ON THE *N*-OXIDATION OF THIENO[*b*]-2,5-NAPHTHYRIDINES

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Abstract: Thieno[*b*]-2,5-naphthyridine-*N*-oxides have been prepared both in a Pd(0)-catalysed ring-closure between *t*-butyl-*N*-(trimethylstannylthienyl)carbamates and 2-chloro-3-formylpyridine-*N*-oxide or 2-(2-bromo-3-pyridyi)-1,3-dioxolane-*N*-oxide using copper(II)oxide as co-reagent, and by oxidation of the parent compounds with *m*-chloroperbenzoic acid.

Introduction

We have been interested for a long time in the effects of the mode of annelation on physical properties and reactivities of tricyclic heterocyclic systems with the phenanthrene annelation pattern [1]. We have previously developed several methods for the preparation of the six isomeric thieno[*c*]-1,5-naphtyridine 5-oxides and 9-oxides and studied the selectivity in *N*-oxidation of the parent compounds. It was found that especially oxidation of thieno[2,3-*c*]-1,5-naphthyridine was higly selective giving almost exclusively the 5-*N*-oxide, while thieno[3,4-*c*]-1.5-naphthyridine on the other hand gave about equal amounts of the 5- and 9-*N*-oxides upon oxidation with *m*-chloroperbenzoic acid [2]. We were therefore interested to find out how reactivity and selectivity would change, moving the nitrogen of the middle ring and therefore decided to study the *N*-oxidation of the analogous thieno[*b*]-2,5-naphthyridines [3].

Experimental

The NMR spectra were recorded on a Varian XL-300 spectrometer. Deuteriochloroform was used as solvent for all substances. The mass spectra were recorded on a JEOL JMS-SX 102 spectrometer (70 eV). The elemental analyses were carried out by Dornis und Kolbe, Mühlheim, Germany. All melting points are uncorrected. *m*-Chloroperbenzoic acid (*m*-CPBA) was purchased from Merck. Dichloromethane and dimethylformamide were distilled and kept over molecular sieves prior to use. Tetrahydrofuran was distilled over sodium. All other solvents were purchased from the manufacturer in analytical grade and used without further purification. 2-(2-Bromo-3-pyridyl)-1,3-dioxolane [4] , thieno[2,3-*b*]-2,5-naphthyridine[5] , thieno[3,2-*b*]-2,5-naphthyridine [5] , thieno[3,4-*b*]-2,5-naphthyridine [4], dichloro(diphenylphosphinebutane)palladium(II) [6], *t*-butyl-*N*-(2-trimethylstannyl-3-thienyl)carbamate [5], *t*-butyl-*N*-(3-trimethyistannyl-2-thienyl)carbamate [5] and *t*-butyl-*N*-(4-trimethylstannyl-3-thienyl)carbamate [5] were prepared by published procedures.

2-(2-Bromo-3-pyridyl)-1,3-dioxolane-*N*-oxide (**5**).

To a stirred mixture of 4.00 g (17.4 mmol) of 2-(2-bromo-3-pyridyl)-1,3-dioxolane (**4**) [4] and 40 ml of

chloroform, 4.95 g (28.7 mmol) of *m*-CPBA was added in small portions over a period of 30 minutes at room temperature. The reaction mixture was stirred for 48 hours at room temperature, when 150 ml of chloroform was added. The organic phase was washed with 1 M sodium carbonate and water, and then dried over magnesium sulfate. Chromatography on silica gel using dichloromethane/methanol (95:5) as eluent gave 3.59 g (83%) of the title compound as white crystals, mp 103-104 °C; ^{1}H NMR : δ 4.11 (m, 4H, CH_2), 6.01 (s, 1H, CH), 7.24 (dd, 1H, H5, J = 6.4, 7.9 Hz), 7.42 (dd, 1H, H4, J = 1.6, 7.9 Hz) , 8.37 (dd, 1H, H6, J = 1.6, 6.4 Hz); MS: m/z 247, 245 (45, 47, M^+), 230 (5, M^+-O), 173,175 (20, 18, M^+-$CHO_2C_2H_4$), 78 (15, pyridine ring), 73 (100, acetal); HRMS: m/z Calcd. for $C_8H_8NO_3Br$: 244.9688 . Found: 244.9688.

