Synthesis of Pyridine-Thioethers *via* Mono- and Tricationic Pyridinium Salts

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Z. Naturforsch. **60b,** 683 – 687 (2005); received March 11, 2005

On nucleophilic substitution with S-nucleophiles at room temperature, 1-(4-dimethylamino)-[2,3,5,6-tetrachloropyridin-4-yl]pyridinium chloride (**2**) yielded tetrachloro-4-sulfanylpyridines and 2,3,5-trichloro-4,6-disulfanylpyridines depending on the reaction conditions. Similarly, the tricationic (3,5-dichloropyridine-2,4,6-triyl)-1,1',1"-tris[4-(dimethylamino)pyridinium] trichloride **3** was reacted with S-nucleophiles to give the corresponding 3,5-trichloro-2,4,6-trisulfanylpyridines under mild conditions.

Key words: Nucleophilic Substitution, Thioethers, DMAP, Chloropyridines

Introduction

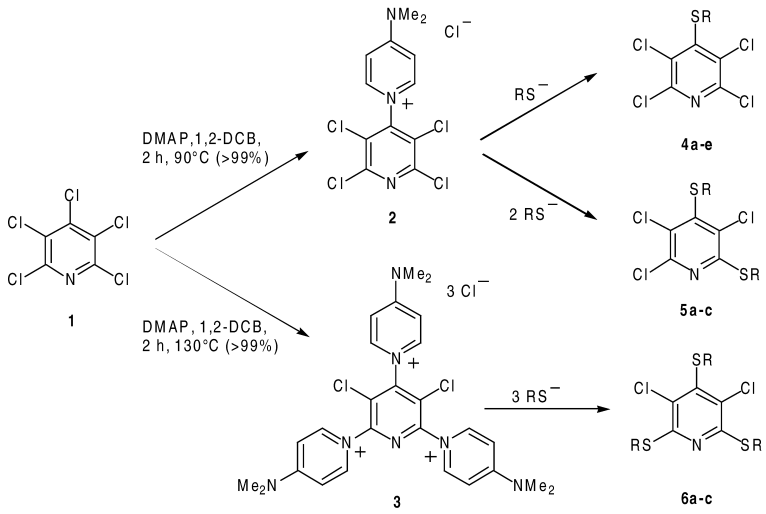
Pyridine and its derivatives continue to be of great interest in organic chemistry, which is reflected in an impressive number of monographs and review articles [*e.g.* 1 – 4]. Despite of the intense work which has been devoted to pyridines [4], a surprisingly large number of simple pyridine derivatives, especially highly substituted rings, have been unavailable to date. This contrasts to the fact that nucleophilic substitution reactions on halogenated heteroaromatics are standard reactions in organic chemistry [1 – 3]. They are known to proceed *via* the *AE*-mechanism [1 – 3], but S_N(*ANRORC*)-[5], *EA*- [6 – 8] and S_{RN1}-mechanisms [9 – 11] are observed as well. It is also known that halogen substituents in the 2-, 3- or 4-positions of pyridine display different reactivities. Thus, 2- and 4-chloropyridine react with a large variety of nucleophiles, whereas the 3-position is inert under these reaction conditions [12 – 15] unless strong bases are used to induce *EA*-mechanisms [16] or metal catalysis is applied [17 – 20]. Tetrachloro-4-sulfanylpyridines, 2,3,5-trichloro-4,6-bis-sulfanylpyridines (most of which are patented [21]), and the very scarcely described class of 3,5-dichloro-2,4,6-tris-sulfanylpyridines have found interest as bactericides [22], pesticides for controlling bacteria, fungi, nematodes, insects, crustaceans, and weeds, and as host compounds [23]. In addition, they are interesting as chemical intermediates for the preparation of sulfones and sulfoxides, which are also useful as fungicides and bactericides [24], herbicides [25], biologically active compounds with fungicidal and phytotoxic activities [26], as well as insectizides and acarizides [27]. Known syntheses of pyridine-sulfanyls start from 2,3,5,6-tetrachloro-pyridine-4-thiol which can be S-methylated by dimethyl sulfate [28], S-alkylated in moderate yields [29, 30], or reacted with perfluorinated carboxylic acids under xenon difluoride catalysis [31, 32].

