On the Reaction of 1,3-Dichloro-2-azoniaallene Salts with Olefins and Diphenylacetylene

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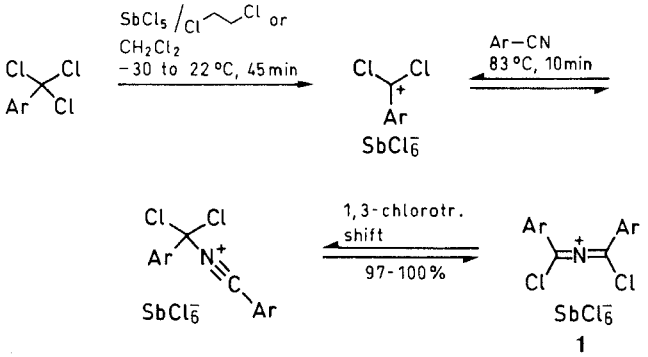
1,3-Diaryl-1,3-dichloro-2-azoniaallene salts **1** react with di-, tri- and tetraalkyl and aryl substituted olefins to form new types of 2-azoniaallene salts **4**, a 4-azapentadienyl salt **5e** or pyridinium salts **8**, respectively. The cycloaddition of olefins to 1,3-dichloro substituted 2-azoniaallene ions proceeds stepwise via carbocations. An X-ray structural analysis of the cycloadduct of **1** with norbornene is presented. With diphenylacetylene, compounds **1** react to give 11*H*-indeno[1,2-*c*]isoquinolinium salts **12**. The free bases are generated from the hexachloroantimonates by treatment with aqueous sodium hydroxide or sodium hydrogen carbonate.

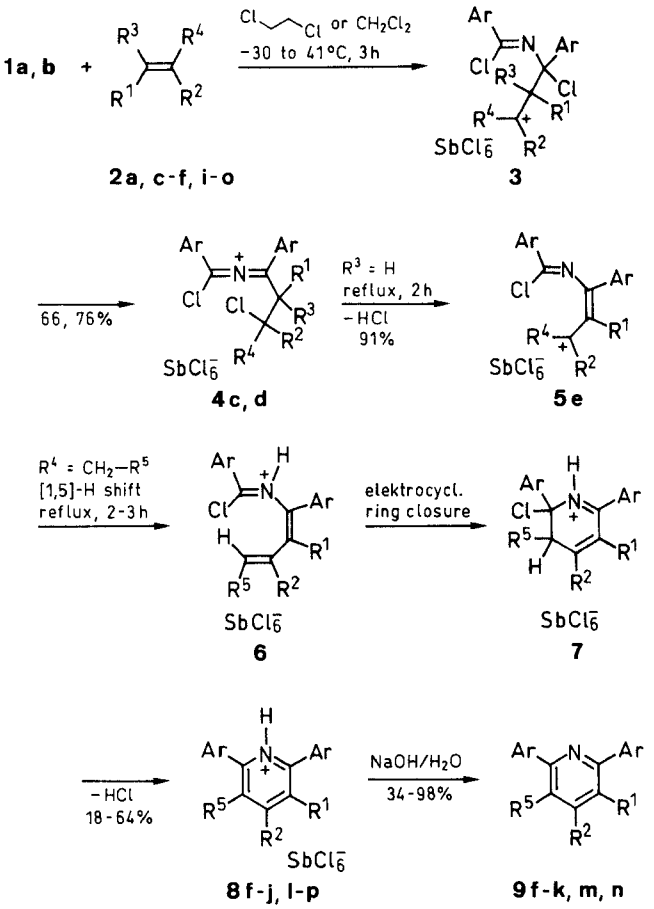
Recently we described the synthesis of the 1,3-dichloro-2-azoniaallene salts **1** by Ritter reaction of α-chlorocarbenium salts with nitriles (Scheme 1).[1-3]



Scheme 1

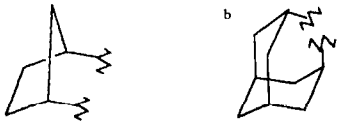
Here, we would like to report reactions of salts **1** with olefins and acetylenes. Depending on the substitution pattern of the olefin, new types of 2-azoniaallene salts **4**, a 4-azapentadienyl salt **5e**, or pyridinium salts **8**, respectively, were obtained. To account for the results the reaction sequence shown in Scheme 2 is proposed. The olefins add to the electron deficient imidic carbon atom of **1** to give carbenium salts **3**. [1,3]-Shift of chloride yields the 2-azoniaallene salts **4**. For R^3 = H spontaneous although slow elimination of hydrogen chloride furnishes the pentadienyl salt **5e**. While appropriately substituted compounds **4** and **5** could be isolated, the intermediates **6** and **7** are only plausible. For $R^4 = CH_2{-}R^5$ a [1,5]-prototropic rearrangement affords the hexatrienyl salts **6**, which undergoes electrocyclic ring closure to **7**. Elimination of hydrogen chloride provides the pyridinium salts **8**.

Stirring solutions of **1a,b** between −30 °C and 23 °C with norbornene **(2a)** in dichloromethane afforded yellow powders of mixtures of the diastereomeric 1:1 adducts **10a,a'** (29%) and **10b,b'** (78%), respectively (Scheme 3). Fractional crystallization of **10a,a'** gave a single diastereomer **10a** suitable for an X-ray structural analysis, which revealed a product with a rearranged norbornane fragment (Figure, Table 1). This, however, is indicative of a stepwise cycloaddition of **1a** to norbornene via a carbenium ion **3** as intermediate. This conclusion is based on results of Mayr et al, who have shown that addition of a carbenium ion to the C=C double bond of norbor-



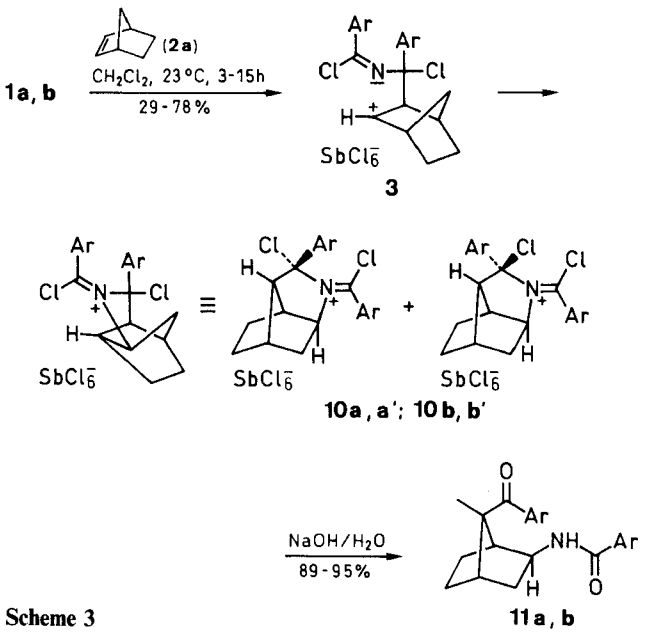
1–9	Ar	R^1	R^2	R^3	R^4	R^5
a	Ph	H	H		[a]	–
b	4-ClC_6H_4	H	H		[a]	–
c	4-ClC_6H_4	Me	Me	Me	Me	–
d	4-ClC_6H_4	H	[b]	Me	[b]	–
e	4-ClC_6H_4	H	Ph	H	Ph	–
f	Ph	Me	Me	H	Me	H
g	Ph	Me	Me_3CCHMe	H	Me	H
h	4-ClC_6H_4	Me	Me	H	Me	H

