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

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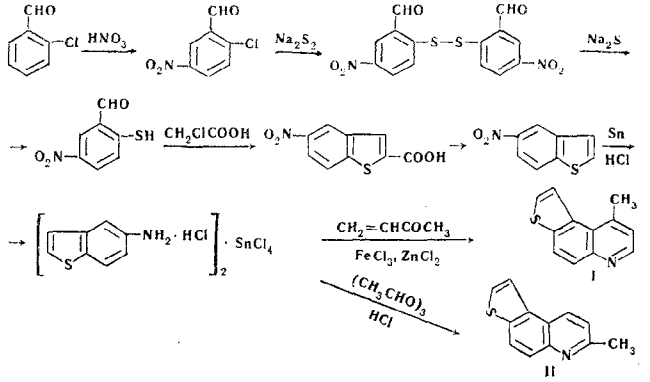
New heterocyclic bases with a condensed heterocyclic ring in the molecule are synthesized. They are 7-methylthieno[3,2-f]quinoline and 9-methylthieno[3,2-f]quinoline.

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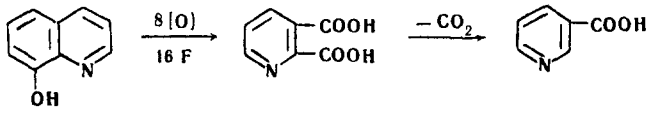
Electrochemical oxidation of 8-hydroxyquinoline at a lead dioxide anode in sulfuric acid gives quinolinic acid, which is decarboxylated to nicotinic acid.

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.

The electrochemical oxidation of quinoline is described in [1–5]; the literature does not contain any information about electrooxidation of 8-hydroxyquinoline. Work on the chemical oxidation of 8-hydroxyquinoline shows that permanganate [6], nitric acid [7–10], or mixed oxygen-ozone oxidation gives quinolinic acid, which is readily decarboxylated to nicotinic acid.

The present communication describes the preparation of nicotinic acid by electrochemical oxidation of 8-hydroxyquinoline:



EXPERIMENTAL

The electrochemical oxidation of 8-hydroxyquinoline was run in a cylindrical electrolyzer with a ceramic diaphragm. The anode was a perforated lead one, previously coated with a layer of lead dioxide by anodic treatment in sulfuric acid. The cathode is also of lead. Working anolyte volume 100 ml, anolyte composition (g/l): 8-hydroxyquinoline 112, sulfuric acid 475; V_2O_5 1; the catholyte was 60% H_2SO_4. Electrolysis conditions: anolyte temperature 75 ± 2°, anode current density 5 amp/dm^2, quantity of electricity passed 125% (theoretical quantity of electricity 16 F per mole of 8-hydroxyquinoline).

After the electrolysis the anolyte was neutralized with 25% NH_4OH, and brought to pH 2. Quinolinic acid was extracted from this solution by n-butanol at 90–95°. When the butanol was distilled off, the quinolinic acid underwent decarboxylation to nicotinic acid, and the latter separated when the remaining small volume of butanol was cooled to 0°. Yield 5.9–6.0 g nicotinic acid, 96–98% pure (60% yield). Recrystallization from water, using decolorizing charcoal, gave nicotinic acid mp 234–236°.

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HYDRAZONES AND HYDRAZIDES OF 4,6-DIMETHYL-5-CARBOXYPYRID-2-ONE AND 4-METHYL-6-CARBOXYMETHYLPYRID-2-ONE

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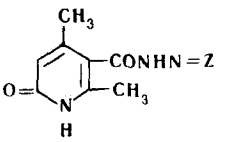
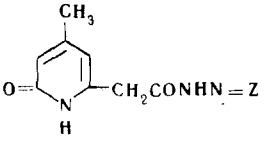
With a view to elucidating antitubercular activity, from the hydrazides of 4, 6-dimethyl-5-carboxypyrid-2-one and 4-methyl-6-carboxymethylpyrid-2-one, are synthesized the hydrazones of acetone, methyl ethyl ketone, acetophenone, benzaldehyde, p-hydroxypropiophenone, p-dimethylaminobenzaldehyde and tetrahydrothiopyr-4-one.

4,6-Dimethyl-5-ethoxycarbonylpyrid-2-one and the isomeric 4-methyl-6-ethoxycarbonylmethylpyrid-2-one, now prepared by us from β-aminocrotonic ester by somewhat modified methods [1, 2], have been used by us to synthesize the corresponding hydrazides (I, II), and a number of hydrazones (III–XI) based on them, with a view to testing their antiturbercular activities.

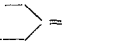


III, IV

III, V	$z=(CH_3)_2C$
IV, VIII	$z=C_6H_5CH$
VI	$z=(CH_3)(C_2H_5)C$
VII	$z=(C_6H_5)(CH_3)C$



V–XI

IX	$z=(p\text{-}HOC_6H_4)(C_2H_5)C$
X	$z=p\text{-}(CH_3)_2NC_6H_4CH$
XI	$z=S$  $=$

EXPERIMENTAL

Hydrazide of 4, 6-dimethyl-5-carboxypyrid-2-one (I). The starting 4, 6-dimethyl-5-ethoxycarbonylpyrid-2-one, mp 136–137°, was pre-