We found that hetarenium-substituted pyridines are suitable starting materials for the synthesis of highly substituted pyridines. In continuation of our work on betainic and oligocationic heteroaromatics [33 – 37] and their synthetic potential toward oxygen nucleophiles [38] we wish to report here a simple approach to some thioethers of chloropyridines starting from a monocationic and a tricationic pyridinium salt, respectively.

Results and Discussion

Syntheses

1-(4-Dimethylamino)-[2,3,5,6-tetrachloropyridin-4-yl]pyridinium chloride (**2**) and (3,5-dichloropyridine-2,4,6-triyl)-1,1',1"-tris[4-(dimethylamino)pyridinium] trichloride (**3**) are available in quantitative yields from pentachloropyridine **1** on reaction with 4-(dimethylamino)pyridine [36]. The salts **2** and **3** are



1,2-DCB = 1,2-dichlorobenzene

suitable starting materials for the selective synthesis of sulfanyl-substituted pyridines, taking advantage of the leaving group tendency [36, 38] as well as of the electron-withdrawing properties of the pyridinium substituents. Thus, reaction of **2** with ethanethiol in the presence of triethylamine in acetone gave 2,3, 5,6-tetrachloro-4-ethylsulfanyl-pyridine **4a** in 93% yield at room temperature (Scheme). Details of the reaction conditions are summarized in Table 1. The work-up procedure is simple as possible highly polar by-products which would result from an attack at C-2 of **2** as well as unreacted starting material can easily be removed by filtration through silica gel. It is known that the formation of regioisomers is observed starting from pentachloropyridine; in the case of benzenethiolate the outcome of the substitution is dependent on solvent effects and reaction conditions [39] which is a severe limitation of this procedure. Therefore, the ethylsulfanyl derivative **4a** has hitherto been prepared by a substitution / elimination sequence from pentachloropyridine **1** with dithiocarbonic acid O-ethyl ester in 55% yield [40], starting from chloro-(tetrachloro-pyridin-4-yl)-sulfane and $P(OEt)_3$ [41], or by reaction of ethyl bromide with tetrachloro-4-mercaptopyridine [42]. 2,3,5,6-Tetrachloro-4-isopropylsulfanyl-pyridine **4b** was hitherto available starting from **1** on reaction with potassium *iso*-propyltrithiocarbonate [43]; an additional approach is described in a patent [24]. Starting from hetarenium salt **2** this compound is formed in quantitative yield with sodium 2-propanethiolate

Table 1. Reaction conditions for the synthesized compounds.

	R	Eq. Nucleophile, base	Solvent	Reaction time [h]	Yield [%]
4a	Et	1 EtSH, NEt_3	acetone	18	93
4b	*i*Pr	3 *i*PrSH, Na	–	2	99
4c	*t*Bu	1 *t*BuSH, NEt_3	acetone	18	64
4d	allyl	1 $CH_2{=}CHCH_2SH$, NEt_3	MeOH	4	76
4e	C_5Cl_4N	1 C_5Cl_4N-SH, NEt_3	acetone	12	25
5a	Et	3 EtSH, Na	–	2	50
5b	*i*Pr	3 *i*PrSH, NEt_3	MeOH	18	25
5c	*t*Bu	3 *t*BuSH, NEt_3	MeOH	18	27
6a	Et	exc. EtSH, NEt_3	MeOH	3	80
6b	*i*Pr	exc. *i*PrSH	MeOH	3	99
6c	*t*Bu	exc. *t*BuSH, NEt_3	MeOH	3	70

which can be generated *in situ*. The corresponding *tert*-butyl derivative **4c** is new and is formed starting from **2** by nucleophilic substitution with *tert*-butanethiol in acetone in the presence of triethylamine at room temperature in 64% yield. The allyl derivative **4d** was prepared earlier by *S*-alkylation of tetrachloropyridine-4-thiol with allyl bromide after Kugelrohr distillation [44] and is formed by the method described here within 4 h at room temperature from monocation **2**. Octachloro-4,4'-sulfanediyl-bis-pyridine **4e** was synthesized earlier, *i. a.* by lithiation of tetrachloropyridine in the 4-position and subsequent treatment with SCl_2 [45, 46].