2-Chloro-3-formylpyridine-*N*-oxide (**6**)

A mixture of 500 mg (2.02 mmol) 2-(2-bromo-3-pyridyl)-1,3-dioxoiane-*N*-oxide (**5**), 10 ml of 2 M hydrochloric acid and 30 ml of tetrahydrofuran was refluxed for 60 minutes. The reaction mixture was neutralized with a 2 M sodium hydroxide solution and then extracted continuously with chloroform. The organic phase was then dried and evaporated. Chromatography on silica gel using dichloromethane/methanol (90:10) gave 220 mg (69%) of the title compound as white crystals, mp 151-153 °C; ^{1}H-NMR: δ 7.36 (ddd, 1H, H5, J = 0.8, 6.5, 7.9 Hz), 7.76 (dd, 1H, H4, J = 1.5, 7.9 Hz), 8.54 (dd, 1H, H6, J = 1.5, 6.5Hz), 10.37 (d, 1H, CHO, J = 0.8); MS: m/z 157, 159 (100, 30, M^+), 141 (5, M^+-O), 129 (15, M^+-CHO), 94 (10, M^+-CHO-Cl); HRMS: Calcd. for $C_6H_4NO_2Cl$: 156.9931. Found: 156.9932.

General procedure for the preparation of thieno[*b*]-2,5-naphthyridine-9-oxides (**7**,**8**,**9**)

A 25 ml three-necked flask with magnetic stirrer and nitrogen inlet, was charged with 245 mg (1.00 mmol) of 2-(2-bromo-3-pyridyl)-1,3-dioxolane-*N*-oxide (**5**) or 157 mg (1.00 mmol) of 2-chloro-3-formylpyridine-*N*-oxide (**6**), 30.0 mg (0.05 mmol) of dichloro(diphenylphosphinebutane)palladium (II) [6], 80 mg (1.0 mmol) of copper(II)oxide and 5 ml of *N*,*N*-dimethylformamide. After stirring for 5 minutes at 100 °C 522 mg (1.50 mmol) of the appropriate *t*-butyl-*N*-(trimethylstannylthienyl)carbamate (**1**-**3**) was added all at once to the reaction mixture. After the starting materials were consumed (2 hours), the reaction mixture was allowed to reach room temperature. In the reactions containing 2-(2-bromo-3-pyridyl)-1,3-dioxolane-*N*-oxide 2.5 ml of 2 M hydrochloric acid was added to the reaction mixture. These solutions were then heated to 100 °C for one hour, allowed to reach room temperature and neutralized with 5 ml of 2 M sodium hydroxide solution. For all the reactions the precipitate was filtered off and the filtrate was evaporated. The residue was chromatographed on silica gel, using dichloromethane/methanol (90:10) as eluent. It was then subjected to chromatography on a reversed phase HPLC Polygosil 60 C_{18}-column with acetonitrile/water (45:55) as eluent.

Thieno[3,2-*b*]-2,5-naphthyridine-9-oxide (**7**)

This compound was obtained in a yield of 43 mg (21%) from **5** and 72 mg (35%) from **6** as white crystals, mp 202-204 °C, ^{1}H NMR: δ 7.50 (dd, 1H, H7, J = 6.4, 8.4 Hz), 7.84 (d, 1H, H1, J = 5.5 Hz), 8.00 (d, 1H, H2, J = 5.5 Hz), 8.04 (dd, 1H, H6, J = 0.8, 8.4 Hz), 8.77 (dd, 1H, H8, J = 0.8, 6.4 Hz), 9.29 (s broad, 1H, H5); MS: m/z 202 (100, M^+), 186 (35, M^+-O), 174 (15), 147 (20). HRMS: Calcd. for $C_{10}H_6N_2OS$: C, 59.39; H, 2,99. Found C, 59.26; H, 3.11.

