## STUDY OF THE AZO-COUPLING OF

### 6-HYDROXY(METHOXY)-2-PHENYL-3-HYDROXYPYRIDINES

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Depending on the type of selected reaction, electrophilic substitution in the series of 2-aryl-3-hydroxypyridines is directed either to the aryl or to the pyridine ring of the molecule of the starting compound. Thus, sulfonation and nitration reactions, where the 2-aryl-3-hydroxypyridines react in the cationic form, are directed to the aryl ring. At the same time, in aminomethylation, iodination, and azo-coupling reactions, which proceed either in alkaline or weakly acid media, the hydroxypyridine ring undergoes substitution.

A study of the sulfonation and nitration of the 6-hydroxy(methoxy)-2-phenyl-3-hydroxypyridines [1] disclosed that insertion of the hydroxy or methoxy group into the pyridinol ring does not affect the orientation of electrophilic substitution. It was interesting to study the azo-coupling of the 6-hydroxy(methoxy)-2-phenyl-3-hydroxypyridines in order to obtain compounds that contain the azo group in the pyridine ring.

The azo-coupling of the 2-phenyl-, 2-(p-alkylphenyl)-, 2-anisyl-[2], and 4-methyl-5-phenyl-3-hydroxypyridines [3] had been studied earlier. In view of the low activity of the diazonium ion the substitution of the phenyl ring in the indicated compounds seemed improbable. Actually, it was established that in all cases the azo group enters only into the hydroxypyridine ring.

In view of the fact that the pyridinediols and their ethers are more reactive during electrophilic substitution than are the hydroxypyridines, it could be assumed that also in the case of the 6-hydroxy (methoxy)-2-phenyl-3-hydroxypyridines the azo-coupling would be directed only to the 4 or 5 position of the pyridine ring. As we were able to establish, the azo-coupling of the indicated compounds proceeds with exceeding ease under mild conditions. As the azo-components we used the phenyldiazonium, p-nitrophenyldiazonium, p-bromophenyldiazonium, and p-methoxyphenyldiazonium chlorides



The position of the azo groups in the synthesized azo dyes was established by IR spectroscopy. The use of IR spectroscopy was based on the following: usually a strong intramolecular hydrogen bond is formed



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© 1971 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00. TABLE 1. Azo Derivatives of 6-Methoxy- and 6-Hydroxy-2-phenyl-3-hydroxypyridines



R	Ri	Yield, %	Mp, °C	Found, %			Empirical	Calculated, %		
				С	н	N	formula	C	н	N
CH3	N=N	92	63-64	70,69	4,82	13,42	C <sub>18</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub>	70,81	4,91	13,77
н	N=N	90	91-92 decompn.	69,87 )	4,31	14,26	C17H13N3O2	70,01	4,46	14,43
н	Br	93	67-68 decompn	54,89	3, <b>0</b> 8	10,74	C17H12N3O2Br	55,13	3,24	11,35
H	NO2-N=N	88	94-95 decompn	60,34 • )	3,46	15,93	$C_{17}H_{12}N_4O_4$	60,71	3,57	16,66
н	CH <sub>2</sub> O-	91	5859 decompn	67,11 •)	4,43	12,51	C18H15N3O3	67,29	4,64	13,08

when the azo group is found in the o-position (4-position) to the  $\beta$ -hydroxy group, which shifts the band of the stretching vibrations of the OH group by 300-400 cm<sup>-1</sup>, while when the azo group is found in the p-position (5-position) to the  $\beta$ -hydroxy group the band at  $\nu_{OH}$  practically retains the position of the maximum. From an examination of the solutions of the azo compounds of the 6-methoxy- (I) and 6-hydroxy-2-phenyl-3-hydroxypyridines (II) in CCl<sub>4</sub> it can be seen that they are characterized by intense bands of the stretching vibrations of the OH in the vicinity of 3560 cm<sup>-1</sup>, attached by a weak intramolecular hydrogen  $\pi$ -bond (Fig. 1a). This testifies to the fact that the azo group is found in the 5 position. In the spectrum of compound (II) (Fig. 1b), besides the indicated band at  $\nu_{OH}$ , are observed the intense bands of the stretching vibrations of the keto and NH groups in the 1690 and 3400 cm<sup>-1</sup> regions, respectively. The presence of these bands is explained by the fact that compound (II) exists in the  $\alpha$ -pyridone form. Consequently, the OH group in the 6 position is found in the keto form and for this reason does not form a hydrogen bond with the azo group.

As a result, similar to the nitration of 6-hydroxy-2- (p-nitrophenyl)-3-hydroxypyridine, the azocoupling of 3,6-dihydroxy-2-phenylpyridine or its methyl ether is also directed to the 5 position of the pyridine ring. Consequently, the main orienting agent during the electrophilic substitution of 3,6-dihydroxy-2-phenylpyridine is the  $\alpha$ -hydroxy group, which directs the substitution in the o-position.

#### EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in  $CCl_4$  solutions at a substance concentration of  $2 \cdot 10^{-4}$  mole/liter.

Azo-Coupling Procedure. To a solution of 0.001 mole of 3,6-dihydroxy-2-phenylpyridine or its methyl ether in 50 ml of 1% aqueous KOH solution, cooled to 5-10°C, with constant stirring, was added in small portions a solution of the diazo component, maintaining the pH of the medium within the limits 8-9 by the addition of KOH solution. The reaction mixture was then stirred for 1 h, and the mother liquor was neutralized by the passage of  $CO_2$  gas. The obtained precipitate was separated, washed with water, and recrystallized from an alcohol – water mixture (1:1). The azo derivatives of the 3,6-dihydroxy- and 3-hydroxy-6-methoxy-2-phenylpyridines were obtained. The yields and physicochemical constants are given in Table 1.

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## CONCLUSIONS

1. A study was made of the azo-coupling of the 6-hydroxy(methoxy)-2-phenyl-3-hydroxypyridines.

2. On the basis of the IR spectra it was shown that the azo-coupling is directed to the 5 position of the pyridine ring.

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