yellow-green crystals of IX that decomposed at 275-277°C without melting and had Rf 0.42 were isolated successively. IR spectrum: 1688 cm⁻¹ (C=O). Found: M⁺ 345. Calculated: M 345. Subsequent elution with ether gave 0.41 g (59%) of oxidized product VIII as yellow-green crystals with mp 244-245°C (from ether) and Rf 0.51 (ether). IR spectrum: 1680 (C) and 3248 cm⁻¹ (OH). Found: C 83.8; H 4.9; N 3.7%; M⁺ 361. C₂₅H₁₃NO₂. Calculated: C 83.6; H 4.9; N 3.9%; M 361.

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CHEMISTRY OF HETEROCYCLIC N-OXIDES AND RELATED COMPOUNDS.

10.* REACTION OF PYRIDINE N-OXIDE WITH 4-METHYL-

AND 4-PHENYL-SUBSTITUTED HANTZSCH ESTERS

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The corresponding dehydrogenation products were obtained in the reaction of diethyl 1,4-dihydro-2,4,6-collidine-3,5-dicarboxylates and diethyl 1,4-dihydro-4-phenyl-2,6-lutidine-3,5-dicarboxylate with pyridine N-oxide. The reaction with dihydro-collidine is accompanied by simultaneous demethylation in the 4 position and methylation of the pyridine ring.

In [1-5] we established that the N-oxides of pyridine bases, which have high dehydrogenating activity, can be used for the dehydrogenation of dihydro derivatives of pyridine, naphthalene, anthracene, and completely saturated heterocycles — piperidine and the alkaloid anabasine. Of the investigated compounds, the dehydrogenation of diethyl 1,4-dihydro-2,6lutidine-3,5-dicarboxylate (the Hantzsch ester) takes place especially readily. In a continuation of our research it seemed of interest to study the dehydrogenation of 4-substituted Hantzsch esters by heteroaromatic N-oxides.

In the present communication we present the results of a study of the dehydrogenation of diethyl 1,4-dihydro-2,4,6-collidine-3,5-dicarboxylate and diethyl 1,4-dihydro-4-phenyl-2,6-lutidine-3,5-dicarboxylate with pyridine N-oxide.

In addition to the expected dehydrogenation, which leads to the formation of diethyl 2,4,6-collidine-3,5-dicarboxylate (III) and pyridine, the reaction of diethyl 1,4-dihydro-2,4,6-collidine-3,5-dicarboxylate (I) with pyridine N-oxide (II) also involves the simultaneous demethylation of the starting ester in the 4 position to give considerable amounts of diethyl 2,6-lutidine-3,5-dicarboxylate (IV), as well as the simultaneous methylation of pyridine to give 2- and 4-picolines. Acetaldehyde, ethanol, and propyl, isobutyl, and isoamyl alcohols are formed in very small amounts as side products, probably as a result of hydrolysis, oxidation, and alkylation.

Ester IV is most likely formed as a result of radical demethylation of starting dihydrocollidine I. This is confirmed by the formation of $C_3 - C_5$ alcohols and particularly 2- and 4-picolines, which may be obtained as a result of radical alkylation, and by the fact that demethylation does not occur [6] in the ionic dehydrogenation of dihydrocollidine I by the

*See [1] for Communication 9.

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action of the nitrosyl cation. The dehydrogenation of I probably proceeds in the same way as demethylation; this is in agreement with the concepts of the one-electron mechanism of the acceptance of hydride hydrogen by the N-oxide [7]. Thus the reaction of dihydrocollidine I with pyridine N-oxide can be represented by the following possible scheme on the basis of the products formed:



The reaction of diethyl 1,4-dihydro-4-phenyl-2,6-lutidine-3,5-dicarboxylate (V) with N-oxide II, which is realized under the same conditions, proceeds more unambiguously and leads to the formation of primarily the dehydrogenation product (diethyl 4-phenyl-2,6-lutidine-3,5-dicarboxylate (VI) and the deoxidation product (pyridine).

EXPERIMENTAL

The reactions and the isolation of the reaction products were monitored by paper chromatography in an n-butanol-hydrochloric acid-water system (50:7:14) (system A) with development with Dragendorff's reagent and by thin-layer chromatography (TLC) on activity II aluminum oxide in a chloroform-benzene-alcohol system (22:8:2) (system B) with development with iodine vapors. The reaction products were identified by chromatography and also from the absence of melting-point depressions for mixtures of the bases and their picrates with genuine samples.