1–9	Ar	R^1	R^2	R^3	R^4	R^5
i	4-ClC_6H_4	Et	Me	H	Me	H
j	4-ClC_6H_4	$(CH_2)_4$		H	Me	H
k	4-ClC_6H_4	Cl	Me	H	Me	H
l	4-ClC_6H_4	Ph	Me	H	Me	H
m	4-ClC_6H_4	H	Me	H	Me	H
n	4-ClC_6H_4	H	Ph	H	Me	H
o	4-ClC_6H_4	H	Et	H	Et	Me
p	4-ClC_6H_4	Me	Me	H	Et	Me



Scheme 2

nene gives a cation, which undergoes fast Wagner–Meerwein rearrangements and H-shifts.[4] After quenching with a nucleophile, products exclusively with a rearranged norbornane skeleton similar to **10a** were isolated. On the other hand, concerted cycloadditions, e.g. of chlorosulfonyl isocyanate,[5–7] to the double bond of norbornene yield products without rearrangement of the norbornane skeleton. Thus, norbornene can serve as a mechanistic probe to discriminate between concerted and stepwise cycloadditions of cations to olefins. Hydrolysis of the salts **10a,a'** and **10b,b'**, respectively, afforded the amides **11a,b**.



Scheme 3

When a solution of **1b** and 2,3-dimethyl-2-butene **(2c)** in dichloromethane was stirred between −30 °C and 23 °C the 2-azoniaallene salt **4c** (66%) was produced. A strong and broad IR absorption (in dichloromethane) at 1875 cm^{-1} (shoulder 1840 cm^{-1}) and the observation of four resonances for two pairs of diastereotopic methyl groups in the ^1H and the ^{13}C NMR spectra (Table 2) are in agreement with the geometry of an allene.[9,10] Similarly, from 2-ethylideneadamantane **(2d)** the 2-azoniaallene salt **4d** was obtained (76%). This is a stable 2-azoniaallene salt in spite of an enolizable hydrogen atom in α-position to the C=N=C moiety.[11,12]

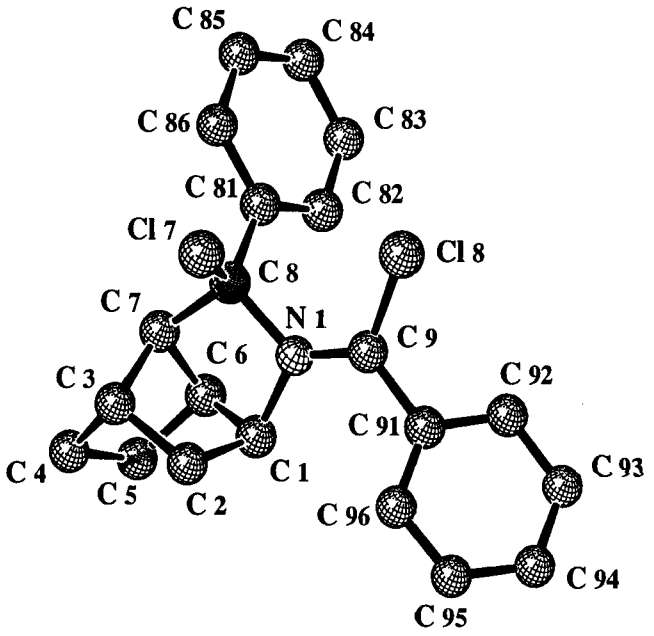


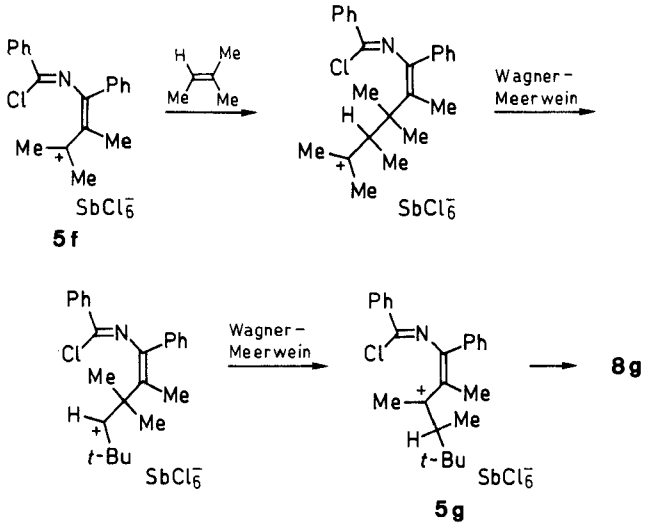
Figure. SCHAKAL Plot of the Cation **10a**

After stirring a solution of **1b** with 1,1-diphenylethene **(2e)** at −30 °C for one hour in dichloromethane the reaction mixture showed a strong IR absorption at 1879 (shoulder 1836) cm^{-1}. Obviously, a 2-azoniaallene salt **4e** was formed. On boiling under reflux, hydrogen chloride was eliminated and the band at 1879 cm^{-1} faded, while a new broad IR absorption at 1675 cm^{-1} developed. Finally, the salt **5e** was isolated almost quantitatively. Indicative for the constitution of **5e** are ^{13}C NMR signals for nonequivalent phenyl and *p*-chlorophenyl groups as well as a ^{13}C resonance at $\delta = 116.2$ for CH (gated decoupling experiment in CD_2Cl_2). According to the IR absorption at 1675 cm^{-1} (dichloromethane) the important canonical form for **5e** is that of a 4-azapentadienyl salt with the positive charge mainly located in the diphenylmethyl group. Stirring a mixture of 2-methyl-2-butene **(2f)** and **1a** at −20 °C in 1,2-dichloroethane produced a solution, which showed a strong IR band at 1865 cm^{-1} indicating the formation of **4f**. After boiling

Table 1. Selected bond lengths (pm), bond angles and torsional angles (deg) of the cation **10a**[8]

