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On the Reaction of Nitrilium Salts with Heterocyclic Nitrones

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Abstract. Nitrilium hexachloroantimonates **1a–c** reactwith pyridine N-oxides **2a, d, f, j, m, o** to afford bicyclic 2,3-dihydropyridinium salts **5a–p**. The constitution of **5f** was secured by an X-ray crystallographic analysis. Compounds **5** proved to be thermally labile (23–82 °C) rearranging to 2-acylamino- pyridinium salts **6a, f–i** or decomposing to tars. The benzimidazole-3-oxide **7** reacts with nitrilium salts **1a, b** to 2-acylaminobenzimidazoles **9a, b**. The experimental results as well as AM1 calculations support a mechanism for the reaction of nitrilium cations with heterocyclic nitrones, which has originally been suggested by Abramovitch [25, 26].

The dipolarophilicity of the nitrile triple bond is only moderate [1]. Electron-withdrawing substituents or Lewis acid catalysis enhance the reactivity of nitriles against 1,3-dipoles [2–6]. Hence, it is tempting to speculate that nitrilium salts **1**, which may be regarded as especially electron deficient nitriles, should be effective dipolarophiles. Known are cycloadditions of organic azides to nitrilium salts leading to trisubstituted tetrazolium salts [7–9]. These reactions are dominated by interaction of the nitrilium LUMO with the azide HOMO [8]. Cycloadditions of the azide ion N_3^- to nitrilium ions are two-step reactions [10–12]. Recently, we reported on preparations of 1,2,4-oxadiazolium salts by cycloaddition of nitrile oxides to nitrilium salts [13].

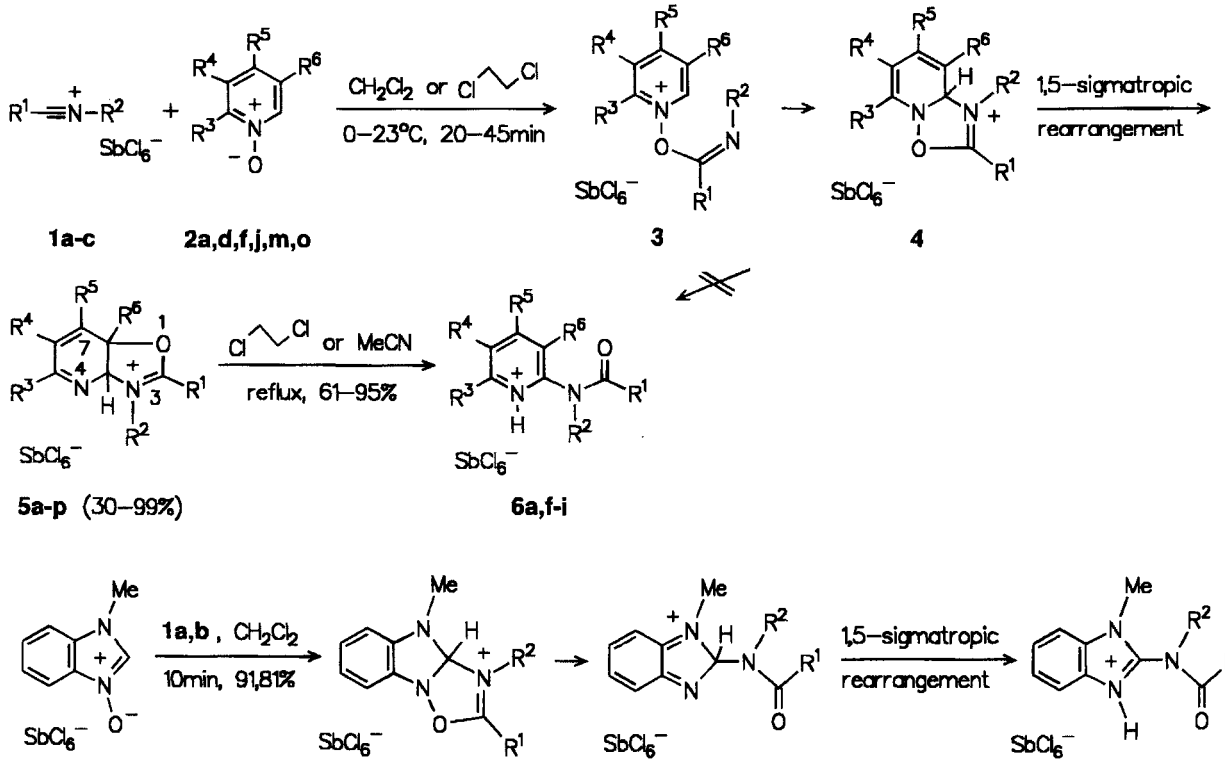
The 1,3-dipolar cycloaddition of nitrones to reactive nitriles constitutes a general synthesis of 2,3-dihydro-1,2,4-oxadiazoles [14–16]. Nitrilium salts in place of nitriles should afford 2,3-dihydro-1,2,4-oxadiazolium salts. We found that nitrones such as benzylideneaniline N-oxide react with nitrilium hexachloroantimonates **1** at low temperatures (< –20 °C). However, only tarry mixtures of compounds were obtained [13].

On the other hand, reactions of imidoyl chlorides as well as of nitrilium hexachloroantimonates with pyridine N-oxides **2** give well defined products [17–25]. For instance, Abramovitch et al. treated **2a** with benzimidoyl chloride or N-phenylbenzonitrilium hexachloroantimonate (**1**, R^1, R^2 = Ph) to obtain mainly 2-(N-benzoylanilino)pyridine. The mechanism originally proposed for this reaction [17] was later questioned by Abramovitch and Shinkai [25], who considered a general mechanism for transformations of pyridine N-oxides with nitrilium salts, isocyanates, benzyne, or acetylenes etc: „Indeed, it is tempting to rationalize most of the results on the basis of a general principle, namely that fused bicyclo-1,2-dihydropyridine-1-oxides (e.g. **4**) are less stable than their 2,3-dihydro counterparts (e.g. **5**) and rearrange readily to these". Since neither intermediate **4** nor **5** was isolated the question of the mechanism remained open.

Cycloadditions of pyridine N-oxides to isocyanates have been studied by Hisano et al. [26–30]. These authors isolated several bicyclic 2,3-dihydropyridines and determined their constitutions by X-ray crystallographic analyses [26].