Thieno[2,3-*b*]-2,5-naphthyridine-9-oxide (**9**)
This compound was obtained in a yield of 23 mg (11%) from **5** and 30 mg (15%) from **8** as white crystals, mp 188-191 °C, ^{1}H NMR: δ 7.50 (dd, 1H, H7, J = 6.2, 8.3 Hz), 7.78 (d, 1H, H2, J = 5.8 Hz), 7.98 (dd, 1H, H6, J = 1.0, 8.3 Hz), 8.74 (dd, 1H, H8, J = 1.0, 6.2 Hz), 9.05 (d, 1H, H1, J = 5.8 Hz), 9.15 (s, 1H, H5); MS: m/z 202 (100, M^+), 186 (35, M^+-O), 174 (20), 146 (10). HRMS: Calcd. for $C_{10}H_6N_2OS$: C, 59.39; H, 2.99. Found C, 59.31; H, 3.06.

General procedure for the reaction of thieno[*b*]-2,5-naphthyridines with *m*-CPBA (**7**,**8**,**9**,**13**,**14**,**16**).
To a stirred mixture, consisting of 186 mg (1.00 mmol) of the appropriate thieno[*b*]-2,5-naphthyridine (**11**, **12**,**15**,) [4] 100 mg of magnesium sulfate and 2 ml of chloroform, 173 mg (1.00 mmol) of *m*-CPBA was added at room temperature. After 12 hours 40 ml of chloroform were added to the reaction mixture. The phases were separated and the organic phase was washed with 10 ml of 1 M sodium carbonate and 10 ml of water, then it was dried over magnesium sulfate. After evaporation the residue was subjected to HPLC chromatography. Compounds **7** and **13** were first chromatographed on a reversed phase HPLC polygosil 60 C_{18}-column using acetonitrile/water (45:55) as eluent, and then HPLC chromatographed on a semipreparative nucleosil silica column using chloroform/2-propanol (99:1) as eluent. Compounds **9** and **16** were chromatographed on a reversed phase HPLC polygosil 60 C_{18}-column using acetonitrile/water (45:55) as eluent. Compounds **8** and **14** were first chromatographed on a reversed phase HPLC polygosil 60 C_{18}-column using acetonitrile/water (45:55) as eluent and then chromatographed on the same column using acetonitrile/water (20:80) as eluent.

Thieno[3,2-*b*]-2,5-naphthyridine-9-oxide (**7**)
This compound was obtained in a yield of 11 mg (5%).

Thieno[3,4-*b*]-2,5-naphthyridine-9-oxide (**8**)
This compound was obtained in a yield of 15 mg (8%) of green-yellowish semi crystals. ^{1}H NMR: δ 7.45 (dd, 1H, H7, J = 6.5, 7.9 Hz), 7.76 (dd, 1H, H6, J = 1.1, 7.9 Hz), 8.06 (d, 1H, H3, J = 3.6 Hz), 8.64 (dd, 1H, H8, J = 1.1, 6.5 Hz), 8.85 (s, 1H, H5), 9.60 (d, 1H, H1, 3.6 Hz); MS: m/z 202 (100, M^+), 186 (75, M^+-O), 174 (70), 130 (60), 86 (70). HRMS: Calcd. for $C_{10}H_6N_2OS$: 202.0201, Found: 202.0201.

Thieno[2,3-*b*]-2,5-naphthyridine-9-oxide (**9**)
This compound was obtained in a yield of 24 mg (12%).

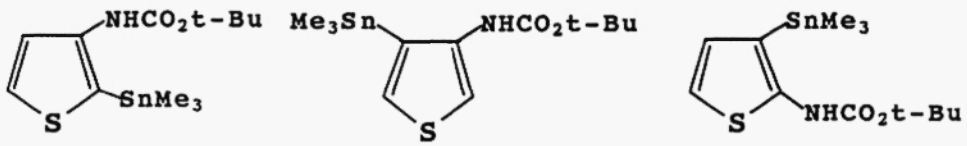
Thieno[3,2-*b*]-2,5-naphthyridine-4-oxide (**13**)
This compound was obtained in a yield of 92 mg (45%) as white crystals, mp 217-220 °C; ^{1}H NMR: δ 7.53 (dd, 1H, H7, J = 4.5, 8.3 Hz), 7.81 (d, 1H, H2, J = 5.5 Hz), 7.99 (d, 1H, H3, J = 5,5 Hz), 8.12 (dd, 1H, H6, J = 1.6, 8.3 Hz), 8.72 (s, 1H, H4), 8.92 (dd, 1H, H8, J = 1.6, 4.5 Hz); MS: m/z 202 (100, M^+), 186 (25, M^+-0), 173 (10), 149 (10). Anal. Calcd. for $C_{10}H_6N_2OS$: C, 59.39; H, 2.99. Found C, 59.28; H, 2.98.

