimonate (**3j**): From **1j**[1,3] (5.15 g, 10 mmol), prepared in situ by stirring a cold (-20°C) mixture of N-phenylbenzimidoyl chloride (2.16 g, 10 mmol) and $SbCl_5$ (2.99 g, 10 mmol) in $ClCH_2CH_2Cl$ (20 ml) for 20 min, and freshly dist. **2g** (1.04 g, 10 mmol) in $ClCH_2CH_2Cl$ (20 ml). Boiling under reflux for 10 min, evaporation of the solvent and crystallization from CH_2Cl_2 (10 ml)/CCl_4 (4 ml) at -15°C afforded a yellow-brown powder (5.92 g, 96%); mp 137-139°C (dec). IR(CH_2Cl_2): 1602, 1639, 3232. ^{1}H NMR: 3.90(m,2H), 4.68(m,1H)(CH_2,CH), 12.33(br,NH). ^{13}C NMR: 35.9, 38.6(CH_2,CH), 122.4-140.8(14 lines,aryl), 178.6(C=N). (Found: C, 40.78; H, 3.02; N, 2.12. Calcd for $C_{21}H_{18}Cl_6NSb$ (MW = 618.9): C, 40.76; H, 2.93; N, 2.26%).

3,4-Dihydro-2-methyl-4-vinylquinolinium Hexachloroantimonate (**3k**): From **1a** (4.53 g, 10 mmol) in $ClCH_2CH_2Cl$ (40 ml) and **2k** (0.54 g, 10 mmol) in $ClCH_2CH_2Cl$ (40 ml); rt -15°C 10 min, 23°C 1 h. Precipitation from CH_2Cl_2 (12 ml)/MeCN (4 ml)/CCl_4 (40 ml) gave a colorless powder (4.72 g, 93%); mp 137-139°C (dec). IR(CH_2Cl_2): 1669, 3217. ^{1}H NMR: 2.68(CH_3), 3.19(m,CH_2), 3.88(m,CH), 5.09(m,J=17.0,1H), 5.26(d,J=10.2,1H), 5.89(m,1H)(vinyl), 12.51(t,J≈54,NH). ^{13}C NMR: 25.6, 36.2, 36.6(CH_3,CH_2,CH), 118.7, 121.4, 129.7, 129.8, 129.9, 132.5, 137.5(aryl,vinyl), 188.8(C=N). (Found: C, 27.92; H, 3.30; N, 3.12. Calcd for $C_{12}H_{14}Cl_6NSb$ (MW = 506.7): C, 28.44; H, 2.78; N, 2.76%).

3,4-Dihydro-2,4,4-trimethylquinolinium Hexachloroantimonate (**3l**): From **1a** (4.53 g, 10 mmol) and **2l** (excess); rt 20 min. Filtration, evaporation, and crystallization at -15°C from CH_2Cl_2 (10 ml)/CCl_4 (20 ml) furnished a yellow powder (4.48 g, 88%); mp 123-125°C (dec). IR(CH_2Cl_2): 1612, 1666, 3216. ^{1}H NMR: 1.33(6H), 2.68(d,J=1.1)(CH_3), 3.03(CH_2), 12.43(br,t,J≈55,NH). ^{13}C NMR: 25.8, 28.0, 32.0, 44.5(CH_3,CH_2,C), 121.5, 126.5, 129.2, 131.6, 132.8, 136.8(aryl), 188.5(C=N). (Found: C, 28.40; H, 3.16; N, 2.83. Calcd for $C_{12}H_{16}Cl_6NSb$ (MW = 508.7): C, 28.33; H, 3.17; N, 2.75%).

Spiro[cyclopentane-1,4'-(3,4-dihydro-2-methylquinolinium)] Hexachloroantimonate (**3m**): From **1a** (4.53 g, 10 mmol) and **2m** (0.82 g, 10 mmol); rt 30 min; from CH_2Cl_2 (6 ml); pale green prisms (4.28 g, 80%); mp 119-121°C (dec). IR(CH_2Cl_2): 1616, 1668, 3216. ^{1}H NMR: 2.71(d,J=1.1,CH_3), 3.10(CH_2), 12.54(br,t,J≈50,NH). ^{13}C NMR: 25.0, 25.8, 39.2, 42.4, 42.7(CH_3,CH_2,C), 121.4, 126.6, 129.0, 132.0, 132.5, 136.5(aryl), 188.5(C=N). (Found: C, 31.39; H, 3.43; N, 2.61. Calcd for $C_{14}H_{18}Cl_6NSb$ (MW = 534.8): C, 31.44; H, 3.39; N, 2.62%).

Spiro[cyclopentane-1,4'-(3,4-dihydro-2,6-dimethylquinolinium)] Hexachloroantimonate (**3n**): From **1h** (4.67 g, 10 mmol) and **2m** (0.82 g, 10 mmol); rt 30 min; from CH_2Cl_2 (20 ml)/CCl_4 (10 ml); pale green needles (4.86 g, 89%); mp 137-139°C (dec). IR(CH_2Cl_2): 1614, 1668, 3220. ^{1}H NMR: 2.42, 2.69(d,

J=1.3)(CH_3), 3.07(d,J=0.5,CH_2), 12.36(br,NH). ^{13}C NMR: 21.8, 25.0, 25.6, 39.1, 42.4, 42.6(CH_3, CH_2,C), 121.2, 127.0, 129.3, 129.8, 136.3, 143.3(aryl), 186.7(C=N). (Found: C, 33.00; H, 3.60; N, 2.64. Calcd for $C_{15}H_{20}Cl_6NSb$ (MW = 548.9): C, 32.83; H, 3.67; N, 2.55%).

