2-ARYL-4H-3,1-BENZOXAZIN-4-ONES. REDUCTION

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The reduction of 2-(2-tosylaminophenyl-4H-3,1-benzoxazin-4-one with zinc dust in acetic acid gives N-(o-tosylaminobenzyl)anthranilic acid, the structure of which was proved by mass spectrometry and the ^{13}C NMR spectra.

The 2-aryl-4H-3,1-benzoxazin-4-one molecule contains two electrophilic centers — the 2-C and 4-C heteroring atoms. Our previous polarographic study of compounds of this type showed that the azomethine group containing the 2-C atom initially undergoes reduction, after which the carbonyl group containing the 4-C atom is reduced [1]. However, it follows from the available data on the chemical reduction of 4H-3,1-benzoxazin-4-ones that only the carbonyl group is reduced and that the final product is the corresponding N-(o-acylamino)-benzyl alcohol [2-4].

It seemed of interest to us to study the capacity for reduction of one of the effective organic luminophores belonging to the examined class of compounds — 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-one.

In the case of reduction with zinc dust in glacial acetic acid, a white crystalline substance with blue fluorescence was isolated from the reaction mixture along with the starting compound. In analogy with the literature data it was natural to assume that we were dealing with N-(o-tosylanthranilamido)benzyl alcohol. However, N-(o-tosylanthranilamido)benzyl alcohol synthesized by acylation of o-aminobenzyl alcohol with tosylanthraniloyl chloride differs substantially from the reduction product with respect to its luminescence properties, and a melting-point depression was observed for a mixture of the two products.

The results of elementary analysis made it possible to assign empirical formula $C_{21}H_{20}N_2O_4S$ to the compound, and the molecular mass determined by mass spectrometry was 396. This is 4 amu higher than in the case of the starting compound and indicates that four hydrogen atoms were added during reduction. Subsequent analysis of the mass spectrum indicated the presence of a tosyl fragment (m/e 155) in the dissociative ionization products. The formation from the molecular ion of a fragment with m/e 241, i.e., 155 amu lower than in the case of the starting compound, also provided evidence for this.

The subsequent fragmentation of the ion with m/e 241 leads to the formation of two fragments (104 and 137), each of which contains a benzene ring. In the first fragment the benzene ring and the nitrogen atom account for 90 amu. A simple arithmetic calculation makes it possible to establish the presence of a methylene group in this fragment. The other fragment has the structure of the anthranilic acid ion. During subsequent fragmentation it loses a molecule of water and is converted to an anthranyl ion (m/e 119). Similar fragmentation of the anthranilic acid ion is observed in the products of hydrolysis of 2-aryl-4H-3,1-benzoxazin-4-ones, for which we established the structures of the fragments by means of ^{18}O-labeled compounds. The presence of a carboxyl group in the reduction product is confirmed by chemical methods and by the mass spectrum, in which the formation of an ion with m/e 195, formed as a result of successive fragmentation, is observed:

$$M^+ \xrightarrow{-\text{Tos}} m/e\ 241 \xrightarrow{-\text{HCOOH}} m/e\ 195$$

The presence of a methylene fragment is also confirmed by NMR spectroscopy. Thus a singlet at δ 4.84 ppm with an integral intensity corresponding to two protons is observed in the ^1H NMR spectra. However, the most convincing data on the presence of a CH_2 group were

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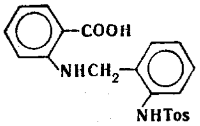
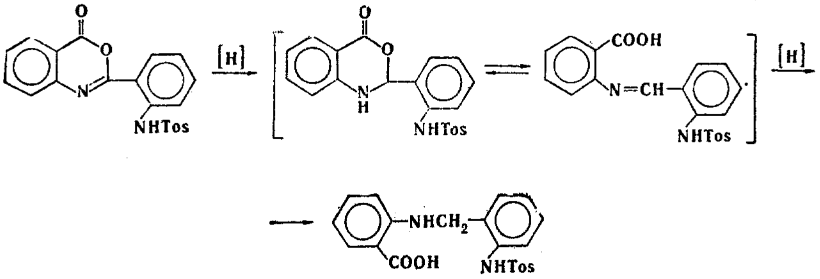
obtained from the ^{13}C NMR spectra without decoupling of the protons, in which a triplet from $^{13}CH_2$ (δ 43.6 ppm from tetramethylsilane) is observed. This chemical shift and the $J_{^{13}CH}$ value of 137 Hz are extremely characteristic for the methylene group of benzylamine [5].

Thus the data obtained enable us to assign the N-(o-tosylaminobenzyl)anthranilic acid structure to the reduction product.



The formation of N-(o-tosylaminobenzyl)anthranilic acid in the reduction of 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-one can be conceived of as being the result of the initial addition of hydrogen to the C=N bond of the oxazine ring. The resulting 2-(2-tosylaminophenyl)-1,2,4H-3,1-benzoxazin-4-one exists in equilibrium with its open form — N-(o-tosylaminobenzylidene)anthranilic acid.* The latter readily undergoes further hydrogenation at the azomethine group to give N-(o-tosylaminobenzyl)anthranilic acid:



EXPERIMENTAL

The mass spectrometric study was carried out with an MS-702 mass spectrometer with a system for direct introduction of the samples into the ion source. The ionizing-electron energy was 70 V, the accelerating voltage was 10 kV, and the sample vaporization temperature was 120°C. The NMR spectra were recorded with a Varian XL-100 spectrometer at 30°C. A standard pulse adapter and an ÉVM-620L computer were used to record the ^{13}C spectra.

Reduction of 2-(2-Tosylaminophenyl)-4H-3,1-benzoxazin-4-one. A 4-g sample of zinc dust was added with stirring in four portions of 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-one in 200 ml of glacial acetic acid, after which the mixture was refluxed for another 2 h. It was then cooled to room temperature and treated with 10 ml of water to dissolve the precipitated zinc acetate. The mixture was then filtered, and the filtrate was poured into 1800 ml of water. The resulting precipitate was removed by filtration and triturated in a mortar with 600 ml of 5% Na_2CO_3. The undissolved portion, which was found to be the starting compound, was separated, and the solution was acidified with hydrochloric acid. The precipitate was recrystallized successively from aqueous alcohol and acetic acid to give 1.65 g (20.8%) of a white crystalline powder with blue fluorescence and mp 182.5-182.7°C. Found, %: C 63.74; H 4.98; N 6.92; S 8.25. $C_{21}H_{20}N_2O_4S$. Calculated, %: C 63.62; H 5.08; N 7.06; S 8.08.

LITERATURE CITED

1. Yu. A. Davydovskaya and B. M. Bolotin, Zh. Vses. Khim. Obshchestva, 16, 117 (1971).
2. W. Elliott, F. Hamilton, and D. K. Ridley, J. Heterocycl. Chem., 5, 707 (1968).
3. B. Witkop, J. B. Patrick, and H. M. Kissman, Chem. Ber., 85, 949 (1952).
4. G. N. Walker, J. Am. Chem. Soc., 77, 6698 (1955).
5. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley-Interscience (1972).
6. J. B. Ekelev, E. C. Rogers, and M. Swisher, J. Am. Chem. Soc., 44, 1756 (1922).

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*The ability of N-arylideneanthranilic acids to exist in equilibrium with 1,2,4H-3,1-benzoxazin-4-ones was demonstrated in [6].