Thieno[3,4-b]-2,5-naphthyridine-4-oxide (**14**)
This compound was obtained in a yield of 24 mg (12%) as white crystals, mp 219-221 °C, ^{1}H NMR: δ 7.49 (dd, 1H, H7, J = 4.6, 8.1 Hz), 7.96 (dd, 1H, H6, J = 1.6, 8.1 Hz), 8.39 (d, 1H, H1, J = 3.7 Hz), 8.45 (s, 1H, H5), 8.62 (d, 1H, H3, J = 3.7 Hz), 8.86 (dd, 1H, H8, J = 1.6, 4.5 Hz); MS: m/z 202 (100, M^+), 186 (90, M^+-O), 174 (20), 142 (10).HRMS: Calcd. for $C_{10}H_6N_2OS$: 202.0201, Found: 202.0198.

Thieno[2,3-b]-2,5-naphthyridine-4-oxide (**16**)
This compound was obtained in a yield of 31 mg (16%) as white crystals, mp 220-221 °C, ^{1}H NMR: δ 7.57 (dd, 1H, H7, J = 4.4, 8.4 Hz), 7.72 (d, 1H, H2, J = 5.6 Hz), 8.15 (d, 1H, H1, J = 5.6 Hz), 8.17 (dd, 1H, H6, J = 1.6, 8.4 Hz), 8.78 (s, 1H, H5), 9.01 (dd, 1H, H8, J = 1.7, 4.4 Hz); MS: m/z 202 (100, M^+), 186 (65, M^+-O), 174 (45), 147 (20). Anal. Calcd. for $C_{10}H_6N_2OS$: C, 59.39; H, 2,99. Found C, 58.99; H, 2.99.

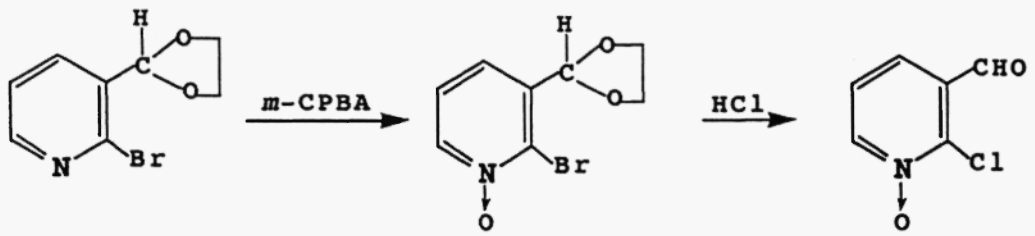
Results and discussion

In order to prepare authentic thieno[*b*]-2,5-naphthyridine-9-*N*-oxides, our aim was to react 2-bromo-3-formylpyridyl-*N*-oxide with the three *ortho*-substituted *t*-butyl-*N*-(trimethylstannylthienyl)carbamates (**1**-**3**) in a Stille coupling. The thiophene derivatives have previously been prepared by us in connection with our improvement of the synthesis of the thieno-[*b*]-fused-2,5-naphthyridines [5]. 2-(2-Bromo-3-pyridyl)-1,3-dioxolane-*N*-oxide (**5**) was prepared by oxidation of (2-bromo-3-pyridyl)-1,3-dioxolane (4) [4] with *m*-chloroperbenzoic acid in 83% yield. However, similarly to the hydrolysis of 2-(2-trimethylstannyl-3-pyridyl)-1,3-dioxolane, which only lead to destannylation [4] it was extremely difficult to hydrolyse **5**. Refluxing with concentrated hydrochloric acid in tetrahydrofuran gave 2-chloro-3-formylpyridine-*N*-oxide (**6**) in 69% yield. The use of hydrobromic acid in tetrahydrofuran gave a complex