3,4-Dihydro-2,4-dimethyl-4-phenylquinolinium Hexachloroantimonate (**3o**): From **1a** (4.53 g, 10 mmol) and **2o** (1.89 g, 16 mmol); rt 1 h; from CH_2Cl_2 (4 ml)/CCl_4 (4 ml); canary crystalline powder (4.79 g, 84%); mp 133-135°C (dec). IR(CH_2Cl_2): 1666, 3216. ^1H NMR: 1.73, 2.66(d,J=1.3)(CH_3), 3.25(dd, J=1.1 and 19.0), 3.70(d,J=19.0)(CH_2), 12.37(br,NH). ^{13}C NMR: 25.7, 27.6, 40.0, 45.0(CH_3,CH_2, C), 188.2(C=N). (Found: C, 35.76; H, 3.24; N, 2.59. Calcd for $C_{17}H_{18}Cl_6NSb$ (MW = 570.8): C, 35.77; H, 3.18; N, 2.45%).

3,4-Dihydro-2,4,6-trimethyl-4-phenylquinolinium Hexachloroantimonate (**3p**): From **1h** (4.67 g, 10 mmol) and **2o** (1.89 g, 16 mmol); rt 10 min; from CH_2Cl_2 (10 ml)/CCl_4 (4 ml); yellow powder (4.68 g, 80%); mp 143-145°C (dec). IR(CH_2Cl_2): 1677, 3206. ^1H NMR: 1.72, 2.38, 2.62(d,J=1.2)(CH_3), 3.20 (dd, J=1.1 and 19.0), 3.66(d,J=19.0)(CH_2), 12.31(br,NH). ^{13}C NMR: 21.7, 25.5, 27.6, 40.1, 44.9(CH_3, CH_2,C), 186.5(C=N). (Found: C, 36.79; H, 3.46; N, 2.60. Calcd for $C_{18}H_{20}Cl_6NSb$ (MW = 584.8): C, 36.97; H, 3.45; N, 2.40%).

6-Chloro-3,4-dihydro-2,4-dimethyl-4-phenylquinolinium Hexachloroantimonate (**3q**): From **1i** (4.87 g, 10 mmol) and **2o** (1.89 g, 16 mmol); rt 24 h; from CH_2Cl_2 (10 ml)/CCl_4 (2 ml); pale yellow powder (3.30 g, 55%); mp 146-148°C (dec). IR(CH_2Cl_2): 1670, 3222. ^1H NMR: 1.72, 2.65(br)(CH_3), 3.25(d,J=19.1), 3.69(d,J=19.1)(CH_2), 12.45(br,NH). ^{13}C NMR: 25.8, 27.4, 40.4, 44.8(CH_3,CH_2,C), 188.8(C=N). (Found: C, 33.67; H, 2.94; N, 2.63. Calcd for $C_{17}H_{17}Cl_7NSb$ (MW = 605.3): C, 33.74; H, 2.83; N, 2.31%).

3,4-Dihydro-1,6-dimethyl-4,4-diphenylquinolinium Hexachloroantimonate (**3t**): From **1h** (4.67 g, 10 mmol) and **2t** (1.80 g, 10 mmol); rt 35 min; from CH_2Cl_2 (20 ml)/CCl_4 (4 ml); pale yellow powder (2.72 g, 42%); mp 206-208°C (dec). IR(CH_2Cl_2): 1616, 1674, 3204. ^1H NMR: 2.31, 2.63(CH_3), 3.94(CH_2), 6.81(m,1H), 12.40(br,NH). ^{13}C NMR: 21.8, 25.5(CH_3), 44.0, 49.9(CH_2,C), 187.3(C=N). (Found: C, 42.55; H, 3.49; N, 2.29. Calcd for $C_{23}H_{22}Cl_6NSb$ (MW = 646.9): C, 42.70; H, 3.43; N, 2.17%).

3,4-Dihydro-4-isopropenyl-2,4,6-trimethylquinolinium Hexachloroantimonate (**3w**): From **1h** (4.67 g, 10 mmol) in $ClCH_2CH_2Cl$ (20 ml) and **2w** (0.82 g, 10 mmol) in $ClCH_2CH_2Cl$ (20 ml); rt 5 min; from CH_2Cl_2 (10 ml)/CCl_4 (4 ml); pale green powder (3.78 g, 69%); mp 128-130°C (dec). IR(CH_2Cl_2): 1608, 1666, 3215. ^1H NMR: 1.48, 1.67(d,J=0.9), 2.41, 2.66(CH_3), 2.93(d,J=19.0), 3.39(d,J=19.0) (CH_2), 4.73(br), 5.04(br)(=CH_2), 12.30(br,t,J≈48,NH). ^{13}C NMR: 19.7, 21.7, 25.4, 25.6, 41.3, 42.0 (CH_3,CH_2,C), 114.7-147.0(8 lines,aryl,vinyl), 186.9(C=N). (Found: C, 33.01; H, 4.03; N, 2.60. Calcd for $C_{15}H_{20}Cl_6NSb$ (MW = 548.8): C,32.83; H,3.67; N, 2.55%).

3,4-Dihydro-2,3,4,6-tetramethylquinolinium Hexachloroantimonate (**3y**): From **1h** (4.67 g, 10 mmol) and **2y** (excess); rt 24 h; from CH_2Cl_2 (10 ml)/CCl_4 (4 ml); colorless needles (3.97 g, 74%); mp 136-138°C (dec). IR(CH_2Cl_2): 1673, 3221. ^1H NMR: main isomer: 1.18(d,J=7.3), 1.19(d,J=7.3), 2.40, 2.69 (d,J= 1.2)(CH_3), 12.43(br,t,J≈50,NH). ^{13}C NMR: (main isomer): 15.4, 21.5, 24.6, 35.4, 42.0(CH_3,CH), 189.6(C=N); (minor isomer, ca 5%): 9.7, 14.0, 21.7, 23.9, 31.6, 40.1(CH_3,CH), 191.0(C=N). (Found: C, 29.79; H, 3.50; N, 2.89. Calcd for $C_{13}H_{18}Cl_6NSb$ (MW = 522.8): C, 29.87; H, 3.47; N, 2.68%).