Slight modifications of the reaction conditions yield the 2,3,5-trichloro-4,6-bis-sulfanylpyridines **5a – c** which – to the best of our knowledge – have never been described before. They are formed in methanol

(**5b**,**c**) or without solvent (**5a**) in moderate yields by a nucleophilic attack on the pyridinium salt **2** at C-4 and C-2 at room temperature.

Using the tricationic (3,5-dichloropyridine-2,4,6-triyl)-tris-pyridinium trichloride **3** as starting material gives the 3,5-dichloro-2,4,6-tris-sulfanylpyridines **6a – c** in fair to excellent yields. To the best of our knowledge, very few representatives of this class of compounds have been described and patented to date, among these the methyl [21, 47] and the phenyl derivative [39]. In addition, two functionalized derivatives are patented [21]. It is described that the preparation of 3,5-dichloro-2,4,6-tris-phenylsulfanyl-pyridine requires temperatures of 140 °C, a reaction time of 18 h, followed by a 12 h period of stirring with excess sodium hydroxide [39]. For the synthesis of 3,5-dichloro-2,4,6-tris-methylsulfanyl-pyridine a multi-step reaction *via* a pyridine-*N*-oxide was published [47]. The compounds **6a – c** prepared as described here are formed at room temperature starting from trication **3** as indicated in Table 1.

In summary, we present an outlook dealing with the synthetic potential of the pyridinium salts **2** and **3** toward S-nucleophiles which might be of value in preparative organic and biological chemistry.

Experimental Section

NMR data of all compounds are presented unless they are described in the literature. The numbering C-2 to C-6 refers to the pyridine ring. NMR spectra were measured at 20 °C ($\delta_{TMS} = 0.00$ ppm). The pyridinium salts 1-(4-dimethylamino)-[2,3,5,6-tetrachloropyridin-4-yl]pyridinium chloride (**2**) and (3,5-dichloropyridine-2,4,6-triyl)-1,1',1"-tris[4-(dimethylamino)pyridinium] trichloride (**3**) were prepared as published earlier [36].

General procedure for the synthesis of the tetrachloro-4-alkylsulfanylpyridines **4a**, **4b**, **4c**, *and* **4e**

A suspension of **2** (10 mmol, 3.74 g) in 75 ml of acetone was cooled to 0 °C and then treated with triethylamine (10 mmol, 1.01 g) and the corresponding thiol [ethanethiol (10 mmol, 0.62 g), 2-propanethiol (10 mmol, 0.76 g), *tert*-butanethiol (10 mmol, 0.90 g), or 2,3,5,6-tetrachloropyridine-4-thiol (10 mmol, 2.51 g)]. Stirring was continued for 18 h at 0 °C (for **4a – c**) or at r. t. (for **4e**). The solvent was then distilled off *in vacuo*, the residue was filtered through silica gel (EtOAc / petroleum ether = 1 / 2) and recrystallized from aqueous ethanol.

*2,4,5,6-Tetrachloro-4-(ethylsulfanyl)pyridine (***4a***)*

M. p. 49 °C (ref. [40]: 47.5 – 48.5 °C, ref. [42]: 49 – 51 °C). NMR data are presented in ref. [40].

*2,3,5,6-Tetrachloro-4-(isopropylsulfanyl)pyridine (***4b***)*

M. p. 42 °C (ref. [43]: 34 – 35 °C (from hexane)). – ^{1}H NMR (200 MHz, [D$_6$]-DMSO): $\delta = 3.77$ (sept, $^3J = 6.3$ Hz, 1H, C*H*), 1.38 (d, $^3J = 6.3$ Hz, 3H, C*H*$_3$), 1.23 (d, $^3J = 6.3$ Hz, 3H, C*H*$_3$). – ^{13}C NMR (50 MHz, [D$_6$]-DMSO): $\delta = 156.1$ (C-4), 146.0 (C-2, C-6), 129.6 (C-3, C-5), 36.2 (*C*H), 23.0 (*C*H$_3$), 22.2 (*C*H$_3$). – IR (KBr): $\nu = 2971$, 1503, 1304, 1239, 1084, 1048, 803, 676 cm^{-1}. – GC-MS: $m/z = 291$ (M, 88), 249 (M - Cl, 100), 211 (M - C$_3$H$_7$-Cl, 23), 43 (C$_3$H$_7$, 96). – C$_8$H$_7$Cl$_4$NS (291.03): calcd. C 33.02, H 2.42, N 4.81, S 11.02; found C 33.27, H 2.46, N 4.75, S 11.13.