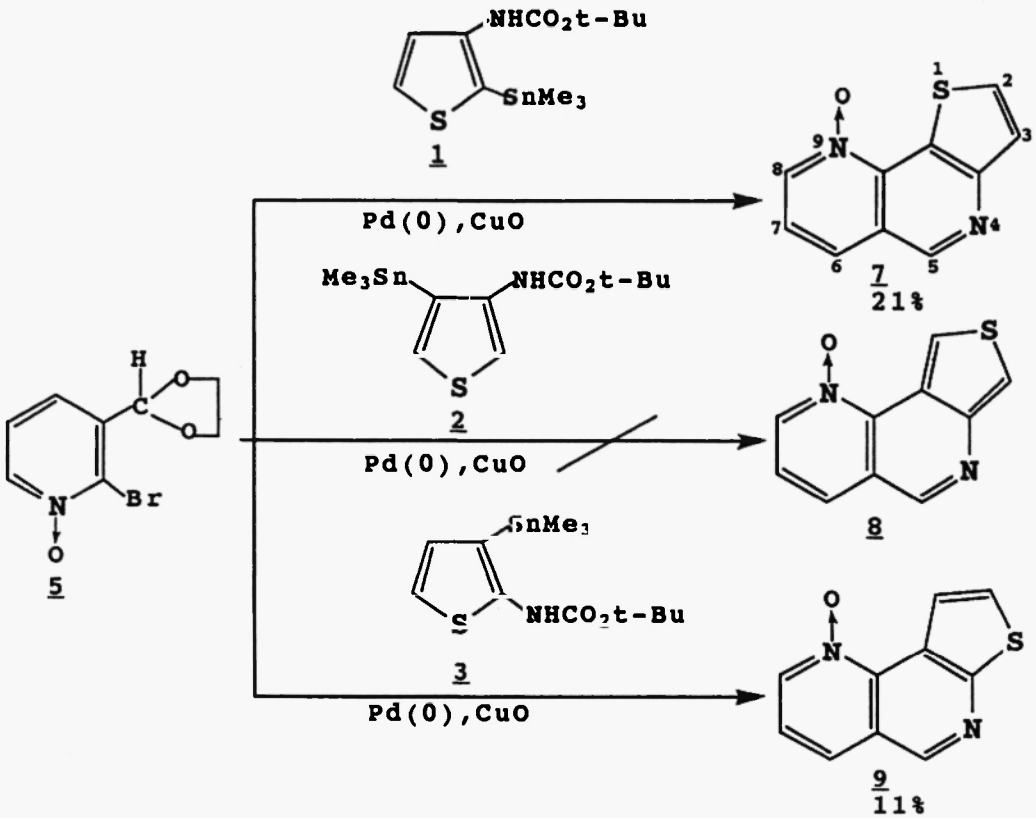
1 **2** **3**

mixture from which 2-bromo-3-formylpyridine-*N*-oxide could be isolated in trace amounts [7]. Attempted deprotection with wet silica gel [8] or with other acids in tetrahydrofuran failed. Therefore we used

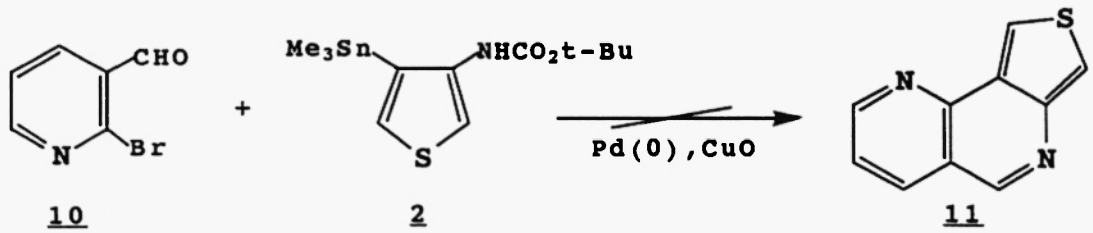


4 **5** 83% **6** 69%

5 directly in the Pd(0)-catalyzed couplings with 1-3 to obtain the intermediate pyridylthiophenes, which without isolation were treated with hydrochloric acid to hydrolyse the acetal, the following ring-closure gave the tricyclic system. However, the yields were low, probably due to the formation of



large amounts of the deoxygenated parent compound. The coupling with **2** failed completely. An attempt to prepare thieno[3,4-*b*]-2,5-naphthyridine (11) from 2-bromo-3-formylpyridine (10) [9,10] and *t*-butyl-*N*-(4-trimethylstannyl-3-thienyl)carbamate (**2**) was also unsuccessful.