3,4-Diethyl-3,4-dihydro-2-phenylquinolinium Hexachloroantimonate (**3z**): From **1j** (5.15 g, 10 mmol) and **2z** (0.84 g, 10 mmol) as described for **3j**. Boiling under reflux for 30 min, evaporation of the solvent and

crystallization at -15°C from CH_2Cl_2 (10 ml)/CCl_4 (4 ml) afforded a yellow-brown powder (2.98 g, 50%); mp 172-173°C (dec). IR(CH_2Cl_2): 1608, 1636, 3238. ^1H NMR: 0.91(t,J=7.3,6H,CH_3), 12.16 (br, NH). ^{13}C NMR: 11.5, 11.9(CH_3), 24.5, 28.3, 39.8, 44.5(CH_2,CH), 181.7(C=N). (Found: C, 37.82; H, 3.76; N, 2.44. Calcd for $C_{19}H_{22}Cl_6NSb$ (MW = 598.9): C, 38.11; H, 3.70; N, 2.34%).

6a,7,8,9,10,10a-Hexahydro-7,10-methano-6-methylphenanthridinium Hexachloroantimonate (**3ac**): From **1a** (4.53 g, 10 mmol) and **2ac** (0.94 g, 10 mmol); rt 40 min; from CH_2Cl_2 (10 ml)/CCl_4 (4 ml); pale yellow powder (4.56 g, 83%); mp 143-145°C (dec). Crystallization at 5°C from MeCN afforded prisms suitable for X-ray structural analysis. IR(CH_2Cl_2): 1674, 3216. ^1H NMR: 2.62(d,J=1.1)(CH_3), 2.49(m, 1H), 2.88(m,1H), 3.28(AB-q,J=10.4,2H), 12.10(br,t,J≈49,NH). ^{13}C NMR: 24.2, 29.2, 31.1, 36.4, 42.8, 47.0, 49.4, 50.0(CH_3,CH_2,CH), 121.1, 129.0, 129.2, 131.0, 131.1, 132.5(aryl), 186.1(C=N). (Found: C, 32.64; H, 3.34; N, 2.79. Calcd for $C_{15}H_{18}Cl_6NSb$ (MW = 546.8): C, 32.95; H, 3.32; N, 2.56%).

6a,7,8,9,10,10a-Hexahydro-7,10-methano-6-methylphenanthridinium Picrate (**3ac'**): A solution of NaOH (2.80 g, 70 mmol) in H_2O (40 ml) was added to a cold (-20°C) solution of **3ac** (5.47 g, 10 mmol) in CH_2Cl_2 (40 ml). After stirring at -20°C for 1 h and warming to 23°C the mixture was filtered. The organic phase of the filtrate was separated. The aqueous phase was extracted with CH_2Cl_2 (2x10 ml). Drying over Na_2SO_4 and evaporation of the solvent afforded a brown oil, which was dissolved in EtOH (10 ml) saturated with picric acid (ca 3 g). After 1 h a yellow crystalline precipitate (3.24 g, 74%) was collected by filtration; mp 186-188°C (dec). IR(nujol): 1615, 1689. ^1H NMR(D_6-DMSO): 2.64(CH_3), 2.43(m,1H), 2.87(m,1H), 3.26(m,2H), 8.59(picryl), 14.0(br,NH). ^{13}C NMR(D_6-DMSO): 23.3, 28.3, 30.0, 35.3, 41.6, 45.2, 48.0, 48.4(CH_3,CH_2,CH), 184.1(C=N). (Found: C, 57.18; H, 4.76; N, 12.55. Calcd for $C_{21}H_{20}N_4O_7$ (MW = 440.4): C, 57.27; H, 4.58; N, 12.72%).

6a,7,8,9,10,10a-Hexahydro-7,10-methano-2,6-dimethylphenanthridinium Hexachloroantimonate (**3ad**): From **1h** (4.67 g, 10 mmol) and **2ac** (0.94 g, 10 mmol); rt 5 min; from CH_2Cl_2 (10 ml)/CCl_4 (6 ml); yellow powder (4.54 g, 81%); mp 161-163°C (dec). IR(CH_2Cl_2): 1620, 1678, 3226. ^1H NMR: 2.36, 2.61 (d,J=1,2)(CH_3), 2.51(m,1H), 2.87(m,1H), 3.25(AB-q,J=10.4,2H), 11.96(br,NH). ^{13}C NMR: 21.5, 24.1, 29.1, 31.0, 36.4, 42.8, 46.9, 49.2, 49.8(CH_3,CH_2,CH), 120.8, 128.8, 128.9, 129.4, 131.3, 143.1(aryl), 184.4(C=N). (Found: C, 34.05; H, 3.57; N, 2.54. Calcd for $C_{16}H_{20}Cl_6NSb$ (MW = 560.8): C, 34.27; H, 3.59; N, 2.50%).

1,2,3,4,4a,12c-Hexahydro-1,3-methano-5-methylbenzo[a]phenanthridinium Hexachloroantimonate (**3ae**): From **1s** (5.03 g, 10 mmol) and **2ac** (0.94 g, 10 mmol); rt 50 min. Et_2O (100 ml) was added to the reaction mixture. Filtration afforded a yellow powder (4.98 g, 83%), which was crystallized at -15°C from CH_2Cl_2 (16 ml)/CCl_4 (6 ml) to give an orange powder (4.86 g, 81%); mp 183-185°C (dec). IR(CH_2Cl_2): 1594, 1681, 3223. ^1H NMR: 2.69(CH_3), 2.55(m,1H), 2.95(m,1H), 3.42(d,J=10.7,1H), 3.72(d,J=10.7, 1H), 11.98(br,NH). ^{13}C NMR: 23.8, 29.9, 30.4, 36.6, 40.9, 47.4, 48.4, 50.8(CH_3,CH_2,CH), 118.5-135.4(10 lines,aryl), 185.8(C=N). (Found: C, 38.23; H, 3.25; N, 2.16. Calcd for $C_{19}H_{20}Cl_6NSb$ (MW = 596.8): C, 38.24; H, 3.38; N, 2.35%).