Here, we report that pyridine N-oxides **2** react with nitrilium salts **1** under much milder conditions than with imidoyl chlorides [17–20]. No side products resulting from reactions of the nucleophilic counterion Cl^- were formed and the salts **5a–p**, which seem to be representatives of a new class of compounds, were isolated in good yields (Scheme 1). Noteworthy, also 4-nitropyridine oxide **2o** reacted smoothly with nitrilium salts, in contrast to a statement of Abramovitch [17, 20]. With 2- or 3-substituted pyridine oxides formation of two isomeric products **5** should be expected.

In fact, from β-picoline **2f** and **1a** a mixture of **5f, g** was formed, which could be separated. The constitution of **5f** was secured by an X-ray structural analysis (Figure 1, Table 1). The structural data may be compared with those for the corresponding ring system formed by cycloaddi-



	R1	R2	R3	R4	R5	R6
a	Me	Me	H	H	H	H
b	Me	*i*-Pr	H	H	H	H
c	Ph	*i*-Pr	H	H	H	H
d	Me	*i*-Pr	Me	H	H	H
e	Ph	*i*-Pr	Me	H	H	H
f	Me	Me	H	H	H	Me
g	Me	Me	H	Me	H	H
h	Me	*i*-Pr	H	Me	H	H

	R1	R2	R3	R4	R5	R6
i	Ph	*i*-Pr	H	Me	H	H
j	Me	Me	H	H	Cl	H
k	Me	*i*-Pr	H	H	Cl	H
l	Ph	*i*-Pr	H	H	Cl	H
m	Me	Me	H	H	CN	H
n	Ph	*i*-Pr	H	H	CN	H
o	Me	Me	H	H	NO_2	H
p	Ph	*i*-Pr	H	H	NO_2	H

Scheme 1

Table 1 Selected bond lengths (pm), bond angles (deg), and torsional angles (deg) of the cation **5f** [34]

O-C1	129.1 (5)	C7-C1-N1	126.2 (4)	O-C1-N1-C2	–5.3 (5)
C1-N1	128.8 (5)	C8-N1-C2	122.0 (4)	O-C1-N1-C8	178.9 (4)
N1-C2	146.9 (5)	N1-C2-N2	108.0 (3)	O-C6-C5-C4	–107.5 (4)
C2-C6	153.3 (4)	C2-N2-C3	116.6 (3)	O-C6-C2-N1	–17.1 (3)
C6-O	149.1 (4)	N2-C3-C4	126.2 (4)	O-C6-C2-N2	101.3 (3)
C1-C7	147.5 (5)	C3-C4-C5	121.3 (4)	C1-N1-C2-C6	14.5 (4)
N1-C8	147.5 (5)	C4-C5-C6	120.6 (4)	C1-N1-C2-N2	–112.6 (3)
C2-N2	145.1 (4)	C5-C6-C2	113.1 (3)	C1-O-C6-C2	15.6 (3)
N2-C3	127.1 (5)	C5-C6-C9	113.1 (3)	C1-O-C6-C5	135.0 (3)
C3-C4	144.3 (6)	C5-C6-O	107.4 (3)	C1-O-C6-C9	–103.5 (3)
C4-C5	130.7 (5)	C6-C2-N2	120.5 (3)	N1-C2-N2-C3	127.3 (4)
C5-C6	149.2 (5)	C9-C6-O	106.5 (3)	N1-C2-C6-C5	–132.4 (3)
C6-C9	150.4 (4)	C9-C6-C2	113.2 (3)	N1-C2-C6-C9	97.3 (3)
O-C1-N1	114.8 (3)	N1-C1-O-C6	–7.2 (4)	C6-O-C1-C7	173.2 (3)
C1-N1-C2	110.7 (3)	C2-N2-C3-C4	–1.8 (6)	N2-C2-N1-C8	63.4 (4)
N1-C2-C6	100.7 (3)	C2-C6-C5-C4	4.9 (5)	N2-C3-C4-C5	–7.6 (6)
C2-C6-O	102.5 (2)	C2-N1-C1-C7	174.3 (3)	N2-C2-C6-C5	–14.0 (4)
C6-O-C1	108.0 (3)	C6-C2-N2-C3	12.7 (5)	N2-C2-C6-C9	–144.4 (3)
O-C1-C7	119.0 (4)	C6-C5-C4-C3	5.2 (6)	C4-C5-C6-C9	135.3 (4)
C1-N1-C8	127.1 (4)	C6-C2-N1-C8	–169.4 (4)	C7-C1-N1-C8	–1.5 (7)

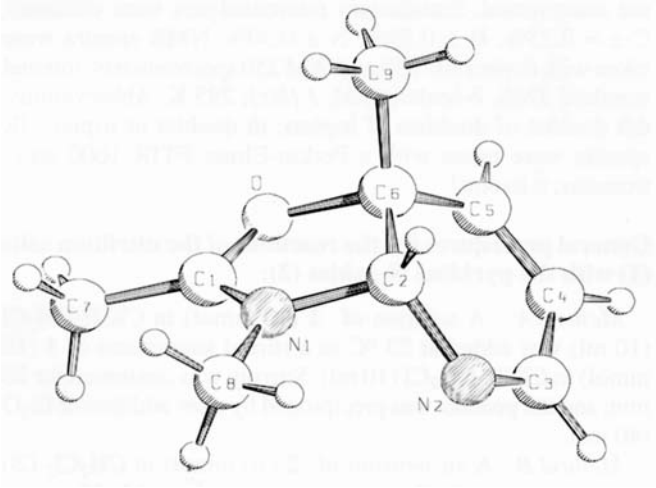


Fig. 1 Plot of the cation **5f**

tion of arylisocyanates to pyridine N-oxides [26]. On the other hand, the bulkier nitrilium salt **1b** afforded only **5h**. Similarly, from α-picoline and **1b**, **c** only the less crowded isomers **5d**, **e** were formed.