C1–C2	155.1(5)	C2–C3–C4	107.2(4)	C1–C2–C3–C7	19.9(4)
C2–C3	154.1(5)	C3–C4–C5	101.9(3)	C2–C3–C7–C8	54.7(4)
C3–C4	153.8(6)	C4–C5–C6	104.2(3)	C3–C7–C8–Cl(7)	44.6(3)
C4–C5	153.2(7)	C6–C1–C2	102.8(3)	C3–C7–C8–C81	171.0(2)
C5–C6	153.3(5)	C1–C6–C7	93.3(2)	C3–C7–C8–N1	−69.0(3)
C6–C7	153.3(5)	C2–C3–C7	102.6(3)	C7–C8–C81–C82	88.2(4)
C3–C7	152.9(5)	C6–C7–C8	103.9(3)	C7–C8–N1–C9	179.3(4)
C7–C8	153.5(4)	C7–C8–Cl(7)	111.8(2)	Cl(7)–C8–N1–C9	62.4(4)
C8–Cl(7)	178.3(3)	C7–C8–N1	100.3(2)	C8–N1–C9–Cl(8)	4.7(6)
C8–N1	152.2(4)	C7–C8–C81	111.2(3)	C8–N1–C9–C91	−174.0(4)
N1–C9	129.6(4)	Cl(7)–C8–N1	107.5(2)	N1–C9–C91–C92	−135.5(4)
C9–Cl(8)	169.0(3)	C8–N1–C9	127.3(3)	C81–C8–N1–C9	−62.0(5)
C8–C81	151.2(4)	N1–C9–Cl(8)	119.1(3)	Cl(7)–C8–C81–C82	−145.6(3)
C9–C91	147.5(4)	N1–C9–C91	125.0(3)	C6–C5–C4–C3	13.8(4)
C1–C2–C3	101.0(3)	Cl(8)–C9–C91	115.9(2)	C5–C4–C3–C7	−45.1(3)

for 3 hours under reflux (83 °C) a black tar was obtained, from which either compound **8f** (37%) or **8g** (18%) was isolated depending on the workup conditions. The ^{1}H NMR spectrum (in CD_3CN, Table 2) of **8g** showed inter alia a singlet for a *tert*-butyl group and a doublet for a methyl group coupled to a CH proton (δ = 3.38 ppm, quartet). The resonance for the pyridinium ^{13}C(5) was found at δ = 124.8, a region characteristic for a pyridinium meta carbon atom. Probably, compound **8g** was formed from an intermediate **5f**, which added another molecule of the olefin **2f** (Scheme 4). Two consecutive Wagner–Meerwein rearrangements lead to **5g**, which cyclized via **6g** and **7g** to produce **8g**. From 2-methyl-2-butene **(2f)** and **1b** the formation of a byproduct corresponding to **8g** was not observed. Only the dimethylpyridinium salt **8h** was isolated (64%).



Scheme 4

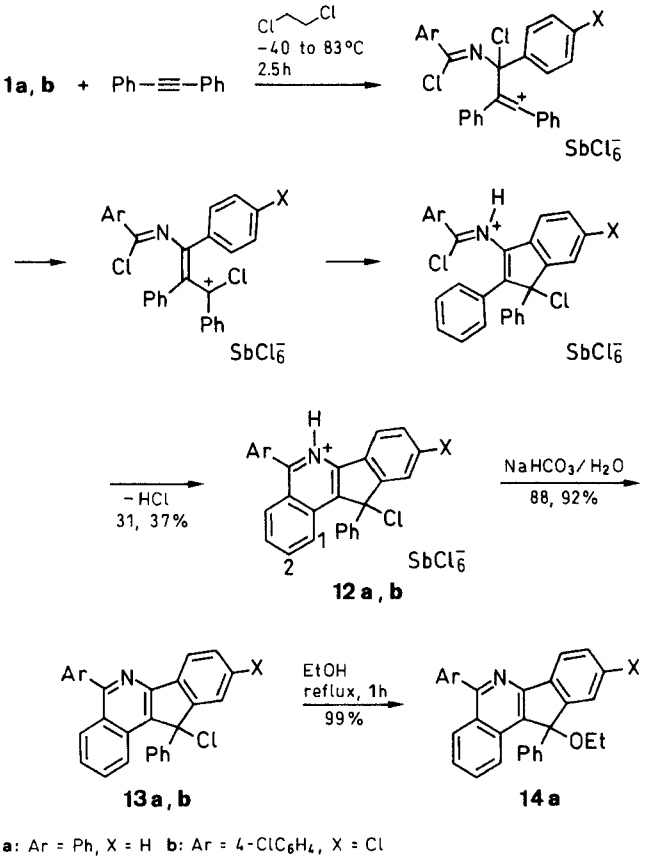
The pyridinium salts **8i–p** were obtained correspondingly. In every case the formation of an intermediate **4** at temperatures below 0 °C was monitored IR spectroscopically (bands around 1870 cm^{-1}).

From 2-ethyl-1-butene **(2o)** and **1b**, instead of the expected pyridinium salt **8o**, a mixture of **8o,p** was obtained. Compound **8p** must have been formed from 3-methyl-2-pentene **(2p)**. It was found that under the reaction conditions the olefin **2o** was quickly isomerized to a mixture of **2o** and **2p**.

With aqueous sodium hydroxide or sodium hydrogen carbonate the pyridinium salts **8** were transformed into the free bases **9**.[13]

The pyridin **9m** shows antimalarial activities.[14] The other compounds **8** and **9** seem to be unreported, with the exception of **9n**.[15]

The allenes **1a,b** reacted with several acetylenes. However, in most cases only black tars were obtained. With diphenylacetylene the heterocycles **12a,b** were isolated in moderate yields. The salts could be transformed into the bases **13a,b** with aqueous sodium hydrogen carbonate. An attempt to recrystallize **13a** from boiling ethanol resulted in a quantitative formation of the ethoxy compound **14a**. The structural assignments are based on the



Scheme 5

NMR spectra (Table 2) and the mass spectra of **13a,b**. The latter showed strong molecular peaks with the isotopic pattern expected for a monochloro and a trichloro compound, respectively. In the ^{13}C NMR spectrum ($CDCl_3$) of **14a** the expected 23 lines were found for the aryl carbon atoms. A resonance at δ = 87.9 was assigned to C(11). The ^{1}H NMR spectrum showed signals for diastereotopic CH_2 protons. For **13b** a gated decoupling experiment proved the presence of the required eleven aromatic C atoms without ^1J couplings to hydrogen atoms. A proposal for the formation of compounds **12–14** is presented in Scheme 5.

Only a few 11*H*-indeno[1,2-*c*]isoquinolines have been reported in the literature.[16–22] Some of them show moderate antitumor and antileucemic activities.[23]

In conclusion, cycloadditions of 1,3-dichloro-2-azoniaallene salts **1** (and most likely also of other 2-azoniaallene salts) to multiple bonds proceed stepwise via cations. In the case of olefins and acetylenes the intermediate carbenium ions may give rise to side reactions, e.g. oligo- and polymerizations, Wagner–Meerwein rearrangements and H-shifts.

All solvents were dried by standard methods. The experiments were carried out with exlusion of moisture. The melting points are uncorrected. IR spectra: IR-Mattson Polaris FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra: Bruker WM-250 and AC-250 spectrometers; internal reference TMS. X-Ray diffraction analysis: ENRAF-Nonius CAD4 diffractometer (graphite monochromator, $\lambda_{Mo-K\alpha}$ = 71.073 pm).