1,2,3,4,4a,14d-Hexahydro-1,4-methano-5-methylnaphtho[1,2-a]phenanthridinium Hexachloroantimonate (**3af**): From **1d** (5.53 g, 10 mmol) in CH_2Cl_2 (30 ml) and **2ac** (0.94 g, 10 mmol) in CH_2Cl_2 (30 ml); rt 30 min; precipitation at 23°C from CH_2Cl_2 (30 ml)/MeCN (5 ml)/CCl_4 (30 ml); red powder (5.28 g, 82%); mp 180-185°C (dec). IR(nujol): 1680, 3249. ^1H NMR: 2.62(CH_3), 2.17(m,1H), 2.84(m,1H), 3.23(d, J=10.6), 4.35(d,J=10.6)(CH_2,CH), 11.89(br,NH). ^{13}C NMR: 23.6, 29.4, 31.1, 37.1, 43.8, 47.9, 48.2,

51.2(CH_3,CH_2,CH), 184.5(C=N). (Found: C, 42.85; H, 3.55; N, 2.12. Calcd for $C_{23}H_{22}Cl_6NSb$ (MW = 646.9): C, 42.70; H, 3.43; N, 2.17%).

8a,9,14,14a-Tetrahydro-9,14-methano-8-methyldibenzo[a,j]phenanthridinium Hexachloroantimonate (**3ah**): From **1s** (5.03 g, 10 mmol) and **2ah**[49] (1.44 g, 10 mmol); rt 40 min. Filtration afforded a pale orange powder, which was crystallized at -15°C from CH_2Cl_2 (5 ml)/CCl_4 (4 ml)/MeCN (5 ml) to give an orange powder (4.06 g, 63%); mp 160-162°C (dec). IR(nujol): 1667, 3268. ^{1}H NMR: 2.84(d,J=1.1,CH_3), 3.36(d,J=10.3), 3.70(d,J=10.3)(CH_2), 3.77(br), 4.19(br)(CH), 12.36(br,NH). ^{13}C NMR: 24.1, 40.4, 46.3, 49.2, 54.7, 55.6(CH_3,CH_2,CH), 118.8-148.3(16 lines,aryl), 185.6(C=N). (Found: C, 42.85; H, 3.15; N, 2.07. Calcd for $C_{23}H_{20}Cl_6NSb$ (MW = 644.9): C, 42.84; H, 3.13; N, 2.17%).

2,3,3a,9b-Tetrahydro-4-methyl-*1H*-cyclopenta[c]quinolinium Hexachloroantimonate (**3ai**): From **1a** (4.53 g, 10 mmol) and **2ai** (0.68 g, 10 mmol); rt 3 h; from CH_2Cl_2 (20 ml)/ CCl_4 (6 ml); pale brown powder (4.04 g, 77%); mp 130-132°C (dec). IR(CH_2C_2): 1613, 1668, 3222. ^{1}H NMR: 2.66(d,J=1.2,CH_3), 12.28 (br,NH). ^{13}C NMR: 24.1, 24.2, 33.5, 36.8, 36.9, 44.6(CH_3,CH_2,CH), 188.8(C=N). (Found: C, 30.07; H, 3.09; N, 2.78. Calcd for $C_{13}H_{16}Cl_6NSb$ (MW = 520.8): C, 29.98; H, 3.10; N, 2.69%).

3,4-Dihydro-2,3-dimethyl-4-phenylquinolinium Hexachloroantimonate (**3ak**): From **1a** (4.53 g, 10 mmol) and **2ak** (1.18 g, 10 mmol); rt 2 h; from CH_2Cl_2 (16 ml)/CCl_4 (4 ml); yellow powder (4.40 g, 77%); mp 125-127°C (dec). IR(CH_2Cl_2): 1661, 3210. ^{1}H NMR (equilibrating mixture (at 23°C ca 1 h) probably of the diastereomers (ca 1:5): main component: 1.31(d,J=7.0), 2.67(d,J=1.2)(CH_3), 3.49(quint,J=7.0), 4.25(d,J=7.0)(CH), 12.61(br,NH); minor component: 1.19(d,J=7.0,CH_3), 4.49(d,J=7.6,CH), 13.60(br, NH). ^{13}C NMR: major component: 15.5, 24.4(CH_3), 42.7, 45.6(CH), 191.0(C=N); minor component: 12.2, 24.0(CH_3), 40.8, 44.4(CH), 192.0(C=N). (Found: C, 35.78; H, 3.22; N, 3.67. Calcd for $C_{17}H_{18}Cl_6NSb$ (MW = 570.8): C, 35.77; H, 3.18; N, 2.45%).

6a,7,8,12b-Tetrahydro-6-methylbenzo[k]phenanthridinium Hexachloroantimonate (**3am**): From **1a** (4.53 g, 10 mmol) in $ClCH_2CH_2Cl$ (40 ml) and **2am** (1.31 g, 10 mmol) in $ClCH_2CH_2Cl$ (40 ml); rt 20 min. Et_2O (200 ml) was added to the reaction mixture. After stirring for 10 min filtration afforded a colorless powder, which was reprecipitated from CH_2Cl_2 (20 ml)/CCl_4 (40 ml); pale yellow powder (4.40 g, 75%); mp 147-149°C (dec). IR(CH_2Cl_2): 1604, 1674, 3210. ^{1}H NMR: 2.76(d,J=1.1,CH_3), 3.41(m), 4.53(d, J=5.5)(CH), 12.46(br,NH). ^{13}C NMR: 19.5, 24.2, 27.8, 36.5, 40.7(CH_3,CH_2,CH), 121.5-136.3 (12 lines, aryl), 191.2(C=N). (Found: C, 37.22; H, 3.27; N, 2.42. Calcd for $C_{18}H_{18}Cl_6NSb$ (MW = 582.8): C, 37.10; H, 3.11; N, 2.40%).