*4-tert-Butylsulfanyl-2,3,5,6-tetrachloropyridine (***4c***)*

M. p. 76 °C. – ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 1.44$ (s, 9H, C*H*$_3$). – ^{13}C NMR (50 MHz, CDCl$_3$): $\delta = 146.9$ (C-4), 146.4 (C-2, C-6), 138.0 (C-3, C-5), 55.3 (*C*), 32.0 (*C*H$_3$). – IR (KBr): $\nu = 2965$, 1499, 1299, 1157, 1079, 797, 671 cm^{-1}. – GC-MS: $m/z = 306$ (M, 100). – C$_9$H$_9$Cl$_4$NS (305.05): calcd. C 35.44, H 2.97, N 4.59, S 10.51; found C 36.27, H 3.18, N 4.43, S 10.96.

*Bis-(2,3,5,6-tetrachloropyridin-4-yl)sulfane (***4e***)*

M. p. 35 – 39 °C. – ^{13}C NMR (50 MHz, CDCl$_3$): $\delta = 146.4$ (C-2, C-2', C-6, C-6'), 144.7 (C-4, C-4'), 129.6 (C-3, C-3', C-5, C-5'). – IR (KBr): $\nu = 1506$, 1352, 1315, 1084, 818, 802 cm^{-1}. – GC-MS: $m/z = 464$ (M, 100). – C$_{10}$Cl$_8$N$_2$S (463.81): calcd. C 25.90, N 6.04; found C 26.09, N 5.87.

*4-Allylsulfanyl-2,3,5,6-tetrachloropyridine (***4d***)*

A suspension of **2** (10 mmol, 3.74 g) in 75 ml of methanol was cooled to 0 °C and treated with triethylamine (22 mmol, 2.8 ml) and allylmercaptane (10 mmol, 0.74 g). After stirring for 4 h at this temperature the mixture was poured on 250 ml of ice and water, and then extracted with dichloromethane. The organic layer was evaporated to give a yellow solid which was recrystallized from aqueous ethanol.

M. p. 43 °C (ref. [44]: 42 – 43 °C). – ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 5.75$ (tt, $^3J = 7.3$ Hz, $^3J = 10.0$ Hz, 1H, C*H*), 5.10 (d, $^4J = 1.1$ Hz, 1H, =C*H*), 5.01 (d, $^3J = 10.0$ Hz, 1H, =C*H*), 3.73 (dt, $^4J = 1.1$ Hz, $^3J = 7.3$ Hz, 2H, C*H*$_2$). – ^{13}C NMR (50 MHz, CDCl$_3$): $\delta = 146.1$ (C-2, C-4), 139.0 (C-4), 131.8 (*C*H), 119.2 (1C, =*C*H$_2$), 117.2 (C-3, C-5), 38.0 (*C*H$_2$). – IR (KBr): $\nu = 1503$, 1456, 1306, 1083 cm^{-1}. – GC-MS: $m/z = 290$ (MH$^+$, 20), 253 (M - Cl, 100), 210 (M - Cl - C$_3$H$_5$, 28). – No satisfactory elemental analysis was obtained.

*2,3,5-Trichloro-4,6-bis(ethylsulfanyl)pyridine (***5a***)*

Sodium (30 mmol, 0.70 g) was dissolved in 50 ml of ethanethiol, then treated with **2** (10 mmol, 3.74 g) and stirred

for 2 h at r. t. The excess mercaptane was distilled off and the residue was chromatographed on silica gel (EtOAc / petroleum ether = 1 / 2) to give **5a** as a yellowish oil.