Table 2. Selected NMR and IR Data of the New Compounds Prepared

Product[a]	Molecular Formula[a]	^{1}H NMR (CD_3CN/TMS)[b] δ, J (Hz)	^{13}C NMR (CD_3CN/TMS)[b] δ, J (Hz)	IR (CH_2Cl_2) ν (cm^{-1})
4c	$C_{20}H_{20}Cl_{10}NSb$ (750.7)	1.67, 1.70, 1.80, 1.83 (CH_3), 7.71–7.98 (aryl)[c]	24.4, 25.0, 29.8, 30.3 (CH_3), 57.9, 74.6 (C), 122.7, 128.2, 131.3, 131.5, 131.8, 133.1, 143.2, 146.9 (aryl), 146.7, 175.1 (C=N)[c]	1875,[d] 1582
4d	$C_{26}H_{26}Cl_{10}NSb \cdot CH_2Cl_2$ (913.7)	1.61 (d, J = 6.5), 1.63 (d, J = 6.6) (CH_3), 4.87 (q, J = 6.6), 4.92 (q, J = 6.5) (CH), 5.45 (CH_2Cl_2), 7.70–8.15 (aryl)[e]	14.4, 15.9 (CH_3), 55.2 (CH_2Cl_2), 85.2, 85.8 (CCl), 124.4, 125.7, 126.0, 126.5, 131.2, 131.5, 131.9, 132.0, 133.3, 133.8, 132.2, 134.3, 145.4, 145.5, 146.0, 147.0 (aryl), 169.9, 174.0 (C=N)[e]	1872,[d] 1582
5e	$C_{28}H_{19}Cl_9NSb$ (810.3)	7.17–8.07 (aryl, CH)[f]	116.2 ($J_{C,H}$ = 163.4, CH), 128.5, 129.7, 129.8, 130.2, 130.5, 131.7, 132.3, 133.1, 133.4, 133.8, 137.8, 137.9, 140.0, 143.6, 147.1 (aryl), 149.8 (C-1, t, $J_{C,H}$ = 5), 176.3 (C-3), 186.0 (C-5)[c]	1675,[d] 1582
8f	$C_{19}H_{18}Cl_6NSb$ (594.8)	2.31, 2.68 (CH_3), 8.05 (CH), 7.64–7.88 (phenyl), 12.52 (NH)	15.8, 21.7 (CH_3), 126.4, 129.1, 129.5, 130.1, 130.3, 131.0, 131.7, 131.8, 135.2, 132.7, 149.8, 151.9 (phenyl, pyridyl), 161.6 (C-4)	1621
8g	$C_{24}H_{28}Cl_6NSb$ (664.9)	1.05 (9H), 1.39 (d, J = 7.0), 2.38 (CH_3), 3.38 (q, J = 7.0, CH), 7.94 (CH), 7.60–7.85 (phenyl), 12.56 (NH)	16.4, 17.2, 27.8 (3-C) (CH_3), 36.3, 45.6 (CH, C), 124.8, 129.6, 129.8, 130.2, 130.5, 131.5, 131.9, 132.7, 132.9, 135.3, 149.7, 153.0, 168.3 (phenyl, pyridyl)	1620, 1594
8h	$C_{19}H_{16}Cl_8NSb$ (663.7)	2.31, 2.68 (CH_3), 8.05 (CH), 7.60–7.86 (aryl), 12.58 (NH)	16.2, 22.1 (CH_3), 127.1, 130.0, 130.1, 130.6, 131.2, 132.5, 136.1, 137.9, 139.1, 149.2, 151.2 (aryl, pyridyl), 162.3 (C-4)	1615[g], 1605
8i	$C_{20}H_{18}Cl_8NSb$ (677.7)	1.07 (t, J = 7.6), 2.74 (CH_3), 2.69 (q, J = 7.6, CH_2), 8.07 (d, J = 1.5, CH), 7.60–7.84 (aryl), 12.58 (NH)	13.6, 21.3 (CH_3), 22.9 (CH_2), 127.9, 129.9, 130.5, 131.0, 132.1, 137.8, 139.1, 141.3, 149.1, 151.6 (aryl, pyridyl), 161.7 (C-4)	
8j	$C_{21}H_{18}Cl_8NSb$ (689.7)	1.87 (m, 4H), 2.68 (m, 2H), 3.15 (m, 2H) (CH_2), 7.93 (CH), 7.57–7.83 (aryl), 12.35 (NH)[h]	21.6, 22.3, 27.2, 31.5 (CH_2), 126.7, 130.2, 130.3, 130.7, 131.1, 132.3, 136.8, 138.2, 139.1, 148.6, 152.1 (aryl, pyridyl), 162.8 (C-4)[h]	1625, 1594
8l	$C_{24}H_{18}Cl_8NSb$ (725.8)	2.46 (d, J = 0.4, CH_3), 8.19 (d, J = 0.4, CH), 7.19–7.93 (phenyl, aryl), 12.77 (NH)	22.6 (CH_3), 127.8, 129.4, 129.8, 129.9, 130.0, 130.7, 130.8, 131.4, 133.0, 134.1, 137.6, 139.4, 140.3, 150.7, 151.6 (aryl, pyridyl), 161.8 (C-4)	1621, 1601
8m	$C_{18}H_{14}Cl_8NSb$ (649.7)	2.75 (CH_3), 8.01 (CH), 7.69–7.91 (aryl), 12.63 (NH)	22.5 (CH_3), 126.6, 129.9, 130.2, 131.2, 139.0, 151.9 (aryl, pyridyl), 162.6 (C-4)	1613
8n	$C_{23}H_{16}Cl_8NSb$ (711.7)	8.30 (CH), 7.54–8.34 (phenyl, aryl), 8.91 (NH)[i]	117.0 (C-3, 5), 127.3, 128.6, 128.8, 129.0, 129.1, 129.4, 134.3, 137.0 (phenyl, aryl), 150.1, 155.1 (C-2, 4, 6)[i]	1605
8o, **8p**[j]	$C_{20}H_{18}Cl_8NSb$ (677.7)	**8o**: 1.41 (t, J = 7.6), 2.36[k] (CH_3), 3.03 (q, J = 7.6, CH_2), 8.04 (d, J = 1.7, CH), 12.60 (NH); **8p**: 2.33[k] (6H), 2.61[k] (3H) (CH_3), ca. 12.50 (NH)	13.0, 15.6, 17.1, 19.0, 28.4 (CH_3, CH_2), 125.3–166.8 (19 lines for aryl, pyridyl)	1605
9f	$C_{19}H_{17}N$ (259.3)	2.24, 2.35 (CH_3), 7.48 (H5), 7.33–8.05 (phenyl)[l]	16.2, 20.4 (CH_3), 120.4, (C-5), 126.8, 127.6, 127.9, 128.3, 128.4, 128.5, 129.4, 139.6, 141.5 (phenyl, C-3), 147.2, 153.8, 158.4 (C-2, 4, 6)[l]	1590, 1551
9g	$C_{24}H_{17}N$ (329.5)	1.00 (9H), 1.30 (d, J = 7.1), 2.31 (CH_3), 3.10 (q, J = 7.1, CH), 7.40–8.02 (phenyl, H5)[l]	16.4, 17.2, 27.8 (3-C) (CH_3), 34.8, 43.2 (CH, C), 118.1 (C-5), 126.9, 127.5, 128.0, 128.1, 128.3, 128.5, 129.4, 140.0, 142.4 (phenyl, C-3), 153.3, 154.5, 159.3 (C-2, 4, 6)[l]	1580[d,m]
9h	$C_{19}H_{15}Cl_2N$ (328.2)	2.25, 2.38 (CH_3), 7.23–7.97 (phenyl, H5)[l]	16.2, 20.5 (CH_3), 120.3 (C-5), 127.9, 128.1, 128.5, 130.7, 133.6, 134.4, 137.5, 139.4 (phenyl, C-3), 147.6, 152.5, 157.0 (C-2, 4, 6)[l]	1594[d,m]
9i	$C_{20}H_{17}Cl_2N$ (342.3)	1.05 (t, J = 7.5), 2.43 (CH_3), 2.63 (q, J = 7.5, CH_2), 7.34–7.94 (aryl, H5)[l]	14.2, 19.6, 22.2 (CH_3, CH_2), 121.2 (C-5), 128.1, 128.2, 128.7, 130.3, 133.7, 134.6, 134.8, 137.7, 140.0 (aryl, C-3), 146.9, 152.7, 157.8 (C-2, 4, 6)[l]	1594[d]
9j	$C_{21}H_{17}Cl_2N$ (354.3)	1.71–1.85 (m, 4H), 2.67 (m, 2H), 2.86 (m, 2H) (CH_2), 7.38 (H4), 7.35–7.95 (aryl)[l]	22.2, 23.1, 27.6, 29.6 (CH_2), 119.7 (C-4), 128.0, 128.2, 128.7, 129.8, 130.6, 133.9, 134.5, 137.8, 139.1 (aryl, C-8a), 147.9, 152.3, 157.3 (C-1, 3, 4a)[l]	1659, 1594
9k	$C_{18}H_{12}Cl_3N$ (348.7)	2.49 (CH_3), 7.54 (H5), 7.23–7.96 (aryl)[l]	20.9 (CH_3), 121.1 (C-5), 128.1, 128.9, 129.4, 131.1, 134.8, 135.3, 136.6, 137.3 (aryl, C-3), 147.3, 153.2, 155.1 (C-2, 4, 6)[l]	1594[d]
9m	$C_{18}H_{13}Cl_2N$ (314.2)	2.44 (CH_3), 7.45 (H3, 5), 7.44 (m), 8.04 (m) (aryl)[l]	21.4 (CH_3), 119.7 (C-3, 5), 128.2, 128.8 (*o,m*-aryl), 135.0, 137.8 (*i,p*-aryl), 148.7, 155.7 (C-2, 4, 6)[l]	1605
9n	$C_{23}H_{15}Cl_2N$ (376.3)	7.83 (H3, 5), 7.48 (m), 7.70 (m) (phenyl, m-aryl), 8.11 (m, o-aryl)[l]	117.1 (C-3, 5), 127.2, 128.4, 128.9, 129.2, 135.3, 137.8, 138.7 (aryl, phenyl), 150.6, 156.3 (C-2, 4, 6)[l]	1601
10a, **10a'**[n]	$C_{21}H_{20}Cl_8NSb$ (691.8)	5.19 (H1)[h]	main isomer: 21.0, 31.3, 34.4, 39.4, 45.8, 65.2, 77.3, 97.6 (sp^3-C); minor isomer: 20.2, 31.8, 32.6, 37.8, 48.4, 66.2, 80.0, 97.2 (sp^3-C)[h]	1575, 1590[e]
10b, **10b'**[o]	$C_{21}H_{18}Cl_{10}NSb$ (760.6)	5.19 (H1)[o]	main isomer: 20.8, 31.0, 34.1, 39.0, 45.5, 64.5, 76.6, 96.5 (sp^3-C), 172.1 (C=N); minor isomer: 19.9, 31.6, 32.4, 37.2, 48.2, 65.4, 79.3, 96.1 (sp^3-C), 174.3 (C=N)[o]	1574[d]