5,6,6a,14b-Tetrahydro-7-methyldibenzo[c,k]phenanthridinium Hexachloroantimonate (**3an**): From **1an** (5.03 g, 10 mmol) in $ClCH_2CH_2Cl$ (40 ml) and **2am** (1.31 g, 10 mmol) in $ClCH_2CH_2Cl$ (40 ml); rt 6 h. Addition of CCl_4 (80 ml) to the reaction mixture and filtration afforded a red-orange powder, which was reprecipitated from CH_2Cl_2 (12 ml)/MeCN (4 ml)/CCl_4 (40 ml); red powder (4.72 g, 75%); mp 145-148°C (dec). IR(nujol): 1662, 3262. ^{1}H NMR: 3.49(m), 4.67(d,J=5.7)(CH), 12.48(br,NH). ^{13}C NMR: 18.6, 24.7, 27.5, 37.0, 40.6(CH_3,CH_2,CH), 193.0(C=N). (Found: C, 41.93; H, 3.55; N, 2.42. Calcd for $C_{22}H_{20}Cl_6NSb$ (MW = 632.9): C, 41.75; H, 3.19; N, 2.21%).

3,4-Dihydro-2,3,4,4-tetramethylquinolinium Hexachloroantimonate (**3as**): From **1a** (4.53 g, 10 mmol) and **2as** (0.70 g, 10 mmol); rt 90 min; from CH_2Cl_2 (20 ml)/Et_2O (40 ml); pale yellow powder (3.26 g, 62%); mp 133-135°C (dec). IR(CH_2Cl_2): 1668, 3216. ^{1}H NMR: 1.09(d,J=7.3), 1.19, 1.40, 2.71(d,J=1.3) (CH_3), 2.99(q,J=7.3,CH), 12.35(br,t,J≈61,NH). ^{13}C NMR: 10.8, 22.3, 24.7, 28.8, 35.1, 46.9(CH_3,CH,

C), 121.5, 127.3, 129.3, 131.1, 133.1, 136.0(aryl), 192.2(C=N). (Found: C, 29.71; H, 3.46; N, 2.59. Calcd for $C_{13}H_{18}Cl_6NSb$ (MW = 522.7): C, 29.87; H, 3.47; N, 2.68%).

Spiro[(tricyclo[3.3.1.1^{3,7}]decane)-2,4'-(3,4-dihydro-2,3-dimethylquinolinium)] Hexachloroantimonate (**3au**): From **1a** (4.53 g, 10 mmol) and **2au**[50] (1.63 g, 10 mmol); rt 10 min; at 23°C from CH_2Cl_2 (12 ml)/MeCN (4 ml)/CCl_4 (40 ml); colorless powder (5.84 g, 95%); mp 179-180°C (dec). IR(CH_2Cl_2): 1670, 3218. ^{1}H NMR: 0.84(d,J=7.2), 2.69(CH_3), 3.96(q,J=7.2,CH), 12.38(br,t,J≈53,NH). ^{13}C NMR: 7.7, 24.8, 27.9, 28.0, 30.3, 33.4, 33.7, 34.1, 34.6, 35.9, 39.4, 42.0, 42.8(CH_3,CH_2,CH,C), 122.0, 128.9, 131.3, 131,8, 132.4, 135.4(aryl), 192.8(C=N). (Found: C, 39.22; H, 4.35; N, 2.65. Calcd for $C_{20}H_{26}Cl_6NSb$ (MW = 614.9): C, 39.07; H, 4.26; N, 2.28%).

Spiro[(tricyclo[3.3.1.1^{3,7}]decane)-2,4'-(3,4-dihydro-2,3-dimethylbenzo[f]quinolinium)] Hexachloroantimonate (**3av**): From **1s** (5.03 g, 10 mmol) and **2au** (1.63 g, 10 mmol) as described for **3au**. Yield: 6.05 g (91%) of an orange powder; mp 154-155°C (dec). IR(CH_2Cl_2): 1670, 3212. ^{1}H NMR(323 K): 0.88 (d, J=7.1), 2.75(CH_3), 4.02(q,J=7.1,CH), 12.49(br,t,J≈53,NH). ^{13}C NMR(323 K): 8.7, 25.0, 28.1, 28.2, 30.8, 33.6, 33.8, 34.0, 35.0, 36.1, 39.6, 42.6, 43.8(CH_3,CH_2,CH,C), 121.4, 128.9, 129.2, 129.5, 129.6, 130.7, 131.4, 132.0, 132.2, 134.6(aryl), 192.7(C=N). (Found: C, 43.21; H, 4.25; N, 2.22. Calcd for $C_{24}H_{28}Cl_6NSb$ (MW = 665.0): C, 43.35; H, 4.24; N, 2.11%).

6a,7,8,9,10,10a-Hexahydro-6,10a-dimethylphenanthridinium Hexachloroantimonate (**3aw**): From **1a** (4.53 g, 10 mmol) and **2aw** (0.96 g, 10 mmol); rt 20 min; from CH_2Cl_2 (10 ml)/CCl_4 (4 ml); colorless powder (3.24 g, 59%); mp 103-107°C (dec). IR(CH_2Cl_2): 1666, 3209. ^{1}H NMR(one stereoisomer, probably the cis form; the compound slowly decomposed in solution): 1.09, 2.72(d,J=1.2)(CH_3), 1.01-2.94(m's,9H, CH_2,CH), 12.60(br,t,J≈50,NH). ^{13}C NMR: 22.2, 24.6, 25.0, 25.1, 29.8, 32.9, 35.7, 49.8(CH_3,CH_2, CH,C), 122.1, 127.2, 129.1, 132.0, 133.1, 134.1(aryl), 190.7(C=N). (Found: C, 32.82; H, 3.80; N, 2.45. Calcd for $C_{15}H_{20}Cl_6NSb$ (MW = 548.8): C, 32.83; H, 3.67; N, 2.55%).

