To prepare IVa, 1 g hydrochloride III was refluxed for 4 hr with 9 ml orthoformic ester, the excess of the latter distilled off under reduced pressure, the residue washed with benzene, and pressed on a porous tile, yield, 0.5 g.

2-Substituted 3', 4'-dihydronaphth-1', 2': 5, 4-oxazoles (IIa-e, and VI). 5 mmole N-acyl derivative of 2-amino-1-keto-1, 2, 3, 4-tetrahydronaphthalene was refluxed for 8 hr with 40 ml $POCl_3$. Most of the latter was then distilled off under reduced pressure, and the residue poured into water. The oxazole which separated was extracted with ether, precipitated as hydrochloride, and then converted to free base. Yields of oxazoles, 30-50%.

To prepare the oxazole IIb, 3.6 g (18 mmole) hydrochloride III was refluxed for 5 hr with 24 ml Ac_2O. Excess of the latter was distilled off, and the residue distilled under reduced pressure. The oxazole obtained was purified by conversion to the hydrochloride, mp 158.5°-163.5° yield 1.7 g (9.2 mmole). Found: Cl 15, 8, 15.7; N 6.22, 6.69%. Calculated for $C_{12}H_{12}CiNO$: Cl 16.0; N 6.27%.

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SYNTHESIS OF 4- AND 8-METHYLTHIENOTHIENOPYRIDINES

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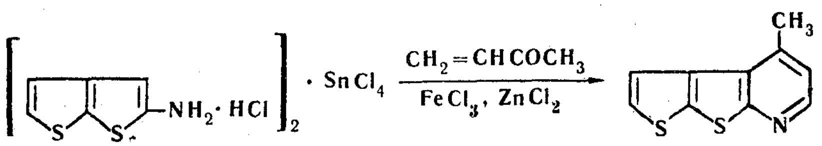
The synthesis of some new heterocyclic bases is described. These are 4-methylthieno (2, 3-b) thieno (2, 3-b)-pyridine (I), and 8-methylthieno (3, 2-b) thieno (2, 3-b) pyridine (II).

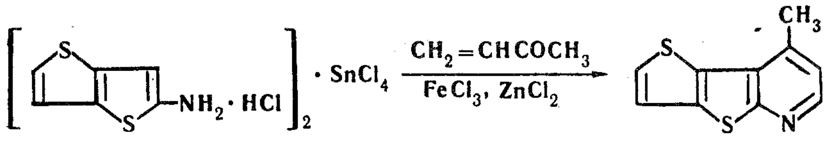
We have previously obtained 4- and 7-methylthieno- and 1-methylthionaphthenopyridine [1, 2]. The present communication describes the synthesis of new heterocyclic bases, 4, -methylthieno [2, 3-b]-thieno [2, 3-b]-(I) and 8-methylthieno [3, 2-b] thieno [2, 3-b] pyridine (II).

Compound I was synthesized by a somewhat modified Doebner-Miller synthesis, by reacting methylvinylketone with the stannic chloride double salt of 2-aminothieno [2, 3-b] thiophene hydrochloride in the presence of ferric chloride plus anhydrous zinc chloride in ethanol solution, heat being used [3].



I

The isomeric base II is obtained by the same method, starting from the stannic chloride double salt with 2-aminothieno [3, 2-b] thiophene hydrochloride [3].



II

We have previously described the synthesis of the starting thieno [2, 3-b]- and thieno [3, 2-b] thiophenes, and the preparation of the double stannic chloride salts with the hydrochlorides of 2-aminothieno [2, 3-b]- and thieno [3, 2-b] thiophenes [4].

Experimental

4-Methylthieno [2, 3-b] thieno [2, 3-b] pyridine. 15.0 g methylvinylketone was added dropwise, over an hour, to a stirred mixture of 64.3 g double salt of stannic chloride with 2-aminothieno [2, 3-b] thiophene hydrochloride, 66.0 g $FeCl_3$, 5.0 g $ZnCl_2$ and 300 ml dry EtOH, at 60-65°. Stirring at that temperature was continued for 1 hr, then the mixture refluxed for the same time, and after this heating was continued for 3 hr more. The EtOH was then distilled off, the residue cooled and made alkaline to litmus with 10% NaOH, and the mixture then steam distilled. The base separated out as a crystalline precipitate when the distillate was cooled. It was filtered off, washed with water, and vacuum-dried over KOH or NaOH. Yield 5.4 g (21.4%), mp 113-119°. After crystallizing from petrol ether it formed colorless plates mp 128-129°. Found: N 6.66, 6.70%. Calculated for $C_{10}H_7NS_2$: N 6.82%.

Picrate, pale yellow plates, mp 191-192° (ex EtOH). Found: N 12.68, 12.71%. Calculated for $C_{16}H_{10}N_4O_7S_2$: N 12.89%.

Ethiodide, grayish prisms, mp 218-219° (ex EtOH). Found: N 3.67, 3.5%. Calculated for $C_{12}H_{12}INS_2$: N 3.87%.

Methiodide, pale yellow prisms, mp 231-232° (ex EtOH). Found: N 3.95, 3.98%. Calculated for $C_{11}H_{10}INS_2$: N 4.03%.

8-Methylthieno [3, 2-b] thieno [2, 3-b] pyridine. 10.0 ml methylvinylketone was added dropwise, over 1 hr, to a mixture of 40.0 g double salt between stannic chloride and 2-aminothieno [3, 2-b] thiophene hydrochloride, 40.0 g $FeCl_3$, 5.0 g anhydrous $ZnCl_2$, and 300 ml dry EtOH, at 65-70°. When the addition was complete, stirring at the same temperature was continued for 1 hr more, after which the mixture was refluxed for an hour, then 50 ml EtOH and 60 g anhydrous $ZnCl_2$ added, and the whole refluxed for 1 hr, after which 30.0 g $FeCl_3$ was added, and the mixture refluxed for 1 hr. The EtOH was distilled off, the residue made alkaline to litmus with aqueous NaOH, with cooling, and then steam distilled. The base distilled over as a colorless oil, which crystallized when the distillate cooled. It was filtered off, washed with water, and vacuum-dried over solid KOH or NaOH. Yield 2.4 g (19.5%), mp 103-104°. Recrystallized from petrol ether it formed colorless plates, mp 113-115°. Found: N 6.77, 6.80%. Calculated for $C_{10}H_7NS_2$: N 6.82%.

Picrate, pale yellow plates, mp 160-161° (ex EtOH). Found: N 12.66, 12.69%. Calculated for $C_{16}H_{10}N_4O_7S_2$: N 12.89%.

Ethiodide, pale gray prisms, mp 219-220° (ex EtOH). Found: N 3.63, 3.70%. Calculated for $C_{12}H_{12}INS_2$: N 3.87%.

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