REACTION OF 5-NITROANTHRANILIC ACID WITH p-TOLUENESULFONYL CHLORIDE IN PYRIDINE

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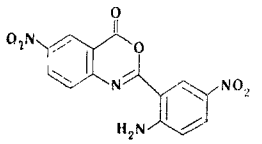
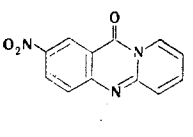
We have previously [1] demonstrated that 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-one is formed in the reaction of anthranilic acid with p-toluenesulfonyl chloride in refluxing pyridine. In an investigation of the reaction of 5-nitroanthranilic acid with p-toluenesulfonyl chloride, we isolated I (mp 298°) and II (mp 256.5°), which differed sharply in composition and properties from the expected 2-(2-tosylamino-5-nitrophenyl)-6-nitro-4H-3,1-benzoxazin-4-one. At room temperature the yields of I and II were 26 and 72%, respectively, compared with 59 and 29% at 114°.

Substance I is 2-(2-amino-5-nitrophenyl)-6-nitro-4H-3,1-benzoxazin-4-one. IR spectrum: 1765 ($\nu_{C=O}$ in benzoxazinones [2]), 3296, and 3443 cm^{-1} (ν_{NH_2}). Found: C 51.2; H 2.7; N 17.2%. $C_{14}H_8N_4O_6$. Calculated: C 51.2; H 2.5; N 17.1%.

Substance II [Found: C 60.2; H 2.8; N 17.2%; mol. wt. 241 (mass spectroscopy). $C_{12}H_7N_3O_3$. Calculated: C 59.8; H 2.9; N 17.4%] differs markedly in its optical and chemical properties from I. Solutions of II luminesce intensely at room temperature, which is not characteristic for nitro-substituted benzoxazinones. Compound II forms a stable hydrochloride. Absorption bands in the region of the stretching vibrations of NH bonds are not observed in the IR spectrum of II. The band at 1710 cm^{-1} is closest to $\nu_{C=O}$ of N-phenyl-substituted tertiary amides [3]. In the IR spectrum of the hydrochloride, $\nu_{C=O}$ is shifted markedly to the higher-wave-number region (1750 cm^{-1}) as compared with II. This sort of shift means that a nitrogen that is capable of salt formation is in direct proximity to the carbonyl group. The presence of a $C_5H_4N^{2+}$ fragment with m/e 78 was established in the mass spectrum of II. The II molecule consequently includes a pyridine ring. On the basis of these data, we assigned the 2-nitro-11H-pyrido[2,1-b]-11-quinazolinone structure to II.



I



II

Using the method in [4] for the synthesis of unsubstituted 11H-pyrido[2,1-b]-11-quinazolinone, we obtained a substance from 5-nitroanthranilic acid and 2-chloropyridine that was identical to II with respect to the IR and UV spectra and melting points.

LITERATURE CITED

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