(1-Methyl-3,3-diphenyl-2-propenylidene)anilinium Hexachloroantimonate (**4u**): From **1a** (4.53 g, 10 mmol) and **2t** (1.80 g, 10 mmol); rt 10 min; from CH_2Cl_2 (6 ml)/pentane (2 ml); yellow-green powder (5.70 g, 90%). Crystallization at -15°C from CH_2Cl_2 (6 ml) afforded a yellow powder (4.37 g, 69%); mp 145-148°C (dec). IR(CH_2Cl_2): 1557, 1606, 3258. ^{1}H NMR: 2.14(CH_3), 6.71(CH), 11.58(br,NH). ^{13}C NMR: 24.4(CH_3), 168.5(Ph_2C), 181.0(C=N), 119.8-140.5(13 lines,CH,phenyl). The crude product contained ca 15% of **3u** (^{1}H NMR). (Found: C, 41.45; H, 3.26; N, 2.57. Calcd for $C_{22}H_{20}Cl_6NSb$ (MW = 632.9): C, 41.75; H, 3.19; N, 2.21%).

(4-Chlorophenyl)(1-methyl-3,3-diphenyl-2-propenylidene)ammonium Hexachloroantimonate (**4v**): From **1i** (4.87 g, 10 mmol) and **2t** (1.80 g, 10 mmol); rt 90 min; from CH_2Cl_2 (20 ml)/CCl_4 (10 ml); yellow powder (3.50 g, 52%); mp 175-177°C (dec). IR(CH_2Cl_2): 1562, 1604, 3252. ^{1}H NMR: 2.14(d,J=0.9, CH_3), 6.72(d,J=0.9,CH), 11.49(br,NH). ^{13}C NMR: 24.5(CH_3), 169.3(Ph_2C), 181.6(C=N). (Found: C, 39.45; H, 2.98; N, 2.53. Calcd for $C_{22}H_{19}Cl_7NSb$ (MW = 667.3): C, 39.60; H, 2.87; N, 2.10%).

1-[(2-Thienyl)ethylidene]anilinium Hexachloroantimonate (**4aq**): From **1a** (4.53 g, 10 mmol) in $ClCH_2CH_2Cl$ (20 ml) and **2aq** (1.68 g, 20 mmol) in $ClCH_2CH_2Cl$ (20 ml); rt 1 h; from CH_2Cl_2 (10 ml)/MeCN (4 ml); yellow leaflets (4.62 g, 86%); mp 167-170°C (dec). IR(CH_2Cl_2): 1584, 1604, 3252. ^{1}H NMR: 3.12(d,J=0.8,CH_3), 11.43(br,NH). ^{13}C NMR: 25.2(CH_3), 126.6, 129.9, 131.2, 132.0, 132.5, 135.1, 145.4, 145.5(aryl), 175.1(C=N). (Found: C, 26.96; H, 2.24; N, 2.68. Calcd for $C_{12}H_{12}Cl_6NSSb$ (MW = 536.7): C, 26.85; H, 2.25; N, 2.61%).

1-[(4-Methoxyphenyl)ethylidene]anilinium Hexachloroantimonate (**4ar**): From **1a** (4.53 g, 10 mmol) in $ClCH_2CH_2Cl$ (20 ml) and **2ar** (2.16 g, 20 mmol) in $ClCH_2CH_2Cl$ (20 ml). The reaction mixture was refluxed for 1 h. Workup afforded a brown oil, which was crystallized at -15°C from CH_2Cl_2 (20 ml)/MeCN (1 ml) to afford yellow leaflets (3.44 g, 61%); mp 148-151°C (dec). IR(CH_2Cl_2): 1578, 1604, 3268. ^1H NMR: 2.77, 3.99(CH_3), 11.61(br,NH). ^{13}C NMR: 20.6, 57.1(CH_3), 167.8(CO), 183.7 (C=N). (Found: C, 32.39; H, 2.82; N, 2.61. Calcd for $C_{15}H_{16}Cl_6NOSb$ (MW = 560.8): C, 32.13; H, 2.88; N, 2.50%).

(1,2,2,3-Tetramethyl-3-butenylidene)anilinium Hexachloroantimonate (**5ax**): From **1a** (4.53 g, 10 mmol) and **2ax** (0.84 g, 10 mmol); rt 2 h. After addition of Et_2O (100 ml) filtration afforded a colorless powder (3.08 g, 57%); mp 208-210°C (dec). IR(nujol): 1637, 3248, 3284. ^1H NMR: 1.61(6H), 1.84(d, J=0.6), 2.37(CH_3), 5.22(br), 5.30(m)(CH_2), 11.55(br,NH). ^{13}C NMR: 20.4, 20.5, 24.6(2C)(CH_3), 52.1(C), 117.4, 145.3(C=), 125.9, 131.1, 131.9, 135.1(phenyl), 203.4(C=N). (Found: C, 31.21; H, 3.73; N, 2.46. Calcd for $C_{14}H_{20}Cl_6NSb$ (MW = 536.9): C, 31.33; H, 3.76; N, 2.61%).

(4-Chlorophenyl)(1,2,2,3-tetramethyl-3-butenylidene)ammonium Hexachloroantimonate (**5ay**): From **1i** (4.87 g, 10 mmol) and **2ax** (0.84 g, 10 mmol); rt 90 min; from CH_2Cl_2 (6 ml)/CCl_4 (4 ml); colorless powder (3.94 g, 69%); mp 154-156°C (dec). IR(CH_2Cl_2): 1636, 3188. ^1H NMR: 1.60(6H), 1.82 (dd,J=0.5 and 1.4), 2.39(CH_3), 5.21(br), 5.30(m)(CH_2), 11.52(br,NH). ^{13}C NMR: 20.5, 20.6, 24.5 (2C)(CH_3), 52.2(C), 117.5, 145.2(C=), 127.9, 131.1, 133.7, 137.3(aryl), 204.0(C=N). (Found: C, 29.34; H, 3.51; N, 2.55. Calcd for $C_{14}H_{19}Cl_7NSb$ (MW = 571.3): C, 29.44; H, 3.35; N, 2.45%).