^{1}H NMR (200 MHz, [D$_6$]-DMSO): $\delta = 3.10$ (m, overlapped, 4H, OC*H*$_2$), 1.32 (m, 3H, α-C*H*$_3$), 1.16 (m, 3H, γ-C*H*$_3$). – ^{13}C NMR (50 MHz, [D$_6$]-DMSO): $\delta = 156.0$ (C-4), 145.9 (C-2), 144.9 (C-6), 131.5 (C-3), 128.9 (C-5), 29.0 (C-4-*C*H$_2$), 25.1 (C-2-*C*H$_2$), 14.8 (*C*H$_3$), 13.7 (*C*H$_3$). – IR (NaCl): $\nu = 2969$, 2928, 1506, 1453, 1296, 1217, 1183, 1080 cm^{-1}. – GC-MS: $m/z = 303$ (M, 100). – $C_9H_{10}NCl_3S_2$ (302.67): calcd. C 35.71, H 3.33, N 4.63; found C 34.99, H 2.67, N 4.63.

General procedure for the synthesis of 4,6-bis(alkylsulfanyl)-2,3,5-trichloro-pyridines **5b** *and* **5c**

The salt **2** (10 mmol, 3.74 g) and triethylamine (390 mmol, 4.15 ml) were dissolved in 150 ml of methanol and then treated with 2-propanethiol (30 mmol, 2.82 ml) and *tert*-butanethiol (30 mmol, 3.38 ml), respectively. The reaction mixture was then stirred for 24 h at r. t. After distilling off the solvent *in vacuo* at low temperatures, the residue was chromatographed on silica gel (EtOAc / petroleum ether = 1 / 1).

*2,3,5-Trichloro-4,6-bis(isopropylsulfanyl)pyridine (***5b***)*

Yellow oil. – ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 3.86$ (sept, $^3J = 6.9$ Hz, 1H, C-2-C*H*), 3.67 (sept, $^3J = 6.6$ Hz, 1H, C-4-C*H*), 1.35 (d, $^3J = 6.9$ Hz, 6H, C*H*$_3$), 1.21 (d, 3$J = 6.6$ Hz, 6H, C*H*$_3$). – ^{13}C NMR (50 MHz, CDCl$_3$): $\delta = 156.7$ (C-2), 151.2 (C-4), 146.2 (C-6), 128.7 (C-3), 125.5 (C-5), 40.0 (C-2-*C*H), 36.5 (C-4-*C*H), 23.3 (*C*H$_3$), 22.6 (-*C*H$_3$). – IR (KBr): $\nu = 2960$, 1506, 1293, 1154, 1078, 804 cm^{-1}. – GC-MS: $m/z = 331$ (MH$^+$, 100), 254 (M - Cl - C$_3$H$_7$, 20). – $C_{11}H_{14}NCl_3S_2$ (330.73): calcd. C 39.95, H 4.27, N 4.24; found: C 40.50, H 4.16, N 4.11.

*2,4-Di(tert-butyl)-3,5,6-trichloropyridine (***5c***)*

Yellow oil. – ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 1.55$ (s, 9H, C*H*$_3$), 1.35 (s, 9H, C*H*$_3$). – ^{13}C NMR (50 MHz, CDCl$_3$): $\delta = 158.3$ (C-2), 154.7 (C-4), 147.0 (C-6), 131.7 (C-3), 126.9 (C-5), 49.2 (*C*), 40.0 (*C*), 31.9 (*C*H$_3$), 29.8 (*C*H$_3$). – IR (KBr): $\nu = 2964$, 2925, 1503, 1478, 1456, 1365, 1290, 1157, 1079, 803 cm^{-1}. – GC-MS: $m/z = 359$ (MH$^+$, 4), 344 (M - CH$_3$, 91), 289 (M - 2 Cl, 100), 252 (M - 3 Cl, 40), 240 (M - 3 Cl - CH$_3$, 31), 58 (C$_4$H$_9$, 77). – $C_{13}H_{18}Cl_3NS_2$ (358.78): calcd. C 43.52, H 5.06, N 3.90; found C 42.28, H 4.79, N 3.55.