All compounds **5** turned out to be thermally labile. Slowly at room temperature and faster in boiling 1,2-dichloroethane or acetonitrile **5a**, **f–i** were transformed into the N-acylaminopyridinium salts **6**. However, the other compounds **5** decomposed to tarry mixtures showing only minor ^{1}H NMR signals for 2-amidopyridinium salts **6**. Thus, the reaction of pyridine N-oxides with nitrilium salts cannot be regarded as a general method for the preparation of 2-acylaminopyridines [17, 25]. The limitations are not caused by lack of basicity of the N-oxide **2** but by instabilities of **5**. On the other hand, the formation of 2,3-dihydropyridinium salts **5** from

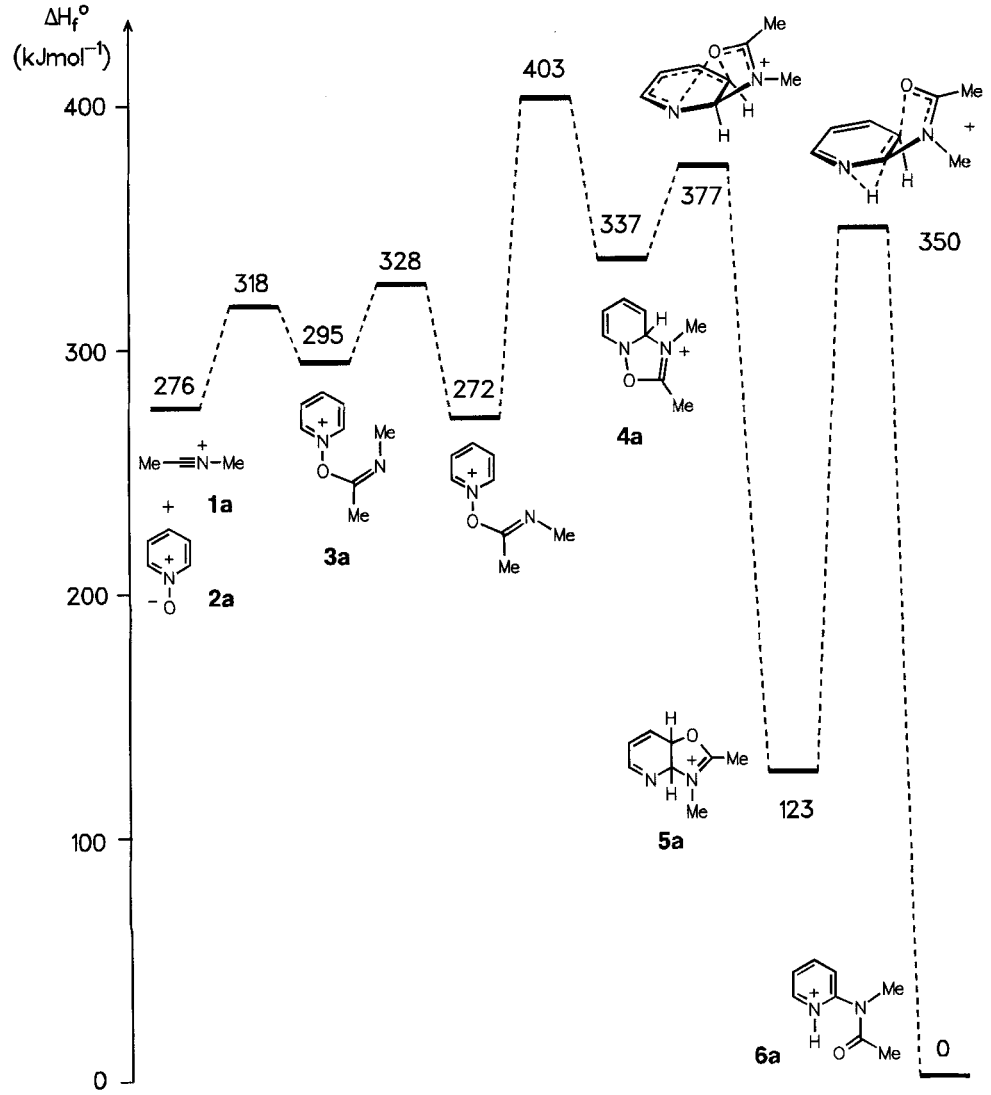


Fig. 2 AM1-calculated heats of formation for the reaction of the cation **1a** with **2a** relative to ΔH_f° = 617 kJ mol^{-1} for **6a**

nitrilium salts **1** and pyridine N-oxides **2** seems to be a general reaction.

The bicyclic compounds show characteristic ^1H and ^{13}C NMR spectra. The following couplings were observed: H3a–H7a ca. 11 Hz, H7–H7a ca. 5 Hz, H6–H7 ca. 10 Hz, H5–H6 ca. 3 Hz. The assignments of C3a and C7a are based on the assumption that C3a shows triplets for the $^3J_{CH}$ couplings (5 to 9 Hz), while C7a gives doublets.

Our experimental results and AM1 calculations are only in accord with Abramovitch's final mechanism [25] represented in Scheme 1. The reaction starts with a non concerted attack of the N-oxide on the nitrilium ion to give – stereochemically controlled [31–33] – a reactive intermediate **4**, which undergoes fast 1,5-sigmatropic rearrangement to the stable salt **5**. Rearomatization of **5** (and not of **4**) furnishes the final product **6**. It is this chance of **4** to escape decomposition by rearrangement to **5**, which renders possible isolation of well defined products from the reaction of nitrilium salts with **2** but not with simple nitrones like benzylideneaniline N-oxide.

An exception to this rule seems to be the reaction of the nitrilium salts **1a, b** with the nitrone **7**. High yields of the 2-acylamino benzimidazoles **9a, b** were obtained, even though the intermediates **8** cannot undergo a stabilizing 1,5-sigmatropic rearrangement. Similar results have been reported by Abramovitch et al. [17, 22]. The mechanism shown in Scheme 1 may account for these reactions.

In Figure 2 the results of AM1 calculations [35, 36] for the reaction of the nitrilium cation **1a** with pyridine N-oxide are shown. The reaction to **6a** was calculated to be exothermic by no less than 276 kJ mol^{-1}. The formation of **4a** occurs stepwise via intermediates **3a** and its more stable (*E*)-isomer. Higher activation enthalpies are required for concerted two-stage or synchronous cycloadditions of the nitrilium ion **1a** to **2a**. According to the calculations the formation of **4a** from **1a** and **2a** is endothermic. With a small activation enthalpy of 40 kJ mol^{-1} the reactive intermediate **4a** rearranged to the much more stable cation **5a**, which on its part needed a high activation enthalpy to be transformed into the final product **6a**. These calculations are in qualitative accord with MINDO/2' and MINDO/3 calculations on related reactions of isocyanates with pyridine N-oxides [24, 30].

