# INVESTIGATION OF DIPIPERIDYLS

## XII.* SYNTHESIS OF 2,2'-DIPYRIDYL-5,5'-DICARBOXYLIC ACID AND ITS ESTERS

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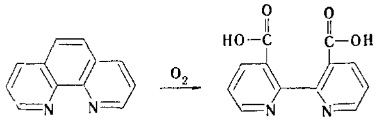
The oxidation of o-phenanthroline with potassium permanganate gives 2,2'-dipyridyl-5,5'-dicarboxylic acid (I). The corresponding esters of I were obtained by esterification with methanol, ethanol, propyl alcohol, isopropyl alcohol, butyl alcohol, and benzyl alcohol.

A number of authors [1-3] have described dicarboxylic acids of 2,3'- and 3,3'-dipyridyls, which are obtained by oxidation of p- and m-phenanthrolines, in the synthesis of 2,3'- and 3,3'-dipyridyls. Smith [4] attempted to obtain o-phenanthroline and, by oxidation of it, 2,2'-dipyridyl-5,5'-dicarboxylic acid (I), but the experiments did not give the desired results, and I was not identified.

2,2'-Dipyridyl and its derivatives are attracting the attention of researchers as physiologically active substances [5,6]. We have accomplished the synthesis of I and a number of its esters, which are of interest as potential physiologically active compounds. Compound I was obtained by oxidation of o-phenanthroline with aqueous potassium permanganate in alkaline media.



I

A study of the IR spectra enables one to adequately judge the structure of acid I. The absence of two carbonyl bands in the spectra of most oxalates is explained by the fact that these compounds usually have trans structures, and the symmetrical stretching vibration of the C=O group therefore should not appear in the IR spectrum. There should be two bands in the spectrum in the case of the cis forms, and this is actually observed. Two absorption bands of the C=O group were detected at 1710 and 1725 $cm^{-1}$ for I. In addition, the splitting of the carbonyl group for I is again caused by the field effect, which appears when two carbonyl oxygen atoms are close enough to one another [7]. This speaks in favor of the cis form of I. If acid I existed in the trans form, one could not exclude the possibility of the formation of an inner salt through the imino and carboxyl groups, and the free OH groups of the carboxyl grouping would not be observed in the spectra. In our case, the stretching vibrations of OH groups appear as a broad band at 2550-3000 $cm^{-1}$ with a major peak at about 2900 $cm^{-1}$ and a side peak at 2580 $cm^{-1}$. There is a strong band at 910 $cm^{-1}$, which vanishes upon complete esterification of I, in the region of the deformation vibrations of the OH group. Bands characteristic for an intramolecular hydrogen bond at 1650-1670 $cm^{-1}$ are absent.

The doublet character in the band of the carbonyl group does not vanish in the spectra of diesters II, and three peaks are observed at 1670, 1708, and 1720 $cm^{-1}$, i.e., the II molecule is not converted to the trans configuration characteristic for 2,2'-dipyridyl [8]. A band at 1270 $cm^{-1}$, which is characteristic for the C—C bond between the pyridine rings in I [9], is observed for both acid I and diesters II.

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*See [10] for communication XI.

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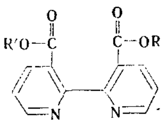
TABLE 1. Esters of 2,2'-Dipyridyl-5,5'-dicarboxylic Acid