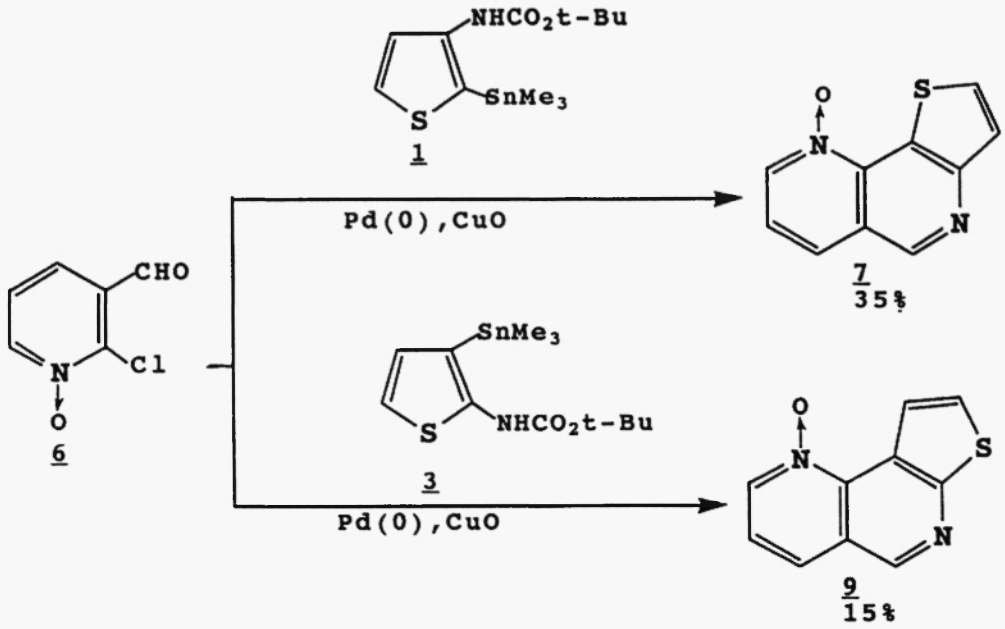


10 2 11

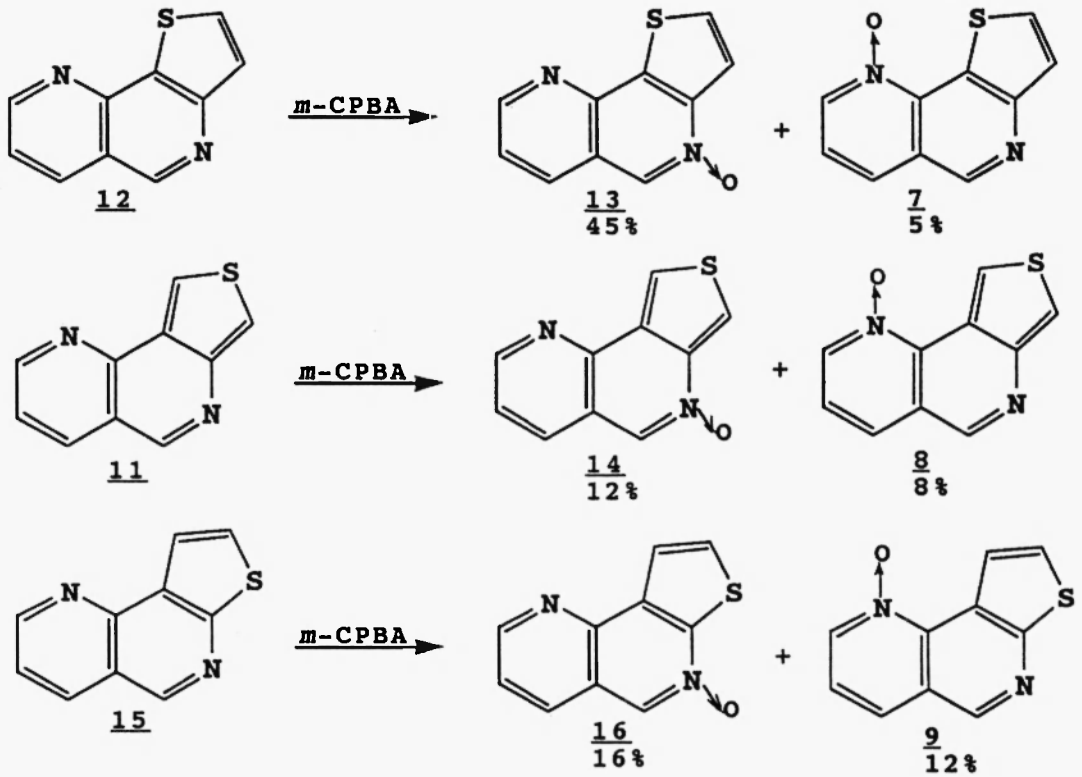
The low reactivity of *t*-butyl-*N*-(4-trimethylstannyl-3-thienyl)carbamate (**2**) had been observed before when trying to cross-couple it with 1-benzyloximethyl-4-bromo-5-formylimidazole [11], which also did not give the desired product. These facts point to that 2 has too low reactivity to be used in this kind of reaction.