Table 2. (continued)

Product[a]	Molecular Formula[a]	^{1}H NMR (CD_3CN/TMS)[b] δ, J (Hz)	^{13}C NMR (CD_3CN/TMS)[b] δ, J (Hz)	IR (CH_2Cl_2) ν (cm^{-1})
11a	$C_{21}H_{21}NO_2$ (319.4)	1.36–2.09 (m, 6H), 2.72 (m, 2H), 3.42 (m, H7), 4.28 (m, H2)[l]	28.3, 28.6, 39.1, 42.1, 45.6, 52.1, 57.9 (CH_2, CH), 126.9, 128.4 (2C), 128.7, 131.1, 133.5, 134.8, 136.7 (phenyl), 166.0, 203.4 (C=O)[l]	1680, 1670[e,m]
11b	$C_{21}H_{19}Cl_2NO_2$ (388.3)	1.37–2.08 (m, 6H), 2.68 (m, 2H), 3.36 (m, H7), 4.24 (m, H2)[l]	28.3, 28.6, 39.0, 42.2, 45.6, 52.2, 57.9 (CH_2, CH), 128.4, 128.7, 129.0, 129.9, 133.3, 135.0, 137.3, 140.1 (aryl), 164.9, 202.2 (C=O)[l]	1667[m]
12a	$C_{28}H_{19}Cl_7NSb$ (739.4)	7.38–8.30 (aryl), 14.01 (NH)[p]	72.1 (C), 122.8, 124.9, 125.7, 126.2, 126.8, 129.3, 129.5, 129.6, 130.2, 130.7, 131.2, 132.0, 132.9, 133.0, 135.3, 136.8, 137.7, 139.8, 142.7, 151.3, 159.4 (aryl)[p]	1640, 1610
12b	$C_{28}H_{17}ClNSb$ (808.3)	7.35–8.12 (aryl), 12.48 (NH)[i]	72.1 (C), 122.2, 123.3, 124.5, 125.7, 126.0, 127.7, 128.3, 128.6, 128.7, 128.9, 129.7, 131.6, 131.7, 131.8, 133.4, 134.2, 135.7, 136.5, 137.9, 148.8, 152.1, 161.9 (aryl)[i]	1630, 1600, 1580[q]
13a	$C_{28}H_{18}ClN$ (403.9)	7.23–8.55 (aryl)[l]	73.3 (C), 121.2, 124.1, 124.5, 126.3, 126.5, 127.0, 128.1, 128.4, 128.7, 128.9, 129.2, 129.4, 130.3, 130.7, 132.5, 133.8, 138.6, 139.7, 139.9, 151.2, 151.8, 164.0[l]	1615, 1550, 1560[e]
13b	$C_{28}H_{16}Cl_3N$ (472.8)	7.24–8.08 (aryl)[l]	72.5 (C), 122.1, 124.1, 125.1, 126.1, 126.7, 126.9, 128.4, 128.6, 128.7, 128.8, 129.6, 130.9, 131.6, 132.3, 134.0, 135.1, 135.2, 136.9, 137.8, 138.9 (aryl), 150.7, 152.6, 162.7 (C-5, 6a, 11b)[l]	1620,[e] 1598[m]
14a	$C_{30}H_{23}NO$ (413.5)	1.13 (t, J = 7.0, CH_3), 3.07 (16 lines, CH_2), 7.13–8.12 (aryl)[l]	15.6 (CH_3), 59.2 (OCH_2), 87.9 (OC), 120.8, 123.8, 124.2, 125.5, 126.3, 126.4, 127.1, 128.2, 128.4, 128.7, 128.8, 128.9, 129.0, 130.3, 130.5, 132.8, 133.6, 139.8, 140.6, 142.8, 149.5, 153.3, 163.2 (aryl)[l]	1620[m]

[a] Satisfactory microanalyses obtained: C ± 0.25, H ± 0.24, N ± 0.31 %.
[b] At 295 K.
[c] In CD_2Cl_2 at 273 K.
[d] Broad.
[e] Shoulder.
[f] Mixture of two diastereomers (≈ 1 : 0.8)
[g] In CD_2Cl_2 at 295 K.
[h] At 333 K.
[i] In DMSO-d_6.
[j] Spectrum of a mixture of **8o** and **8p**, ratio 2 : 1.
[k] Assignment by means of a nuclear Overhauser effect.
[l] In $CDCl_3$.
[m] In CCl_4.
[n] Mixture of two diastereomers, ratio ca 1 : 3.
[o] Mixture of two diastereomers, ratio ca 1 : 2; in CD_3CN/CD_2Cl_2 (1 : 1) at 273 K.
[p] In $CDCl_3/CD_3CN$ (4 : 1).
[q] In KBr.