1,2-Dihydro-2,3-dimethyl-2-isopropenylbenzo[f]quinolinium Hexachloroantimonate (**6**): From **1s** (5.03 g, 10 mmol) and **2ax** (0.82 g, 10 mmol), however in $ClCH_2CH_2Cl$ (40 ml); rt 25 min; from CH_2Cl_2 (10 ml) /MeCN (1 ml)/CCl_4 (4 ml); orange powder (4.40 g, 75%); mp 150-153°C (dec). IR(nujol): 1681, 3242. ^1H NMR: 1.67(6H), 2.72(d,J=1.2)(CH_3), 2.95(d,J=9.7), 3.44 (d,J=9.7)(CH_2), 5.28(br), 5.39(=CH_2), 12.54(br,NH). ^{13}C NMR: 20.9, 25.0, 25.9, 43.4, 45.0(CH_3,CH_2,C), 114.4, 150.3(vinyl), 186.8(C=N). (Found: C, 37.20; H, 3.41; N, 2.32. Calcd for $C_{18}H_{20}Cl_6NSb$ (MW = 584.9): C, 36.97; H, 3.45; N, 2.40%).

4-Butyl-2-methylquinolinium Hexachloroantimonate (**7c**): A mixture of DDQ (2.27 g, 10 mmol) and **3c** (5.37 g, 10 mmol) in $ClCH_2CH_2Cl$ (80 ml) was boiled under reflux for 30 min. Cooling to 23°C, filtration, and evaporation of the filtrate afforded a dark brown powder. Crystallization at -15°C from CH_2Cl_2 (10 ml)/CCl_4 (4 ml) furnished a brown powder (4.30 g, 80%); mp 145-147°C (dec). IR(CH_2Cl_2): 1610, 1646, 3218. ^1H NMR: 0.99(t,J=7.3), 2.93(CH_3), 1.50(m,2H), 1.79(m,2H), 3.30(m, 2H)(CH_2), 7.73(H3), 13.24(br,NH). ^{13}C NMR: 14.1, 21.1, 23.3, 32.8, 33.4(CH_3,CH_2), 121.0, 124.1, 126.5, 127.2, 130.2, 135.5, 138.1, 157.7, 163.4(aryl). (Found: C, 31.29; H, 3.49; N, 2.58. Calcd for $C_{14}H_{18}Cl_6NSb$ (MW = 534.8): C, 31.44; H, 3.39; N, 2.62%).

2-Methyl-4-phenylquinolinium Hexachloroantimonate (**7g**): From **3g** (5.57 g, 10 mmol) as described for **7c**. Crystallization at -15°C from CH_2Cl_2 (20 ml) afforded a yellow-green powder (3.68 g, 66%); mp 203-205°C (dec). IR(CH_2Cl_2): 1608, 1636, 3206. ^1H NMR: 3.01(CH_3), 13.36(br,NH). ^{13}C NMR: 21.2(CH_3), 120.8-159.8(13 lines,aryl). (Found: C, 34.67; H, 2.66; N, 2.69. Calcd for $C_{16}H_{14}Cl_6NSb$ (MW = 554.8): C, 34.64; H, 2.54; N, 2.52%).

2,6-Dimethyl-4-phenylquinolinium Hexachloroantimonate (**7h**): From **3h** (5.71 g, 10 mmol) as described for **7c**. Crystallization at -15°C from CH_2Cl_2 (20 ml) afforded pale green prisms (4.78 g, 84%); mp 208-

210°C (dec). IR(CH_2Cl_2): 1608, 1644, 3210. ^1H NMR: 2.53, 2.99(CH_3), 13.26(br,NH). ^{13}C NMR: 21.0, 21.9(CH_3), 120.5-158.9(13 lines,aryl). (Found: C, 35.92; H, 2.86; N, 2.52. Calcd for $C_{17}H_{16}Cl_6NSb$ (MW = 568.8): C, 35.90; H, 2.84; N, 2.46%).

6-Chloro-2-methyl-4-phenylquinolinium Hexachloroantimonate (**7i**): From **3i** (5.91 g, 10 mmol) as described for **7c**. Crystallization at -15°C from CH_2Cl_2 (20 ml) afforded pale green needles (5.07 g, 86%); mp 208-210°C (dec). IR(CH_2Cl_2): 1608, 1634, 3195. ^1H NMR: 3.03(CH_3), 13.50(br,NH). ^{13}C NMR: 21.3(CH_3), 122.8-158.7(13 lines,aryl). (Found: C, 32.72; H, 2.36; N, 2.64. Calcd for $C_{16}H_{13}Cl_7NSb$ (MW = 589.2): C, 32.62; H, 2.22; N, 2.38%).