General procedure for the synthesis of the 2,4,6-tris(alkylsulfanyl)-3,5-dichloropyridines **6a – c**

A solution of triethylamine (0.05 mol, 5.0 g) and **3** (5.34 g, 10 mmol) in 100 ml of anhydrous methanol was treated dropwise ar r. t. with the corresponding thiols [ethanethiol (3.0 mmol, 186 mg), 2-propanethiol (3.0 mmol, 229 mg), *tert*-butanethiol (3.0 mmol, 271 mg), respectively]. After stirring for 3 h, the reaction mixture was poured on cold water which was then extracted twice with dichloromethane. The organic layer was dried over sodium sulfate and evaporated. The residue was chromatographed on silica gel (EtOAc / petroleum ether = 1 / 2).

*3,5-Dichloro-2,4,6-tris(ethylsulfanyl)pyridine (***6a***)*

M. p. 25 °C. – ^{1}H NMR (200 MHz, [D$_6$]-DMSO): $\delta = 3.19$ (q, $^3J = 7.3$ Hz, 4H, C-2/6-C*H*$_2$), 3.04 (q, $^3J = 7.3$ Hz, 2H, C-4-C*H*$_2$), 1.33 (t, $^3J = 7.3$ Hz, 6H, C*H*$_3$), 1.13 (t, $^3J = 7.3$ Hz, 3H, C*H*$_3$). – ^{13}C NMR (50 MHz, [D$_6$]-DMSO): $\delta = 157.2$ (C-4), 155.1 (C-2, C-6), 127.3 (C-3, C-5), 28.7 (C-4-*C*H$_2$), 24.6 (C-2/6-*C*H$_2$), 14.7 (CH$_3$), 14.4 (2 *C*H$_3$). – IR (KBr): $\nu = 2968$, 2927, 1493, 1284, 1210, 1077 cm^{-1}. – GC-MS: $m/z = 327$ (M, 56), 293 (M -Cl, 100). – $C_{11}H_{15}Cl_2NS_3$ (328.35): calcd. C 40.24, H 4.60, N 4.27; found C 40.88, H 4.54, N 3.77.

*3,5-Dichloro-2,4,6-tris(isopropylsulfanyl)pyridine (***6b***)*

M. p. 42 °C. – ^{1}H NMR (200 MHz, [D$_6$]-DMSO): $\delta = 3.85$ (q, $^3J = 6.8$ Hz, 2H), 3.80 (q, $^3J = 6.8$ Hz, 1H), 1.40 (t, $^3J = 6.8$ Hz, 12H, C-2-CH$_3$), 1.22 (t, $^3J = 6.8$ Hz, 6H, CH$_3$). – ^{13}C NMR (50 MHz, [D$_6$]-DMSO): $\delta = 163.3$ (C-4), 149.0 (C-2, C-6), 127.5 (C-3, C-5), 35.3 (*C*H), 22.8 (6 *C*H$_3$). – IR (KBr): $\nu = 2965$, 2927, 1681, 1504, 1457, 1293 cm^{-1}. – GC-MS: $m/z = 370$ (M, 100), 334 (M$^+$, -Cl, 78), 259 (M - Cl - C$_3$H$_7$S, 15). – No satisfactory elemental analysis was obtained.

*2,4,6-Tris(tert-butylsulfanyl)-3,5-dichloropyridine (***6c***)*

Yellow oil. – ^{1}H NMR (200 MHz, [D$_6$]-DMSO): $\delta = 1.67$ (s, 9H, C-4-C*H*$_3$), 1.39 (s, 18H, C-2-C*H*$_3$). – ^{13}C NMR (50 MHz, [D$_6$]-DMSO): $\delta = 162.3$ (C-4), 157.1 (C-2, C-6), 116.2 (C-3, C-5), 30.4 (3 *C*(CH$_3$)$_3$), 21.8 (9 *C*H$_3$). – IR (NaCl): $\nu = 2930$, 1737, 1677, 1458, 1387, 1245 cm^{-1}. – GC-MS: $m/z = 413$ (M, 12), 323 (M - C$_4$H$_9$S, 100), 235 (M - 2 C$_4$H$_9$S, 47). – $C_{17}H_{27}NCl_2S_3$ (412.51): calcd. C 49.50, H 6.60, N 3.40; found C 49.32, H 6.30, N 3.36.

Acknowledgement

We thank the Deutsche Forschungsgemeinschaft for financial support.

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