# SYNTHESIS OF 7-METHYL- AND 9-METHYLTHIENO[3, 2-f]QUINOLINE

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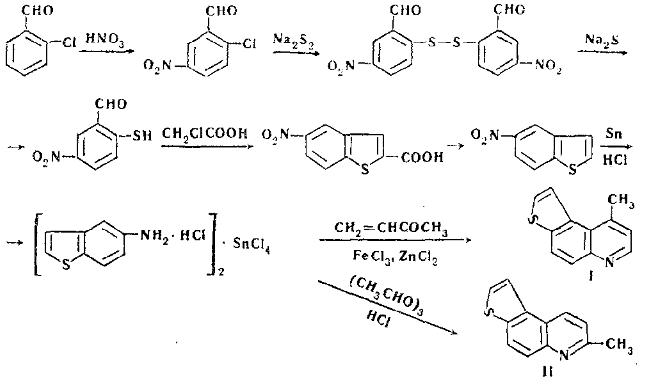
New heterocyclic bases with a condensed heterocyclic ring in the molecule are synthesized. They are 7-methylthieno[3, 2-f]quinoline and 9-methylthieno[3, 2-f]quinoline.

We previously synthesized methyl-substituted thieno[2,3-b]- and -[3,2-b]pyridines and thionaphtheno[2,3-b]- and -[3,2-b]pyridines, respectively, isosteres of 2- and 4-methylquinoline and -5,6 and -7,8-benzoquinoline [1–4]. We have now been able to prepare the new heterocyclic bases 9-methyl- and 7-methylthieno[3,2-f] quinoline (I–II), which are isosteres of 4- and 2-methyl-5,6-benzoquinoline.



5-Nitro-2-chlorobenzaldehyde was prepared by nitrating, with mixed nitric and sulfuric acids [5], o-chlorobenzaldehyde. Treatment with sodium disulfide in ethanol solution converted it to di(4-nitro-2-formylphenyl)disulfide, reduced by sodium sulfide in boiling ethanol to 5-nitro-2-mercaptobenzaldehyde. Reaction of the latter with chloroacetic acid in alkaline solution gave 5-nitrothionaphthene-2-carboxylic acid [6], converted on heating in quinoline to 5-nitrothionaphthene [7]. The tin double salt of 5-aminothionaphthene hydrochloride was obtained by reducing 5-nitrothionaphthene with tin in hydrochloric acid, yield 60%.

Condensation of this salt with methylvinylketone in ethanol gave 9-methylthieno[3,2-f]quinoline (mp 158–159° (ex petrol ether). Found: N 6.92%. Calculated for $C_{12}H_9NS$: N 7.02%). Reaction with paraldehyde in dilute hydrochloric acid (1:1) gave 7-methylthieno[3,2-f]quinoline (mp 81–82° (ex petrol ether). Found: N 6.93%. Calculated for $C_{12}H_9NS$: N 7.02%).

Unsubstituted thieno[3,2-f]quinoline was previously synthesized from 5-aminothionaphthene, using the Skraup reaction.

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# ELECTROSYNTHESIS OF NICOTINIC ACID FROM 8-HYDROXYQUINOLINE

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Electrochemical oxidation of 8-hydroxyquinoline at a lead dioxide anode in sulfuric acid gives quinolinic acid, which is decarboxylated to nicotinic acid.

Until recently pyridine bases were practically the only source of nicotinic acid; at the present time quinoline and its derivatives assume great importance. Choice of oxidizing agent plays an important part in the preparation of nicotinic acid. Owing to the cheapness and availability of electrical energy, electrochemical methods of oxidation are definitely of interest.