| Comp. | R | R' | Reaction conditions |  | Mp, °C (crystalliz. solvent) | $R_f$* | Empirical formula | Found, % |  |  | Calc., % |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | time,h | temp., °C |  |  |  | C | H | N | C | H | N |  |
| IIa | $C_3H_7$ | H | 2 | 40—45 | 137 (toluene) | 0,027 | $C_{15}H_{14}N_2O_4$ | 62,8 | 4,9 | 9,7 | 62,9 | 4,9 | 9,8 | 67 |
| III | $CH_3$ | $CH_3$ | 5 | 90—100 | 150 (alcohol) | 0,62 | $C_{14}H_{12}N_2O_4$ | 61,7 | 4,3 | 10,2 | 61,7 | 4,4 | 10,3 | 88 |
| IV | $C_2H_5$ | $C_2H_5$ | 9 | 90—100 | 81 (water) | 0,63 | $C_{16}H_{16}N_2O_4$ | 63,9 | 5,2 | 9,2 | 64,0 | 5,3 | 9,3 | 84 |
| V | $C_3H_7$ | $C_3H_7$ | 30 | 110—115 | 37—39 (alcohol) | 0,64 | $C_{18}H_{20}N_2O_4$ | 65,8 | 6,0 | 8,3 | 65,8 | 6,1 | 8,5 | 80 |
| VI | *i*-$C_3H_7$ | *i*-$C_3H_7$ | 16 | 110—115 | 158 (water) | 0,61 | $C_{18}H_{20}N_2O_4$ | 65,7 | 6,0 | 8,4 | 65,8 | 6,1 | 8,5 | 86 |
| VII | $C_4H_9$ | $C_4H_9$† | 40 | 125—130 | — | 0,65 | $C_{20}H_{24}N_2O_4$ | 67,4 | 7,1 | 7,9 | 67,4 | 7,0 | 7,8 | 71 |
| VIII | $C_6H_5CH_2$ | $C_6H_5CH_2$ | 24 | 160—170 | 118 (alcohol–water) | 0,59 | $C_{26}H_{20}N_2O_4$ | 73,5 | 4,6 | 6,7 | 73,6 | 4,7 | 6,6 | 68 |

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*The following solvent systems were used: $CHCl_3$ ($NH_3$-saturated)–$C_6H_6$–$CH_3OH$ (35 : 5 : 1.5) for IIa, and $CHCl_3$–$C_6H_6$–$CH_3OH$ (15 : 18 : 1.5) for III-VIII.

†Bp 169-170° (1 mm), $n_D^{20}$ 1.5742.

Depending on the ratio of I and the alcohol used in the reaction, one can obtain mono- (IIa) and diesters (II). The diesters have the odor of honey and are insoluble in water, quite soluble in chloroform, and less soluble in alcohol. Acid I is not chromatographed by thin-layer chromatography (TLC) on activity II aluminum oxide; monoester IIa has a very low $R_f$ value even in a strongly polar system. An increase in the size of the alkyl radical lowers the basic properties of II, and this leads to an increase in the $R_f$ (Table 1).

## EXPERIMENTAL

The IR spectra of KBr pellets and $10^{-3}$-$10^{-5}$ solutions in tetrachloroethylene were recorded with a UR-10 spectrophotometer.

The course of the reactions and the purity of the products were monitored by TLC in a loose layer of activity II $Al_2O_3$ (development with iodine vapors). The starting o-phenanthroline was not additionally purified.

2,2'-Dipyridyl-5,5'-dicarboxylic Acid (I). Potassium hydroxide (20 g) and 50 g of $KMnO_4$ were added to 25 g (about 0.14 mole) of o-phenanthroline dissolved in 3 liters of water, and the mixture was heated on a boiling-water bath until it became completely colorless. The precipitated manganese dioxide was removed by filtration, after which it was boiled with water and again removed by filtration (this operation was repeated 10 times). The solution was evaporated to 0.5 liter and cooled, and the precipitated unchanged o-phenanthroline (3.2 g) was separated. The filtrate was neutralized to pH 3.6 with 15% HCl solution and cooled, and the resulting colorless plates were recrystallized from water to give 28.71 g (84.41%) of a product with mp 250-251°. Found,%: C 59.1; H 3.6; N 11.3. $C_{12}H_8N_2O_4$. Calculated,%: C 59.0; H 3.5; N 11.5.

2,2'-(5-Carboxy-5'-propoxycarbonyl)dipyryidyl (IIa). A 200-g (about 2 mole) sample of $H_2SO_4$ (sp. gr. 1.84) was added to a suspension of 25 g (about 0.1 mole) of I and 300 ml (about 5 moles) of propanol at 40-45° with vigorous stirring until I had dissolved completely (2 h). Compound IIa was extracted with chloroform and recrystallized from ethanol.

2,2'-(5,5'-Dialkoxycarbonyl)dipyridyls (III-VIII). A total of 4 moles of concentrated $H_2SO_4$ (concentrated HCl for VIII) was added to a mixture of 25 g (about 1 mole) of I and 20 moles of alcohol, and the mixture was heated for 5-40 h. The excess alcohol was removed by distillation, 100 ml of water was added to the residue, and the mixture was neutralized with saturated sodium carbonate solution. The esters were extracted with chloroform, and the extract was dried with sodium sulfate. The solvent was removed by distillation, and the residue was recrystallized or vacuum distilled.

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