Using 6 in a coupling in the presence of cupric oxide with 3, improved the yield of thieno[3,2-*b*]-2,5-

naphthyridine-9-oxide (**7**), compared with the route *via* the bromodioxolane **5**. The 2-chloropyridine grouping being reactive enough to give oxidative insertion once again showing the advantage of the cupric oxide methodology [12]. However, when **6** was coupled with **3** giving **9**, the yields for the two routes were comparable.



The thieno[*b*]-2,5-naphthyridines (**11**,**12**,**15**) were oxidized in chloroform with one equivalent of *m*-chloroperbenzoic acid. The thieno[3,2-*b*]-2,5-naphthyridine (**12**) system, was the only one where large selectivity between the two nitrogens could be found, 45% of the 4-nitrogen was *N*-oxidized to give **13**, while only 5% of the 9-nitrogen was *N*-oxidized to give **7**. This is similar to the behaviour of thieno[3,2-*c*]-1,5-naphthyridine where the amount of *N*-oxidation at the 5-nitrogen was 48% and at the 9-nitrogen 13% [2]. In the *N*-oxidation of thieno[3,4-*b*]-2,5-naphthyridine (**11**) no selectivity at all was found as 12% of **14** and 8% of **8** were obtained. This is similar to what was found for the thieno[3,4-*c*]-1,5-naphthyridine where the amount of *N*-oxidation at the 5- and 9-nitrogens was found to be 19% and 21%, respectively [2]. For the thieno[2,3-*b*]-2,5-naphthyridine (**15**) no selectivity was found either, as 16% of the 4-*N*-oxide (**16**) and 12% of the 9-*N*-oxide (**9**) were isolated. This was different to the results for the *N*-oxidation of the thieno[2,3-*c*]-1,5-naphthyridine where the amount of *N*-oxidation at the 5- and 9-nitrogens was found to be 70% and 3%, respectively. As we had authentic **7** and **9** the identification of **13** and **16** from the oxidation experiments were straight-forward. For **8** and **14**, we had no authentical samples, however, the characteristic shielding of the hydrogens and carbons α to the NO group made it very easy to determine the identity of each isomer.



12 → 13 (45%) + 7 (5%)

11 → 14 (12%) + 8 (8%)

15 → 16 (16%) + 9 (12%)

^{13}C NMR spectra

Unambiguous assignments of the ^{13}C NMR signals and the carbon-proton coupling constants of the thieno[*b*]-2,5-naphthyridines are given in Tables 1 and 2. Assignments were confirmed by proton decoupled ^{13}C spectra, proton-coupled ^{13}C spectra and ^{1}H-^{13}C HETCOR spectra. Comparing with

Table 1. ^{13}C NMR chemical shifts (in ppm) of the thieno[*b*]-2,5-naphthyridine-N-oxides.