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Experimental

All solvents were dried by standard methods. All experiments were carried out with exclusion of moisture. The melting points are uncorrected. Satisfactory microanalyses were obtained: C ± = 0.35%; H ± 0.29%; N ± 0.30%. NMR spectra were taken with Bruker AC 250 and WM 250 spectrometers; internal standard TMS, δ-scale [ppm], *J [Hz]*; 295 K. Abbrevations: ddt doublet of doublets of triplets; dt doublet of triplets. IR spectra were taken with a Perkin-Elmer FTIR 1600 spectrometer, $\tilde{\upsilon}$ in cm^{-1}.

General procedures for the reactions of the nitrilium salts (1) with the pyridine N-oxides (2):

Method A: A solution of **2** (10 mmol) in $ClCH_2CH_2Cl$ (10 ml) was added at 23 °C to a stirred suspension of **1** (10 mmol) in $ClCH_2CH_2Cl$ (10 ml). Stirring was continued for 20 min, and the product was precipitated by slow addition of Et_2O (40 ml).

Method B: A suspension of **2** (10 mmol) in CH_2Cl_2 (20 ml) was added at 0 °C to a stirred suspension of **1** (10 mmol) in CH_2Cl_2 (20 ml). After stirring at 0 °C for 45 min the product was precipitated at 0 °C by slow addition of Et_2O (100 ml).

Method C: A suspension of **2** (10 mmol) in CH_2Cl_2 (20 ml) was added at 0 °C to a stirred suspension of **1** (10 mmol) in CH_2Cl_2 (20 ml). After stirring at 0 °C for 10 min and at 23 °C for another 20 min the product was precipitated by slow addition of Et_2O (50 ml).

3a,7a-Dihydro-2,3-dimethyloxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5a**)

From **1a** [37] (3.91 g, 10 mmol) and **2a** (0.95 g, 10 mmol); method A. Yield: 4.28 g (88%); reprecipitation from CH_2Cl_2 (10 ml)/MeCN (1 ml)/Et_2O (25 ml) afforded a yellow-brown powder (3.76 g, 77%); m.p. 109–111 °C (dec.).
$C_8H_{11}Cl_6N_2OSb$ (485.7). – ^1H NMR (CD_3CN/TMS): 2.42, 3.46 (CH_3), 5.67 (dd, J=4.7, 11.7, H7a), 5.99 (br, d, J=11.7, H3a), 6.44 (dd, J=3.1, 9.8, H6), 6.58 (ddt, J=1.1, 4.7, 9.8, H7), 8.02 (br, m, $J \approx 3.1$, H5). – ^{13}C NMR (CD_3CN/TMS): 13.9, 33.2 (CH_3), 75.7 (C3a, 7a), 125.0, 125.5 (C6, C7), 157.3 (C5), 177.0 (C2). – IR (CH_2Cl_2): 1600, 1655, 1670 (sh).

3a,7a-Dihydro-3-isopropyl-2-methyloxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5b**)

From **1b** [38] (4.19 g, 10 mmol) and **2a** (0.95 g, 10 mmol); method A. Yield: 4.78 g (90%); reprecipitation from CH_2Cl_2 (15 ml)/MeCN (5 ml)/Et_2O (35 ml) afforded a colorless powder (3.83 g, 72%); m.p. 136–137 °C (dec.).
$C_{10}H_{15}Cl_6N_2OSb$ (513.7). – ^1H NMR (CD_3CN/TMS): 1.47 (d, J=6.8), 1.62, (d, J=6.7), 2.47 (CH_3), 4.42 (sept, J=6.8, CH), 5.58 (dd, J=4.8, 11.6, H7a), 6.22 (br, dt, J=0.9, 11.6, H3a), 6.43 (dd, J=3.2, 9.7, H6), 6.61(ddt, J=1.3, 4.7, 9.8 H7), 7.98 (br, m, H5). – ^{13}C NMR (CD_3CN/TMS): 14.5, 19.3, 22.2 (CH_3), 53.3 (CH), 74.3, 75.1 (C3a, C7a), 125.0, 125.4 (C6, C7), 156.7 (C5), 176.8 (C2). – IR (CH_2Cl_2): 1600 (sh), 1620, 1660 (sh).

3a,7a-Dihydro-3-isopropyl-2-phenyloxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5c**)

From **1c** [38] (4.81 g, 10 mmol) and **2a** (0.95 g, 10 mmol); method A. Yield: 5.24 g (91%); reprecipitation from CH_2Cl_2 (20 ml)/MeCN (1 ml)/Et_2O (80 ml) afforded a colorless pow-

der (4.95 g, 86%); m.p. 128–131°C.
$C_{15}H_{17}Cl_6N_2OSb$ (575.8). – ^{1}H NMR (CD_3CN/TMS): 1.61(d, J=6.6), 1.68 (d, J=6.7) (CH_3), 4.61(sept, J=6.6) (CH), 5.84 (dd, J=4.9, 11.4, H7a), 6.48 (m, H3a, H6), 6.69 (ddt, J=1.3, 4.8, 9.8, H7), 8.06 (m, H5), 7.68–7.91(aryl). – ^{13}C NMR (CD_3CN/TMS): 20.2 (^1J=129), 23.3 (^1J=129) (CH_3), 54.6 (^1J=144, CH), 74.5 (ddt, J=164.3, 15.6, 4.8, C3a), 75.3 (dd, J=165.7, 8.8, C7a), 121.2 (t, J=8.2, *i*-C), 125.0 (^1J=176.5, C6), 125.5 (^1J=176.3, ^3J=9.8, C7), 130.6 (dd, J=166.5, 7.4, *m*-C), 131.2 (dt, J=165.8, 6.8, *o*-C), 136.8 (dt, J=164.4, 7.3, *p*-C), 157.0 (^1J=185, C5), 172.9 (C2, gated decoupling experiment). – IR (CH_2Cl_2): 1575, 1605.