Diethyl 1,4-dihydro-2,4,6-collidine-3,5-dicarboxylate (I) and diethyl 1,4-dihydro-4phenyl-2,6-lutidine-3,5-dicarboxylate were obtained by the method in [6].

<u>Reaction of Diethyl 1,4-Dihydro-2,4,6-collidine-3,5-dicarboxylate (I) with Pyridine N-Oxide (II).</u> A mixture of 20.3 g (75 mmole) of ester I and 7.13 g (75 mmole) of oxide II was heated for 1 h at 210-220°C (until a negative test for the presence of ester I with picric acid was obtained). The resulting distillate (7.2 g) was analyzed by gas-liquid chromatography (GLC) with a Vyrukhrom chromatograph with a 2 m by 4 mm stainless steel column; the sorbent was 20% β , β '-thiodipropionitrile on a Chromaton N-AW support-silanized with hexamethyldisilazan, the carrier-gas (nitrogen) flow rate was 45 ml/min, the temperature was 80°C, the air:hydrogen:nitrogen ratio was 10:1:1, and detection was realized with a flame-ionization detector. The mixture consisted of the following components: 47.8% pyridine, 19.8% 2-picoline, 3.4% 4-picoline, 2.2% acetaldehyde, 7% ethanol, 0.45% propanol, 0.51% isobutanol, and 0.48% isoamyl alcohol.

The cooled reaction mixture was washed with water and distilled with superheated steam to give 5.13 g (27%) of diethyl 2,6-lutidine-3,5-dicarboxylate (IV) with R_f 0.9 (system B) and mp 72°C (mp 73°C [8]).

The undistillable resinous residue was mixed with aluminum oxide and subjected to continuous extraction with hexane. Removal of the solvent by distillation gave 6.03 g (30.3%) of collidinedicarboxylic acid ester III with R_f 0.81 (system B). The picrate had mp 155-156°C (from ethanol) and was identical to the picrate of ester III obtained by the method in [6]. Found: N 11.23%. $C_{14}H_{19}NO_4 \cdot C_6H_3N_3O_7$. Calculated: N 11.33%. Dehydrogenation of Diethyl 1,4-Dihydro-4-phenyl-2,6-lutidine-3,5-dicarboxylate (V) with <u>Pyridine N-Oxide (II)</u>. A mixture of 6.58 g (20 mmole) of ester V and 1.9 g (20 mmole) of oxide II was heated at 220-230°C, and the resulting distillate (1.54 g) contained, according to GLC, 58.5% pyridine, 1.8% 2-picoline, 15% acetaldehyde, 4.3% ethanol, 0.45% propanol, 0.8% isobutanol, and 0.7% isoamyl alcohol.

The resinified reaction mass was cooled, washed with water, mixed with aluminum oxide, and subjected to fractional extraction with petroleum ether (40-70°C). The fractions containing ester VI were combined, the solvent was removed by distillation, and the residue was washed in the cold with two portions of petroleum ether to give 3.76 g (57.5%) of ester VI with $R_f 0.94$ (system A) and mp 62-63°C (mp 63-64.5°C [6]). A total of 0.4 g (6%) of starting dihydro ester V, with mp 157-158°C, was isolated from the subsequent fractions.

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CHEMISTRY OF HETEROCYCLIC N-OXIDES AND RELATED COMPOUNDS.

11.* REACTION OF PYRIDINE N-OXIDE WITH METAL KETYLS

AND BENZOPHENONE DIANIONS

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The reaction of pyridine N-oxide with metal ketyls of benzophenone was studied. It is shown that diphenyl(2-pyridyl)carbinol N-oxide is formed with the lithium and sodium derivatives of benzophenone, whereas diphenyl(2-pyridyl)carbinol is formed with the potassium derivative of benzophenone. Diphenyl(2-pyridyl)carbinol N-oxide is obtained in lower yields in the reaction of pyridine N-oxide with benzophenone dianions. Pyridine and 4,4'- and 2,2'-dipyridyls are simultaneously formed in all of the reactions.

The N-oxides of aromatic heterocycles have increased reactivity with respect to the action of various electrophilic, nucleophilic, and radical reagents [2]. However, up until now, reactions with anion radicals were unknown in the N-oxide series.

We have shown that the diphenylhydroxymethyl group enters the 2 position of the pyridine ring to give diphenyl(2-pyridyl)carbinol N-oxide (III) in 28% yield in the reaction of pyridine N-oxide (I) with benzophenonyllithium ketyl (II) in dioxane at a reagent ratio of 1:1.

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