1,3-Dichloro-1,3-diphenyl-2-azoniaallene Hexachloroantimonate (1a);[1]
A solution of $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 mL) was added dropwise with stirring to a cold (−30 °C) solution of $PhCCl_3$ (1.96 g, 10 mmol) and PhCN (1.03 g, 10 mmol) in CH_2Cl_2 (45 mL). An orange precipitate was formed. The mixture was stirred at −30 °C for 15 min, warmed to 23 °C and boiled under reflux for 30 min. The reaction mixture was used for cycloaddition reactions without isolation of **1a**.[1]

1,3-Dichloro-1,3-bis(4-chlorophenyl)-2-azoniaallene Hexachloroantimonate (1b):[1]
From 4-$ClC_6H_4CCl_3$ (2.30 g, 10 mmol) and 4-ClC_6H_4CN (1.38 g, 10 mmol) as described for **1a**. The product crystallized at −20 °C from the reaction mixture to afford moisture sensitive orange prisms; yield: 5.87 g (88 %); mp 144–147 °C (dec).

Reaction of 1a,b with Olefins 2; General Procedure:
A solution of the olefin **2** (10 mmol) in CH_2Cl_2 (5 mL) was added to a cold (−40 °C) suspension of **1** (10 mmol, prepared without isolation) in CH_2Cl_2 (55 mL). The mixture was stirred at −30 °C for 1 h and at 23 °C for 2 h. The solvent was evaporated and the residue was purified.

1,5-Dichloro-1,3-bis(4-chlorophenyl)-4,4,5-trimethyl-2-azoniahexa-1,2-diene Hexachloroantimonate **(4c)**: From **2c** (0.84 g, 10 mmol) and **1b** (6.67 g, 10 mmol). Evaporation of the solvent afforded a brown foam, which was dissolved in MeCN (5 mL). At −30 °C Et_2O (15 mL) was added slowly. The yellow-brown precipitate (4.93 g, 66 %) was twice reprecipitated from CH_2Cl_2 (5 mL)/MeCN (1 mL)/Et_2O (25 mL) to furnish a pale yellow powder; yield: 2.48 g (33 %); mp 125–130 °C (dec).

1-Chloro-1,3-bis(4-chlorophenyl)-4-(2-chlorotricyclo[3.3.1.1^{3,7}]dec-2-yl)-2-azoniapenta-1,2-diene Hexachloroantimonate · CH_2Cl_2 **(4d)**: From **2d**[24,25] (1.80 g, 11 mmol) and **1b** (6.67 g, 10 mmol). However, the reaction mixture was boiled under reflux for 30 min. Concentration to a volume of 15 mL and slow addition of Et_2O (20 mL) afforded a moisture sensitive yellow powder (6.96 g, 76 %), which was washed with Et_2O (10 mL). Reprecipitation from CH_2Cl_2 (20 mL)/MeCN (5 mL)/Et_2O (35 mL) furnished a pale yellow powder; yield: 5.98 g (65 %); mp 110–115 °C (dec above 150 °C).

1-Chloro-1,3-bis(4-chlorophenyl)-5,5-diphenyl-2-azapenta-2,4-dienylium Hexachloroantimonate **(5e)**: From **2e** (3.60 g, 20 mmol) and **1b** (6.67 g, 10 mmol). After stirring at −30 °C for 1 h the dark red solution showed a strong IR absorption at 1879 cm^{-1} (1836 sh). The mixture was boiled under reflux for 90 min. Evaporation of the solvent afforded a foam, which was stirred under Et_2O (30 mL) for 2 h. The dark red powder (7.39 g, 91 %) was crystallized from CH_2Cl_2 (10 mL)/Et_2O (30 mL) to afford dark red prisms; yield: 6.55 g (81 %); mp 144–148 °C (dec).

3,4-Dimethyl-2,6-diphenylpyridinium Hexachloroantimonate **(8f)**: From **2f** (1.05 g, 15 mmol) and **1a** (5.98 g, 10 mmol), however, at −20 °C and in $ClCH_2CH_2Cl$ (60 mL) as solvent. At −20 °C the mixture showed a strong IR absorption at 1865, 1830 (sh) cm^{-1}. After stirring for 1 h at −15 °C the mixture was boiled under reflux for 3 h. Evaporation of the solvent afforded a black foam, which was dissolved in CH_2Cl_2 (15 mL). On slow addition of pentane (15 mL) a brownish powder precipitated, which was reprecipitated from CH_2Cl_2 (15 mL)/pentane (15 mL) to give a pale yellow powder; yield: 2.21 g (37 %); mp 214–216 °C.

3-Methyl-2,6-diphenyl-4-(1,2,2-trimethylpropyl)pyridinium Hexachloroantimonate (**8g**): From **2f** (1.05 g, 15 mmol) and **1a** (5.98 g, 10 mmol), however, at −40 °C and in $ClCH_2CH_2Cl$ (60 mL) as solvent. After stirring for 1 h at −30 °C the mixture was boiled under reflux for 3 h. Evaporation of the solvent afforded a black foam, which was dissolved in CH_2Cl_2 (5 mL). On slow addition of Et_2O (15 mL) an almost colorless powder precipitated (1.23 g, 18%), which was washed with CH_2Cl_2 (5 mL)/Et_2O (10 mL). The Et_2O containing product was dissolved in CH_2Cl_2 (20 mL), and the solution was evaporated. The residue was once more dissolved in CH_2Cl_2 (20 mL). Evaporation of the solvent gave an Et_2O-free product; yield: 1.11 g (17%); mp 240–244 °C.

2,6-Bis(4-chlorophenyl)-3,4-dimethylpyridinium Hexachloroantimonate (**8h**): From **2f** (1.05 g, 15 mmol) and **1b** (6.67 g, 10 mmol). At −10 °C the mixture showed a strong IR absorption at 1867 cm^{-1}. The mixture was boiled under reflux for 3 h. Evaporation of the solvent and stirring the residue under Et_2O (20 mL) afforded a pale yellow powder; yield: 4.28 g (64%); mp 236–241 °C (dec).