3a,7a-Dihydro-3-isopropyl-2,5-dimethyloxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5d**)

From **1b** (4.19 g, 10 mmol) and **2d** (1.09 g, 10 mmol); method B. Yield: 4.68 g (89%) of a colorless powder, which soon decomposed in solution; m.p. 111–116 °C (dec.).
$C_{11}H_{17}Cl_6N_2OSb$ (527.7). – ^{1}H NMR (CD_2Cl_2/TMS, 273 K): 1.57 (d, J=6.8), 1.77 (d, J=6.7), 2.22 (d, J=2.0), 2.64 (CH_3), 4.43 (sept, J=6.8, CH), 5.71 (dd, J= 4.8, 11.0, H7a), 6.26 (br, J=10.9, H3a), 6.42 (d, J=9.8, H6), 6.61(dd, J=4.8, 9.8, H7). – ^{13}C NMR (CD_2Cl_2/TMS, 273 K): 14.5, 19.3, 22.8, 26.8 (CH_3), 53.4 (CH), 73.7, 74.5 (C3a, C7a), 124.1, 128.1 (C6, C7), 163.6, 175.4 (C5, C2). – IR (CH_2Cl_2): 1608, 1631, 1674.

3a,7a-Dihydro-3-isopropyl-5-methyl-2-phenyloxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5e**)

From **1c** (4.81 g, 10 mmol) and **2d** (1.09 g, 10 mmol); method B. Yield: 5.25 g (89%) of a colorless powder, which soon decomposed in solution; m.p. 88–93 °C (dec.).
$C_{16}H_{19}Cl_6N_2OSb$ (589.8). – ^{1}H NMR (CD_3CN/TMS, 263 K): 1.60 (d, J=6.6), 1.71 (d, J=6.7), 2.21 (d, J=1.9) (CH_3), 4.56 (sept, J=6.6, CH), 5.78 (dd, J=4.8, 11.3, H7a), 6.43 (m, H3a, H6), 6.66 (dd, J=4.8, 9.8; H7). – ^{13}C NMR (CD_3CN/TMS, 263 K): 20.0, 23.5, 26.9 (CH_3), 54.1(CH), 74.0, 74.6 (C3a, C7a), 163.7, 172.0 (C5, C2). – IR (CH_2Cl_2): 1576, 1602, 1616 (sh), 1671.

3a,7a-Dihydro-2,3,7a-trimethyloxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5f**)

From **1a** (3.91 g, 10 mmol) and **2f** (1.09 g, 10 mmol); method C.Yield: 2.80 g (56%); reprecipitation at 0 °C from MeCN (20 ml)/Et_2O (100 ml) afforded a colorless powder (2.22 g, 44%); m.p. 178–183 °C (dec.). Crystals suitable for the X-ray structural analysis were obtained by slow crystallization at –15 °C from CH_2Cl_2/MeCN.
$C_9H_{13}Cl_6N_2OSb$ (499.7). – ^{1}H NMR (CD_3CN/TMS): 1.73, 2.40, 3.45 (CH_3), 5.72 (br, H3a), 6.41 (m, H6, H7), 8.03 (br, m, H5). – ^{13}C NMR (CD_3CN/TMS): 14.2, 26.9, 33.4 (CH_3), 81.1, 85.1 (C3a, C7a), 123.5, 129.9 (C6, C7), 157.5 (C5), 176.3 (C2). – IR (CH_2Cl_2): 1602, 1651, 1670.

X-Ray diffraction analysis of 5f [34]

$[C_9H_{13}N_2O]SbCl_6$, crystal size 0.2 × 0.2 × 0.3 mm^3, monoclinic, space group $P2_1/n$, Z = 4, a = 1022.2(1), b = 1118.5(1), c = 1540.0(2) pm, β = 100.6(1)°, V = *1730.9(3)*·10^6 pm^3, d_{calc} = 1.92 M g m^{-3}, T = 293 K, $\mu_{Mo\text{-}K\alpha}$ = 25.12 cm^{-1}, ω/2T-scan, 2.22 ≤ T ≤ 24.96°, 3207 collected reflections, 3026 independent reflections, 2232 observed reflections [$I > 2\sigma(I)$]. The cell constants and the intensities of the reflections were measured on an Enraf-Nonius CAD4 diffractometer with a graphite monochromator, $\lambda_{Mo\text{-}K\alpha}$ = 71.073 pm. The structure was solved by direct methods using the program SHELXL-93. The hydrogen atoms were fixed on calculated positions. The anisotropic refinement led to agreement factors R_1 = 0.025 [$I > 2\sigma(I)$](observed reflections), R_2 = 0.044 (all reflections).

3a,7a-Dihydro-2,3,6-trimethyloxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5g**)

On addition of Et_2O (50 ml) to the mother liquor of the first precipitation of **5f** a yellow powder (**5g**, 1.48 g, 30%) precipitated. Reprecipitation at 0 °C from CH_2Cl_2 (20 ml)/Et_2O (30 ml) afforded a pale yellow powder (1.18 g, 24%); m.p. 84–87 °C (dec.).
$C_9H_{13}Cl_6N_2OSb$ (499.7). – ^{1}H NMR (CD_3CN/TMS, 263 K): 2.03 (t, J = 1.6), 2.40, 3.46 (CH_3), 5.65 (m, cpld. to 2.03, J=5.1, 11.3, H7a), 5.91 (br, d, J = 11.3, H3a), 6.29 (m, cpld. to 2.03, 5.65, H7), 7.89 (m, J=2.1, H5). – ^{13}C NMR (CD_3CN/TMS, 263 K): 13.9, 19.8, 33.2 (CH_3), 75.3, 76.8 (C3a, C7a), 118.8, 134.8 (C7, C6), 160.4 (C5), 176.9 (C2). – IR (CH_2Cl_2): 1608, 1652.