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References

1. Klages, F.; Grill, W. *Liebigs Ann.Chem.* **1955**, *594*, 21-32.
2. Meerwein, H. *Angew.Chem.* **1955**, *67*, 374-380.
3. Meerwein, H.; Laasch, P.; Mersch, R.; Spille, J. *Chem.Ber.* **1956**, *89*, 209-224.
4. Meerwein, H.; Laasch, P.; Mersch, R.; Nentwig, J. *Chem.Ber.* **1956**, *89*, 224-233.
5. Coy, H.N.M. *Ber.Dtsch.Chem.Ges.* **1897**, *30*, 1682-1693.
6. Ruske, W. *Friedel-Crafts and Related Reactions,* Olah, G.A. Ed., Vol.III, p.383-497, J.Wiley, New York 1964.
7. Sato, Y.; Yato, M.; Ohwada, T.; Saito, S.; Shudo, K. *J.Am.Chem.Soc.* **1995**, *117*, 3037-3043.
8. Johnson, F.; Madronero, R. *Adv.Heterocycl.Chem.* **1966**, *6*, 95-146.
9. Martin, D.; Weise, A. *Chem.Ber.* **1967**, *100*, 3736-3746.
10. Kühle, E. *Angew.Chem.* **1969**, *81*, 18-32; *Angew.Chem.,Int.Ed.Engl.* **1969**, *8*, 20.
11. Lykkeberg, J.; Klitgaard, N.A. *Acta Chem.Scand.* **1970**, *24*, 2268-2271.
12. Parra, V.G.; Madronero, R.; Vega, S. *Synthesis* **1977**, 345-346.
13. Lindeman, S.V.; Ponomarev, I.I.; Struchkov, Yu.T.; Vinogradova, S.V. *Izv.Akad.Nauk, Ser.Khim.* **1990**, *39*, 412-416; *Chem.Abstr.* **1990**, *113*, 97559.
14. Hori, M.; Iemura, R.; Hara, H.; Sukamoto, T.; Ito, K.; Ohtaka, H. *Chem.Pharm.Bull.* **1991**, *39*, 367-371.
15. Al-Talib, M. *J.Prakt.Chem.* **1993**, *335*, 711-713.
16. Zielinski, W.; Kudelko, A.; Holt, E.M. *Heterocycles* **1996**, *43*, 1201-1209.
17. Madronero, R.; Vega, S. *Synthesis* **1987**, 628-630.
18. Borodaev, S.V.; Zubkova, O.V.; Luk'yanov, S.M. *Zh.Org.Khim.* **1988**, *24*, 2330-2332.
19. Conde, S.; Corral, C.; Madronero, R. *Tetrahedron* **1974**, *30*, 195-200.
20. Schmidt, R.R. *Angew.Chem.* **1965**, *76*, 991; *Angew.Chem.,Int.Ed.Engl.* **1965**, *3*, 804.
21. Al-Talib, M.; Jochims, J.C.; Wang, Q.; Hamed, A.; Ismail, A.E. *Synthesis* **1992**, 875-878.

22. Schmidt, R.R. *Angew.Chem.* **1973**, *85*, 235-270; *Angew.Chem.,Int.Ed.Engl.* **1973**, *12*, 212.
23. Al-Talib, M.; Jochims, J.C.; Hamed, A.; Wang, Q.; Ismail, A.E. *Synthesis* **1992**, 697-701.
24. Schmidt, R.R. *Tetrahedron Lett.* **1968**, *9*, 3443-3446.
25. Fodor, G.; Nagubandi, S. *Tetrahedron* **1980**, *36*, 1279-1300.
26. Lora-Tamayo, M.; Madronero, R.; Gracián, D.; Gómez-Parra. V. *Tetrahedron* **1966**, Suppl.8, Part I, 305-312.
27. Zielinski, W. *Heterocycles* **1985**, *23*, 1639-1644.
28. Garcia, A.; Lete, E.; Villa, M.J.; Dominguez, E.; Badia, M.D. *Tetrahedron* **1988**, *44*, 6681-6686.
29. Petterson, R.C.; Bennett, J.T.; Lankin, D.C.; Lin, G.W.; Mykytka, J.P.; Troendle, T.G. *J.Org.Chem.* **1974**, *39*, 1841-1845.
30. Johnson, F.; Duquette, L.G.; Parker, W.L.; Nasutavicus, W.A. *J.Org.Chem.* **1974**, *39*, 1434-1437.
31. Schinzer, D.; Bo, Y. *Angew.Chem.* **1991**, *103*, 727-728; *Angew.Chem.,Int.Ed.Engl.* **1991**, *30*, 687.
32. Scheinbaum, M.L.; Dines, M.B. *Tetrahedron Lett.* **1971**, *12*, 2205-2208.
33. Luk'yanov, S.M.; Borodaev, S.V.; Zubkova, O.V. *Zh.Org.Khim.* **1992**, *28*, 2577-2581.
34. Beifuss, U.; Ledderhose, S. *J.Chem.Soc.,Chem.Commun.* **1995**, 2137-2138.
35. Jones, G. Ed. *Quinolines*: Weissberger, A.; Taylor, E.C. Ed's *The Chemistry of Heterocyclic Compounds*: Part 1-3, Wiley, New York, 1977, 1982, 1990.
36. Suwinski, J. *Zesz.Nauk.Politech.Slask.,Chem.* **1976**, *75*, 45-54; *Chem.Abstr.* **1977**, *87*, 39205.
37. Bhandari, K.; Virmani, V.; Murti, V.A.; Jain, P.C.; Anand, N. *Indian J.Chem.* **1979**, *17B*, 104-106.
38. Wendelin, W.; Keimelmayr, H.; Huber, M. *Sci.Pharm.* **1989**, *87*, 391-406.
39. Adam, G.; Andrieux, J.; Plat, M.M. *Tetrahedron Lett.* **1983**, *24*, 3609-3612.
40. Cacchi, S.; Palmieri, G. *Tetrahedron* **1983**, *39*, 3373-3383.
41. Goti, A.; Romani, M. *Tetrahedron Lett.* **1994**, *35*, 6567-6570.
42. Jochims, J.C.; Hehl, S.; Herzberger, S. *Synthesis* **1990**, 1128-1133.
43. Moustafa, A.H.; Jochims, J.C. *unpublished results.*
44. Jochims, J.C.; Abu-El-Halawa, R. *Synthesis* **1990**, 488-490.
45. A computer print-out of refined coordinates, structure factors, bond distances etc. is available from the Cambridge Crystallographic Centre, respectively from the British Library, Lending Devision, on request.
46. Bachmann, W.E.; Boatner, C.H. *J.Am.Chem.Soc.* **1936**, *58*, 2097-2101.
47. Sah, P.P.T. *Rec.Trav.Chim.Pays-Bas* **1940**, *59*, 1021-1028.
48. Fieser, L.F.; Holmes H.L.; Newman, M.S. *J.Am.Chem.Soc.* **1936**, *58*, 1055.
49. Wittig, G.; Knaus, E. *Chem.Ber.* **1958**, *91*, 895-907.
50. Landa, S.; Vais, J.; Burkhard, J. *Collect.Czech.Chem.Commun.* **1967**, *32*, 570-575.

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