2,6-Bis(4-chlorophenyl)-3-ethyl-4-methylpyridinium Hexachloroantimonate (**8i**): From **2i** (0.93 g, 11 mmol) and **1b** (6.67 g, 10 mmol) as described for **8g**. At −30 °C the mixture showed a strong IR absorption at 1864 cm^{-1}. After boiling under reflux for 3 h and evaporation of the solvent the residue was suspended in CH_2Cl_2 (10 mL) and pentane (10 mL) was added dropwise. The solid was filtered off and washed with CH_2Cl_2 (2 mL)/pentane (2 mL) to give a brownish powder (4.32 g, 64%), which was reprecipitated from CH_2Cl_2 (10 mL)/MeCN (2 mL)/pentane (15 mL) to afford a pale yellow powder; yield: 2.74 g (41%); mp 240–242 °C.

1,3-Bis(4-chlorophenyl)-5,6,7,8-tetrahydroisoquinolinium Hexachloroantimonate (**8j**): From **2j** (1.06 g, 11 mmol) and **1b** (6.67 g, 10 mmol) as described for **8g**. At −30 °C the mixture showed a strong IR band at 1865 cm^{-1}. After boiling for 3 h the mixture was concentrated to a volume of 25 mL. Pentane (10 mL) was added and the pale yellow powder (3.12 g, 45%) formed was filtered off. Crystallization from MeCN (20 mL, −20 °C) afforded a pale yellow powder; yield: 2.06 g (30%); mp 216–218 °C.

2,6-Bis(4-chlorophenyl)-4-methyl-3-phenylpyridinium Hexachloroantimonate (**8l**): From **2l** (5.29 g, 40 mmol) and **1b** (6.67 g, 10 mmol). The mixture was stirred at −30 °C for 4 h (IR absorption at 1870 cm^{-1}), then at 23 °C for 2 h, and was finally boiled under reflux for 2 h. After concentration to a volume of 20 mL and cooling the brown powder formed was filtered off. On stirring with CH_2Cl_2 (10 mL)/Et_2O (40 mL) a pale yellow powder was obtained; yield: 1.52 g (21%); mp 230–234 °C (dec).

2,6-Bis(4-chlorophenyl)-4-methylpyridinium Hexachloroantimonate (**8m**): From **2m** (1.12 g, 20 mmol, condensed into CH_2Cl_2 at −30 °C) and **1b** (6.67 g, 10 mmol). After concentration to a volume of 20 mL and cooling a yellow powder was filtered off; yield: 1.62 g (25%); mp 253–256 °C (dec).

2,6-Bis(4-chlorophenyl)-4-phenylpyridinium Hexachloroantimonate (**8n**): From **2n** (3.55 g, 30 mmol) and **1b** (6.67 g, 10 mmol) as described for **8h**. The mixture was concentrated to a volume of 30 mL. The red precipitate (3.34 g, 47%) was filtered off and stirred under CCl_4 (40 mL). Yield 3.34 g (47%) of a red powder, which was crystallized from MeCN (70 mL, −20 °C) to afford yellow needles; yield: 2.00 g (28%); mp 301–303 °C (dec).

Mixture of 2,4-Bis(4-chlorophenyl)-4-ethyl-3-methylpyridinium Hexachloroantimonate (**8o**) *and 2,4-Bis(4-chlorophenyl)-3,4,5-trimethylpyridinium Hexachloroantimonate* (**8p**): From **2o** (1.09 g, 13 mmol) and **1b** (6.67 g, 10 mmol) as described for **8g**. Concentration of the mixture to a volume of 10 mL and slow addition of Et_2O afforded a pale yellow powder, which according to the ^1H NMR spectra consisted of a mixture of **8o** and **8p** (ratio ca 2:1); yield: 3.84 g (57%).

3,4-Dimethyl-2,6-diphenylpyridine (9f); Typical Procedure:
A mixture of **8f** (1.19 g, 2 mmol), CH_2Cl_2 (10 mL) and $NaHCO_3$ (2.52 g, 30 mmol) in H_2O (15 mL) was stirred for 2 h. Filtration from a mucous impurity and workup of the organic phase afforded a brown oil (0.49 g, 94%), which crystallized from hot EtOH (2 mL, −20 °C) to give a pale brown powder; yield: 0.38 g (73%); mp 47–48 °C.

3-Methyl-2,6-diphenyl-4-(1,2,2-trimethylpropyl)pyridine (**9g**):
From **8g** (1.33 g, 2 mmol) as described for **9f**. Yield: 0.66 g (86%) of a pale yellow foam, which crystallized from EtOH (3 mL, −20 °C) to give a pale yellow powder; yield: 0.42 g (55%); mp 75–78 °C.

2,6-Bis(4-chlorophenyl)-3,4-dimethylpyridine (9h):
A solution of NaOH (6.00 g, 150 mmol) in H_2O (30 mL) was added at 0 °C to the mixture of **8h** (prepared from 10 mmol of **1b**). After stirring for 30 min the organic layer was worked up affording an oil, which crystallized from hot EtOH (30 mL, −20 °C) to give colorless needles; yield: 1.82 g (56%); mp 118–120 °C.

2,6-Bis(4-chlorophenyl)-3-ethyl-4-methylpyridine (**9i**): From **8i** (3.38 g, 5 mmol) as described for **9f**. Yield: 1.54 g (90%) of a brown oil, which was crystallized from hot EtOH (8 mL, −20 °C) to afford a colorless powder; yield: 1.27 g (74%); mp 69–74 °C.

1,3-Bis(4-chlorophenyl)-5,6,7,8-tetrahydroisoquinoline (**9j**): From **8j** (3.45 g, 5 mmol) as described for **9f**. Yield: 1.65 g (93%) of a yellow foam, which was crystallized from hot EtOH (20 mL, −20 °C) to afford orange prisms; yield: 1.28 g (72%); mp 126–128 °C.

3-Chloro-2,6-bis(4-chlorophenyl)-4-methylpyridine (**9k**): A solution of the hexachloroantimonate was prepared from **2k** (1.00 g, 11 mmol) and **1b** (6.67 g, 10 mmol) as described for **8g**. The mixture was boiled under reflux for 5 h. After concentration to a volume of 30 mL the base was obtained as described for **9f**. A black oil was formed, which was stirred under EtOH (5 mL) for 1 h. The pale brown powder (1.18 g, 34%) was filtered off and recrystallized from hot EtOH (30 mL, −20 °C) to give a beige powder; yield: 1.04 g (30%); mp 139–142 °C.

2,6-Bis(4-chlorophenyl)-4-methylpyridine (**9m**): From **8m** (3.25 g, 5 mmol) as described for **9f**. Yield: 1.38 g (88%) of a yellow powder, which was purified by flash chromatography (silica gel, eluent pentane/$CHCl_3$, 5:1) to give a colorless powder; yield: 0.86 g (55%); mp 155–158 °C.

2,6-Bis(4-chlorophenyl)-4-phenylpyridine (**9n**): From **8n** (3.56 g, 5 mmol) as described for **9f**. Yield: 1.84 g (98%) of a brown powder, which was crystallized at −20 °C from hot *i*-PrOH (200 mL, −20 °C) to give colorless needles; yield: 1.45 g; mp 183–186 °C (Lit.[15] mp 183 °C).