3a,7a-Dihydro-3-isopropyl-2,6-dimethyloxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5h**)

From **1b** (4.19 g, 10 mmol) and **2f** (1.09 g, 10 mmol); method C. Precipiation with Et_2O afforded an oil, which slowly solidified on stirring. Yield: 4.74 g (90%); reprecipitation at 0 °C from CH_2Cl_2 (20 ml)/Et_2O (50 ml) afforded a colorless powder (4.48 g, 85%); m.p. 125–126 °C.
$C_{11}H_{17}Cl_6N_2OSb$ (527.7).– ^{1}H NMR (CD_3CN/TMS, 263 K): 1.46 (d, J=6.8), 1.61(d, J=6.7), 2.02 (t, J=1.4), 2.45 (CH_3), 4.40 (sept, J=6.7, CH), 5.54 (dd, J=5.1, 11.1, H7a), 6.13 (br, (d, J=11.0, H3a), 6.30 (m, H7), 7.86 (t, J=2.2, H5). – ^{13}C NMR (CD_3CN/TMS, 263 K): 14.5, 19.3, 19.8, 22.3 (CH_3), 52.9 (CH), 73.7, 76.3 (C3a, C7a), 118.8, 134.6 (C7, C6), 160.1 (C5), 176.7 (C2). – IR (CH_2Cl_2): 1604, 1628.

3a,7a-Dihydro-3-isopropyl-6-methyl-2-phenyloxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5i**)

From **1c** (4.81 g, 10 mmol) and **2f** (1.09 g, 10 mmol); method C. Yield: 5.34 g (91%); reprecipitation from CH_2Cl_2 (30 ml)/MeCN (1 ml)/Et_2O (100 ml) afforded a colorless powder (4.98 g, 84%); m.p. 140–142 °C.
$C_{16}H_{19}Cl_6N_2OSb$ (589.8). – ^{1}H NMR (CD_3CN/TMS, 263 K): 1.59 (d, J=6.5), 1.70 (d, J=6.7), 2.05 (t, J=1.5) (CH_3), 4.60 (sept, J=6.7, CH), 5.81 (m, cpld. to 2.05, H7a), 6.37(m, cpld. to 2.05, H3a, H7), 7.93 (m, J=1.4, H5), 7.69–7.89 (phenyl). – ^{13}C NMR (CD_3CN/TMS, 263 K): 19.9, 20.2, 23.4 (CH_3), 54.3 (CH), 73.9, 76.5 (C3a, C7a), 118.7, 121.2, 130.6, 131.3, 134.8, 136.8 (C7, C6, phenyl), 160.4 (C5), 172.7 (C2). – IR (CH_2Cl_2): 1575, 1592, 1610.

7-Chloro-3a,7a-dihydro-2,3-dimethyloxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5j**)

From **1a** (3.91 g, 10 mmol) and **2j** (1.30 g, 10 mmol); method B. Yield: 4.80 g (92%); reprecipitation from CH_2Cl_2 (40 ml)/

MeCN (8 ml)/Et_2O (200 ml) afforded a pale yellow powder (4.04 g, 78%); m.p. 111–113 °C (dec.).
$C_8H_{10}Cl_7N_2OSb$ (520.1). – ^1H NMR (CD_3CN/TMS): 2.46, 3.48 (CH_3), 5.66 (d, J=11.7, H7a), 6.17 (br, m, J=11.7, H3a), 6.64 (d, J=3.7, H6), 7.92 (dd, 2.4, 3.8, H5). – ^{13}C NMR (CD_3CN/TMS): 14.0, 33.7 (CH_3), 79.1, 79.3 (C3a, C7a), 123.5, 135.3 (C6, C7), 156.0 (C5), 177.0 (C2). – IR (CH_2Cl_2): 1590, 1655, 1669.

7-Chloro-3a,7a-dihydro-3-isopropyl-2-methyloxazolo[4,5-b] pyridin-3-ium hexachloroantimonate (**5k**)

From **1b** (4.19 g, 10 mmol) and **2j** (1.30 g, 10 mmol); method B. Yield: 5.16 g (94%); reprecipitation at 0 °C from CH_2Cl_2 (40 ml)/MeCN (20 ml)/Et_2O (300 ml) afforded a colorless powder (4.12 g, 75%); m.p. 126–127 °C (dec.).
$C_{10}H_{14}Cl_7N_2OSb$ (548.2). – ^1H NMR (CD_3CN/TMS, 263 K): 1.44 (d, J=6.8), 1.61(d, J=6.7), 2.48 (CH_3), 4.43 (sept, J=6.7, CH), 5.57 (d, J=11.7, H7a), 6.33 (dd, $J\approx$2, 11.7, H3a), 6.65 (d, J=3.7, H6), 7.88 (dd, J=2.4, 3.7, H5). – ^{13}C NMR (CD_3CN/TMS, 263 K): 14.6, 19.0, 22.0 (CH_3) 53.7 (CH), 77.4, 78.6 (C3a, C7a), 123.3, 135.4 (C6,C7), 155.4 C5, 176.7 (C2; at 263 K). – IR (CH_2Cl_2): 1587, 1631, 1664.

7-Chloro-3a,7a-dihydro-3-isopropyl-2-phenyloxazolo[4,5-b] pyridin-3-ium hexachloroantimonate (**5l**)

From **1c** (4.81 g, 10 mmol) and **2j** (1.30 g, 10 mmol); method B. Yield: 5.16 g (85%); reprecipitation at 0 °C from CH_2Cl_2 (40 ml)/MeCN (8 ml)/Et_2O (200 ml) afforded a colorless powder (4.44 g, 73%); m.p. 120–122 °C.
$C_{15}H_{16}Cl_7N_2OSb$ (610.2). – ^1H NMR (CD_3CN/TMS, 263 K): 1.60 (d, J=6.6), 1.68 (d, J=6.7, CH_3), 4.61(sept, J=6.6) (CH), 5.83 (d, J=11.9, H7a), 6.58 (dd, J= 2.5, 11.9, H3a), 6.69 (d, J=3.7, H6), 7.70–7.97 (m, aryl, H5). – ^{13}C NMR (CD_3CN/TMS, 263 K): 19.9, 23.3 (CH_3), 55.0 (CH), 77.6, 78.7 (C3a, C7a), 120.9, 123.4, 130.7, 131.5, 135.3, 137.1 (aryl, C6, C7), 155.6 (C5), 172.3 (C2). – IR (CH_2Cl_2): 1577, 1605, 1663.