Compound	C1	C2	C3	C5	C6	C7	C8
7		133.5	124.8	149.6	124.9	120.9	138.3
8	125.8		120.2	151.4	124.5	122.3	140.9
9	125.0	126.9		149.0	124.8	121.7	139.8
13		130.4	120.0	132.9	133.3	123.1	151.7
14	117.1		122.1	132.2	133.1	123.0	150.8
16	122.3	128.2		132.1	133.4	123.0	151.9

the spectra of the parent compounds, the thieno[*b*]1,5-naphthyridines, we could observe some characteristic changes of the chemical shifts. These were that *N*-oxidation primarily leads to shielding of the carbon atoms α and γ to the NO group in the naphthyridine part, but not in the thiophene part. Except for C2 in 7 and C7 in 8, all the one bond ^{1}H-^{13}C coupling constants for the carbon nuclei were larger than those observed for the corresponding carbons in the parent compound. Similar

changes were found in the isomeric thieno[*c*]-1,5-naphthyridines [2] , and have also been found in other aromatic heterocycles upon *N*-oxidation [13,14]. The two and three bond ^{1}H-^{13}C coupling constants in the naphthyridine part fall in defined intervals, J_{78} = 8.6-8.9, J_{86} = 7.3-7.6 and J_{87} = 3.3-

Table 2. J_{CH} values (Hz) of the thieno[*b*]-2,5-naphthyridines-*N*-oxides (**7**, **8**, **9**, **13**, **14**, **16**).

Compound		C1	C2	C3	C5	C6	C7	C8
7	$^{1}J_{CH}$		184.0	173.0	183.5	168.9	168.6	187.0
	$^{2}J_{CH}$		5.6	3.4			3.7	4.5
	$^{3}J_{CH}$				4.4	6.7, 2.9		8.0
8								
	$^{1}J_{CH}$	200,1		189.5	183.8	163.1	163.8	187.4
	$^{2}J_{CH}$						4 3	4 2
	$^{3}J_{CH}$	4.8		4.0	5.1	5.5, 2.7		8.0
9								
	$^{1}J_{CH}$	181.2	187.3		185.1	170.6	168.6	186.7
	$^{2}J_{CH}$	4.0	7.8				3.8	3.8
	$^{3}J_{CH}$				4.9	6.7, 3.3		8.4
13								
	$^{1}J_{CH}$		188.9	180.1	183.8	165.1	166.4	181.4
	$^{2}J_{CH}$		6.1	4.1			8.9	3.4
	$^{3}J_{CH}$				3.0	6.1, 3.7		7.4
14								
	$^{1}J_{CH}$	195.9		192.6	184.6	163.8	165.9	180.8
	$^{2}J_{CH}$						8.6	3.3
	$^{3}J_{CH}$	4.3		5.7	4.9	6.0, 3.3		7.3
16								
	$^{1}J_{CH}$	175.3	187.4		186.8	164.9	166.3	180.9
	$^{2}J_{CH}$	3.9	6.7				8.9	3.5
	$^{3}J_{CH}$				5.3	6.0, 3.9		7.6

3.5 Hz for **13**, **14** and **16** J_{78} = 3.7-4.3, J_{86} = 8.0-8.4 and J_{87} = 3.8-4.5 Hz for **7**, **8** and **9** J_{56} = 3.0-5.3, J_{68} = 5.5-6.7 and J_{65} = 2.7-3.9 Hz for **7**, **8**, **9**, **13**, **14** and **16**. The one, two and three-bond coupling constants in the thiophene part of the *N*-oxidized thieno[*b*]-2,5-naphthyridines, were for the four *N*-oxidized in the same range as for the thieno[*c*]iso-quinoline-*N*-oxides [15] and for the nine *N*-oxidized in the same range as for the thieno[*c*]-1,5-naphthyridine-9*N*-oxides [2]. This assured the unambiguous assignments of the protons and carbons in the thiophene part.

Acknowledgements

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[7] ^{1}H NMR: δ 10.30 (d, 1H, CHO, J = 0.8 Hz), 8.57 (dd, 1H, H6, J = 6.8, 1.0 Hz), 7,69 (dd, 1H, H4, J = 7.6, 1.0 Hz), 7.37 (ddd, 1H, H5, J = 7.6, 6.8, 0.8 Hz); MS: m/z 203 (95,M^+ + 2), 201 (100, M^+), 187 (45, M^+ + 2 -O), 185 (50, M^+ - O); HRMS calcd. for $C_6H_4NO_2Br$: 200.9425. Found: 200.9421.

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