Diastereomeric Mixture of the Racemates (1S,R,3S,R,4R,S,5S,R,8S,R)-(**10a**), *and (1S,R,3R,S,4R,S,5S,R,8S,R)-3-Chloro-2-[(Z)-(chlorophenylmethylene)azonia]-3-phenyltricyclo[4.3.0.0^{4,8}]nonane Hexachloroantimonate* (**10a'**): From **2a** (1.88 g, 20 mmol) in CH_2Cl_2 (10 mL) and **1a** (5.98 g, 10 mmol). However, the mixture was stirred at 23 °C for 15 h. Evaporation of the solvent afforded a black oil, which was triturated with Et_2O (25 mL). The residue was dissolved in CH_2Cl_2 (15 mL). Slow addition of Et_2O (15 mL) furnished a yellow-green powder of **10a, a'** (1.97 g, 29%), from which **10a** crystallized at −20 °C from MeCN (5 mL) to give colorless prisms suitable for an X-ray structural analysis; yield: 1.60 g (24%); mp 168–170 °C (dec).

10a: monoclinic, space group $P2_1/n$, $Z = 4$, $a = 1152.4(2)$, $b = 1602.0(1)$, $c = 1607.4(3)$ pm, $\beta = 99.50(1)°$, $V = 2926.6(7).10^6$ pm^3, $d_{calc} = 1.58$ Mgm^{-3}, $T = 298$ K, $\mu = 17.0$ cm^{-1}, variable $\omega/2\theta$-scan (between 1.37 and 5.49° min^{-1}), $4° \leq 2\theta \leq 56°$, 6983 independent reflections, 5264 observed reflections ($I > 1.5\sigma$). The structure was solved by direct methods (program ENRAF-Nonius SDP). Positions of H atoms from difference Fourier synthesis. The antisotropic refinement led to agreement factors $R = 0.042$ and $R_w = 0.049$.

Diastereomeric Mixture of the Racemates (1S,R,3S,R,4R,S,5S,R,8S,R)-(**10b**), *and (1S,R,3R,S,4R,S,5S,R,8S,R)-3-Chloro-2-{(Z)-[chloro(4-chlorophenyl)methylene]azonia}3-(4-chlorophenyl)tricyclo[4.3.0.0^{4,8}]nonane Hexachloroantimonate* (**10b'**): From **2a** (1.88 g, 20 mmol) and **1b** (6.67 g, 10 mmol). However, the mixture was

stirred at 23 °C for 3 h. Evaporation of the solvent afforded a red oil, which was precipitated from CH_2Cl_2 (10 mL)/Et_2O (15 mL) to give an orange powder (5.90 g, 78%). This was reprecipitated from CH_2Cl_2 (5 mL)/Et_2O (10 mL) to afford a pale yellow powder; yield: 3.25 g (43%); mp 157–164 °C (dec).

(1R,S,2R,S,4R,S,7S,R)-2-Benzoylamino-7-benzoylbicyclo[2.2.1]-heptane (11a):
A solution of NaOH (0.64 g, 16 mmol) in H_2O (30 mL) was added with stirring to a solution of **10a, 10a'** (1.38 g, 2 mmol) in CH_2Cl_2 (30 mL). After stirring for 30 min the inorganic precipitate was centrifuged off. The organic phase was separated, washed with H_2O, dried over Na_2SO_4 and evaporated. The colorless residue (0.57 g, 89%) was crystallized at −20 °C from EtOH (5 mL) to afford a colorless powder; yield: 0.45 g; mp 133–135 °C.

(1R,S,2R,S,4R,S,7S,R)-2-(4-Chlorobenzoylamino)-7-(4-chlorobenzoyl)bicyclo[2.2.1]heptane (**11b**): From **10b, 10b'** (2.28 g, 3 mmol) as described for **11a**. Yield: 1.11 g, (95%) of a faint yellow powder, which was crystallized at −20 °C from EtOH (5 mL) to give a pale gray powder; yield: 0.71 g (61); mp 139–141 °C.

11-Chloro-5,11-diphenyl-11*H*-indeno[1,2-*c*]isoquinolinium Hexachloroantimonate · Et_2O (12a):
From diphenylacetylene (1.78 g, 10 mmol) and **1a** (5.98 g, 10 mmol) as described for **8g**. However, the reaction was carried out in $ClCH_2CH_2Cl$ (90 mL) and the mixture was boiled under reflux for 90 min. After cooling to 23 °C the solvent was evaporated and the residue was dissolved in CH_2Cl_2 (20 mL)/MeCN (4 mL). Slow addition of Et_2O (40 mL) afforded a brown precipitate, which was washed with CH_2Cl_2 (20 mL)/Et_2O (20 mL) to give a yellow-brown powder (3.36 g). Reprecipitation from MeCN (40 mL) /Et_2O (160 mL) gave a yellow powder; yield: 2.56 g (31%); mp 259–262 °C.

9,11-Dichloro-5-(4-chlorophenyl)-11-phenyl-11H-indeno[1,2-c]isoquinolinium Hexachloroantimonate (**12b**): From diphenylacetylene (1.78 g, 10 mmol) and **1b** (6.67 g, 10 mmol) as described for **8g**. However, the mixture was boiled for 1 h. After cooling to 23 °C Et_2O (60 mL) was added dropwise, and a brown powder (2.99 g, 37%) was filtered off. Stirring under CH_2Cl_2 (10 mL)/MeCN (10 mL) and slow addition of Et_2O (40 mL) afforded a yellow powder (2.35 g); mp 293–294 °C.

11-Chloro-5,11-diphenyl-11*H*-indeno[1,2-*c*]isoquinoline (13a); General Procedure:
A mixture of **12a** (2.44 g, 3 mmol) in CH_2Cl_2 (30 mL) and $NaHCO_3$ (3.78 g, 45 mmol) in H_2O (30 mL) was stirred at 23 °C for 30 min. Workup of the organic phase afforded a yellow foam (1.07 g, 88%), which was crystallized at −20 °C from CH_2Cl_2 (10 mL)/pentane (60 mL) to give a colorless powder; yield: 0.76 g (63%); mp 233–235 °C.

9,11-Dichloro-5-(4-chlorophenyl)-11-phenyl-11H-indeno[1,2-c]isoquinoline (**13b**): From **12b** (2.25 g, 3 mmol) as described for **13a**. Yield: 1.31 g (92%) of a yellow foam, which was stirred with CH_2Cl_2 (5 mL) for 5 min. Pentane (10 mL) was added and the pale yellow powder (1.04 g) was filtered off; yield: 1.04 g (73%); mp 192–195 °C.

11-Ethoxy-5,11-diphenyl-11*H*-indeno[1,2-*c*]isoquinoline (14a):
A solution of **13a** (0.81 g, 2 mmol) in EtOH (20 mL) was boiled under reflux for 1 h. The solvent was evaporated and the residue was dissolved in CH_2Cl_2 (20 mL). Treatment with aq $NaHCO_3$ as described for **13a** and workup afforded an orange-brown foam (0.82 g, 99%), which was sublimed (1 d at ca 200 °C/0.1 Torr) to give a colorless powder; yield: 0.45 g (54%); mp 230–231 °C.

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