7-Cyano-3a,7a-dihydro-2,3-dimethyloxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5m**)

From **1a** (3.91 g, 10 mmol) and **2m** (1.20 g, 10 mmol); method B. The oily precipitate was stirred at 0 °C for 1h in Et_2O (100 ml). The solvent was removed and the residue was again stirred at 0 °C for 1h in Et_2O (100 ml). Decantation, drying of the residue, and stirring the resulting foam at 0 °C for 1h in pentane (100 ml) afforded a pale yellow powder (5.00 g, 98%); m.p. 65–75 °C (dec.).
$C_9H_{10}Cl_6N_3OSb$ (510.7). – ^1H NMR (CD_3CN/TMS, 263 K): 2.46, 3.47 (CH_3), 5.75 (d, J=11.8, H7a), 6.19 (br, d, J=11.8, H3a), 7.11 (d, J=3.3, H6), 8.21 (m, H5). – ^{13}C NMR (CD_3CN/TMS, 263 K): 14.0, 33.4 (CH_3), 73.3, 76.3 (C3a, C7a), 110.7, 115.8 (CN, C7), 134.8 (C6), 155.6 (C5), 177.2 (C2). – IR (nujol): 1594, 1651,1667.

7-Cyano-3a,7a-dihydro-3-isopropyl-2-phenyloxazolo[4,5-b] pyridin-3-ium hexachloroantimonate (**5n**)

From **1c** (4.81 g, 10 mmol) and **2m** (1.20 g, 10 mmol) as described for **5m**. Yield: 5.52 g (92%) of a colorless powder; m.p. 108–110 °C (dec.).
$C_{16}H_{16}Cl_6N_3OSb$ (600.8). – ^1H NMR (CD_3CN/TMS): 1.61(d, J=6.6), 1.66 (d, J=6.8) (CH_3), 4.65 (sept, J=6.7, CH), 5.90 (d, J= 11.7, H7a), 6.60 (dd, J=2.6, 11.7, H3a), 7.13 (d, J=3.4, H6), 8.23 (t, J=3.0, H5), 7.71–7.94 (phenyl). – ^{13}C NMR (CD_3CN/TMS): 20.0, 23.2 (CH_3), 55.3 (CH), 72.8, 75.2 (C3a, C7a), 110.8, 115.8 (CN, C7), 120.7, 130.8, 131.5, 134.8, 137.4 (C6, phenyl), 155.3 (C5), 172.6 (C2). – IR (CH_2Cl_2): 1576, 1603, 1658.

3a,7a-Dihydro-2,3-dimethyl-7-nitrooxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5o**)

From **1a** (3.91 g, 10 mmol) and **2o** (1.40 g, 10 mmol); method B. After stirring at 0 °C for 45 min MeCN (8 ml) was added to the viscous brown product. Centrifuging from an impurity and slow addition of Et_2O (200 ml) at 0 °C afforded an oil, which was stirred at 0 °C in Et_2O (100 ml) for 1h. Decantation and drying of the residue afforded a yellow solid foam (4.14 g, 78%); m.p. 110–120 °C (dec.).
$C_8H_{10}Cl_6N_3O_3Sb$ (530.7). – ^1H NMR (CD_3CN/TMS, 263 K): 2.49, 3.56 (CH_3), 6.14 (d, J=11.3, H7a), 6.39 (br, d, J=11.3, H3a), 7.55 (d, J=3.5, H6), 8.38 (dd, J=2.6, 3.5, H5). – ^{13}C NMR (CD_3CN/TMS, 263 K): 14.1, 34.0 (CH_3), 72.6, 80.7 (C3a, C7a), 124.5 (C6), 145.4 (C7), 155.8 (C5), 177.8 (C2). – IR (nujol): 1658, 1680 (sh).

3a,7a-Dihydro-3-isopropyl-7-nitro-2-phenyloxazolo[4,5-b]pyridin-3-ium hexachloroantimonate (**5p**)

From **1c** (4.81 g, 10 mmol) and **2o** (1.40 g, 10 mmol); method B. After stirring at 0 °C for 45 min and filtration of the reaction mixture an oil was precipitated at 0 °C by slow addition of Et_2O (100 ml). The precipitate was stirred at 0 °C for 1h in Et_2O (100 ml). Removing the solvent and drying the residue afforded a yellow foam, which solidified to a yellow powder (5.04 g, 81%) on stirring at 0 °C for 1h in pentane (100 ml); m.p. 85–100 °C (dec.).
$C_{15}H_{16}Cl_6N_3O_3Sb$ (620.8). – ^1H NMR (CD_3CN/TMS, 263 K): 1.64 (d, J=6.5), 1.71 (d, J=6.7 (CH_3), 4.72 (sept, J=6.7) (CH), 6.35 (d, J=11.3, H7a), 6.77 (dd, J=2.6, 11.3, H3a), 7.58 (d, J=3.6, H6), 7.67–7.95 (phenyl), 8.40 (dd, J=2.6, 3.5, H5). – ^{13}C NMR (CD_3CN/TMS, 263 K): 20.2, 23.2 (CH_3), 55.4 (CH), 72.3, 79.1 (C3a, C7a), 120.6, 124.2, 130.8, 131.7, 137.5, 145.5 (C6, C7, aryl), 155.5 (C5), 173.2 (C2). – IR (CH_2Cl_2): 1555, 1576, 1591, 1600 (sh), 1607 (sh).

2-(N-Methylacetamido)pyridinium hexachloroantimonate (**6a**)

A solution of **5a** (4.86 g, 10 mmol) in $ClCH_2CH_2Cl$ (40 ml) was boiled under reflux for 3h. Cooling to 23 °C and slow addition of CCl_4 (50 ml) to the black solution afforded a red-brown powder (3.70 g, 76%), which was reprecipitated from CH_2Cl_2 (40 ml)/MeCN (10 ml)/Et_2O (100 ml) to give a yellow powder (2.96 g, 61%); m.p. 195–199 °C (dec.).
$C_6H_{11}Cl_6N_2OSb$ (485.7). – ^1H NMR (CD_3CN/TMS): 2.51, 3.58 (CH_3), 7.69 (m, 2H), 8.40–8.56 (m, 2H, aryl), 15.3 (br NH). – ^{13}C NMR (CD_3CN/TMS): 25.9, 37.2 (CH_3), 117.1

(C3), 122.0 (C5), 139.0 (C4), 148.6, 151.5 (C6, C2), 178.4 (CO). – IR (CH_2Cl_2): 1675, 1630, 1600.

