was 150°C, the ionizing voltage was 70 V, and the emission current was 1.0 mA. The high-resolution mass spectra were recorded with an MS-902 spectrometer. The mass spectra are presented in Table 1.

LITERATURE CITED


SYNTHESIS OF 5-SUBSTITUTED 6-METHOXY-1,2,3,4-
TETRAHYDRO-8-CARBOLIN-1-ONES

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The nitration and bromination of 6-methoxy-1,2,3,4-tetrahydro-8-carbolin-1-one were studied. 5-Nitro and 5-bromo derivatives were obtained. 5-Acetyl-1,2,3,4-tetrahydrocarbolin-1-one oxime was obtained, and its Beckmann rearrangement was studied. The use of lithium aluminum hydride leads to reduction of the 5-acetyl group to give an alcohol group, whereas reduction of the acetyl group to an ethyl group occurs in the case of reduction with a palladium catalyst. Saponification of 5-substituted carbolin-1-ones with alcoholic alkali makes it possible to obtain 4-substituted tryptamines with a carbonyl group in the 2 position. The structures of the compounds were established by means of the PMR and mass spectra.

Studies of the electrophilic substitution reactions of 5-methoxyindole and its derivatives by a number of researchers [1-5] have shown that the direction of attack by the electrophilic reagent in this case is determined mainly by the methoxy group of the benzene ring in the para position relative to the indole nitrogen atom. Instead of the electrophilic substitution in the 3 position that is classical for other indoles, the new substituent enters the 6 position in 5-methoxyindole compounds.

In the opinion of Yudin, Kost, and co-workers [5], realization of the process in acidic media, in which indoles that are protonated at the pyrrole nitrogen atom undergo substitution, is decisive for this sort of reaction pathway. According to the data in [4], the introduction in the 2 position of 5-methoxyindoles of an additional alkoxy carbonyl group, which changes the electron density distribution and evidently the site of protonation of the molecule, has a substantial effect on the direction of electrophilic attack. Thus, for example, the bromination of 2-ethoxycarbonyl-5-methoxyindole in acidic media leads to the formation of a 4-bromo derivative rather than a 6-bromo derivative in high yield.

6-Methoxy-1,2,3,4-tetrahydro-β-carbolin-1-one (I) is a 5-methoxyindole derivative with a carbonyl function included in an additional six-membered ring.

We have previously shown [6] that the dichlorophosphoryl derivative of this compound is readily acetylated by acetic anhydride in the 5 position, which corresponds to the 4 position of 2-ethoxycarbonyl-5-methoxyindole.

It seemed of interest to ascertain how general this pathway of electrophilic substitution reactions is for I and to use the resulting synthetic possibilities for the preparation of previously difficult-to-obtain 5,6-disubstituted β-carbolines and the corresponding 4,5-disubstituted tryptamines.

It should be noted that electrophilic substitution reactions in the 6-methoxy-1,2,3,4-tetrahydro-β-carbolin-1-one series have not been previously studied.

We investigated the nitration and bromination of I.

The nitration of carbolinone I or its diacetyl derivative (II) with fuming nitric acid or a mixture of fuming nitric acid and concentrated sulfuric acid at 0°C was accompanied by pronounced resinification and did not make it possible to isolate the individual nitration products. 5-Nitro-6-methoxy-1,2,3,4-tetrahydro-β-carbolin-1-one (III) was obtained in 66% yield when the reaction was carried out in glacial acetic acid with equimolar ratios of carbolinone I and the nitrating agent. The mass spectrum of nitro compound III contains a molecular-ion peak with m/e 261 and ion peaks with m/e 231 ([M -- NO]⁺), and 204 ([M -- CONHCH₂]⁺), as well as an intense peak with m/e 244 ([M -- OH]⁺), the formation of which is evidently due to the ortho orientation of the methoxy and nitro groups. The subsequent fragmentation of the [M -- OH]⁺ ion entails cleavage of the piperidine ring and elimination of a CO group.

The PMR spectrum of III contains two triplets of the CH₂CH₂ group of the tetrahydro-pyridine ring at 3.91 and 3.15 ppm, a singlet of a 6-methoxy group at 4.09 ppm, two doublets of aromatic protons attached to C₇ and C₈ at 7.74 and 7.38 ppm with spin–spin coupling constant (SSCC) J = 9 Hz, and a broad singlet of the proton of the NH group at 10.46 ppm; the spectrum does not contain the signal of the proton attached to C₅ of the aromatic ring that