2-(N-Methylacetamido)-3-methylpyridinium hexachloroantimonate (**6f**)

A solution of **5f** (5.00 g, 10 mmol) in $ClCH_2CH_2Cl$ (100 ml) was boiled under reflux for 3h. Evaporation of the solvent and precipitation of the residue from CH_2Cl_2 (50 ml)/MeCN (15 ml)/Et_2O (300 ml) furnished a yellow powder (4.50 g, 90%); m.p. 182–187 °C (dec.).
$C_9H_{13}Cl_6N_2OSb$ (499.7). – ^1H NMR (CD_3CN/TMS, 323 K): 2.11 br, 2.43, 3.33 (br) (CH_3), 7.92 (m, 1H), 8.53 (m, 2H, aryl), 12.07 (br, NH). – ^{13}C NMR (CD_3CN/TMS, 323 K): 17.0, 22.2, 37.2 (br, CH_3), 127.1, 138.4, 141.0 (br), 149.7 (br), 152.3, 171.8 (br, aryl, CO). – IR (KBr): 1606, 1622 sh, 1648.

2-(N-Methylacetamido)-5-methylpyridinium hexachloroantimonate (**6g**)

A solution of **5g** (5.00 g, 10 mmol) in $ClCH_2CH_2Cl$ (100 ml) was boiled under reflux for 1h. Cooling and slow addition of Et_2O (250 ml) afforded a yellow powder (4.13 g, 83%); m.p. 183–190 °C (dec.).
$C_9H_{13}Cl_6N_2OSb$ (499.7). – ^1H NMR (CD_3CN/TMS): 2.46, 2.47, 3.53 (CH_3), 7.58 (d, J=9.0, H3), 8.22 (br, m, H6), 8.33 (br, m, H4). – ^{13}C NMR (CD_3CN/TMS): 17.8, 25.7, 37.2 (CH_3), 116.9 (C3), 133.3, 137.7, 149.6 (2C?) (C2, C4, C5, C6), 177.9 (CO). – IR (CH_2Cl_2): 1556,1599, 1644, 1681.

2-(N-Isopropylacetamido5-methylpyridinium hexachloroantimonate (**6h**)

A solution of **5h** (5.28 g, 10 mmol) in MeCN (30 ml) was boiled under reflux for 3h. Evaporation of the solvent and precipitation of the residue from CH_2Cl_2 (30 ml)/MeCN (30 ml)/Et_2O (200 ml) furnished a colorless powder (4.63 g, 88%); m.p. 210–212 °C.
$C_{11}H_{17}Cl_6N_2OSb$ (527.7). – ^1H NMR (CD_3CN/TMS): 1.18 (d, J=6.8), 2.00, 2.59 (CH_3), 4.73 (sept, J=6.8, CH), 7.81 (d, J=8.3, H3), 8.53 (m, H4, H6), 9.63 (br, NH). – ^{13}C NMR (CD_3CN/TMS): 18.4, 21.3 (2C), 23.4 (CH_3), 51.0 (CH), 128.9, 139.6, 143.2 (br), 145.5 (br), 151.2 (aryl), 170.9 (CO). – IR (KBr): 1563, 1601, 1626, 1673.

2-(N-Isopropylbenzamido)-5-methylpyridinium hexachloroantimonate (**6i**)

From **5i** (5.90 g, 10 mmol) as described for **6h**. Precipitation from CH_2Cl_2 (25 ml)/Et_2O (130 ml) furnished a colorless powder (5.60 g, 95%); m.p. 160–162 °C.
$C_{16}H_{19}Cl_6N_2OSb$ (589.8). – ^1H NMR (CD_3CN/TMS): 1.30 (d, J=6.8), 2.48 (CH_3), 4.81(sept, J=6.8, CH), 7.36–7.47 (phenyl), 7.78 (d, J=8.3, H3), 8.35 (m, H4, H6), 11.87 (br NH). – ^{13}C NMR (CD_3CN/TMS): 18.2, 21.1 (2C) (CH_3), 53.0 (CH), 128.7, 128.9, 129.7, 132.0, 135.4, 138.9, 142.3,146.3, 150.7 (aryl), 170.8 (CO). – IR (CH_2Cl_2): 1596, 1640, 1658, 1686.

2-(N-Methylacetamido)-1-methylbenzimidazolium hexachloroantimonate (**9a**)

A solution of **7** [39] (1.48 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (–25 °C) suspension of **1a** (3.91 g, 10 mmol) in CH_2Cl_2 (20 ml). After stirring at –25 °C for 10 min CCl_4 (100 ml) was added. The oily precipitate was crystallized at –15 °C from CH_2Cl_2 (40 ml)/MeCN (4 ml)/CCl_4 (100 ml) to give a colorless powder (4.88 g, 91%); m.p. 178–180 °C.
$C_{11}H_{14}Cl_6N_3OSb$ (538.7). – ^1H NMR (CD_3CN/TMS): 2.28 (br), 3.48 (br), 3.85 (CH_3), 7.65–7.80 (aryl), 12.0 (br, NH). – ^{13}C NMR (CD_3CN/TMS): 22.7, 33.1, 38.0 (br, CH_3), 114.0, 115.1, 127.7, 128.3, 129.1, 132.0 (aryl), 146.8, 172.1 (br NCN, CO). – IR (CH_2Cl_2): 1724.

2-(N-Isopropylacetamido)-1-methylbenzimidazolium hexachloroantimonate (**9b**)

From **1b** (4.19 g, 10 mmol) as described for **9a**. After stirring at –25 °C for 10 min Et_2O (200 ml) was added dropwise. Stirring at 23 °C for 30 min afforded a yellow precipitate, which was reprecipitated from CH_2Cl_2 (40 ml)/MeCN (4 ml)/Et_2O (300 ml) to furnish a pale yellow powder (4.60 g, 81%); m.p. 158–162 °C.
$C_{13}H_{18}Cl_6N_3OSb$ (566.8). – ^1H NMR (CD_3CN/TMS): 1.28 (br, d, J=6.7), 2.09 (br, 3.94) (CH_3), 4.72 (sept, J=6.7, CH), 7.69–7.90 (aryl), 9.24 (br, NH). – ^{13}C NMR (CD_3CN/TMS) : 21.2 (br), 23.0, 32.7, CH_3), 53.2 (CH), 114.7, 115.7, 128.3, 129.5, 132.4 (aryl), 143.9, 170.8 (NCN, CO). – IR (CH_2Cl_2): 1703, 1717 (sh).

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