2-ARYL-4H-3,1-BENZOXAZIN-4-ONES
NITRATION

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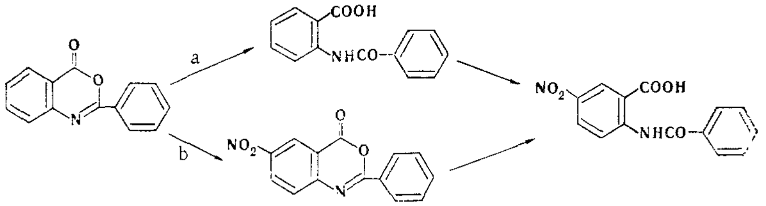
2-(3-Nitrophenyl)-4H-3,1-benzoxazin-4-one is formed in the nitration of 2-phenyl-4H-3,1-benzoxazin-4-one, while 2-(2-tosylamino-5-nitrophenyl)-4H-3,1-benzoxazin-4-one is formed in the nitration of 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-one.

No nitration products can be detected in the nitration of 2-phenyl-4H-3,1-benzoxazin-4-one in dichloroethane with a fourfold excess of fuming nitric acid. Only N-benzoylanthranilic acid, which is the product of hydrolysis of the starting compound, is isolated from the reaction mixture. However, if the amount of nitric acid is doubled, the chief reaction product proves to be N-benzoyl-5-nitroanthranilic acid (path a or b):



Path a seems preferable to us, for, as seen from the fact presented above, hydrolysis proceeds completely in those cases where nitration does not occur. N-Benzoyl-5-nitroanthranilic acid can be easily converted to 6-nitro-2-phenyl-4H-3.1-benzoxazin-4-one by heating with acetic anhydride.

The nitration proceeds completely differently in sulfuric acid. In this case, the chief reaction product is 2-(3-nitrophenyl)-4H-3.1-benzoxazin-4-one. In addition, a small amount of N-(3-nitrobenzoyl)anthranilic acid is formed. The latter is probably obtained as a result of hydrolysis of the already nitrated benzoxazinone when the reaction mixture is poured over ice. If in this case hydrolysis occurred initially followed by nitration, as in the nitration in dichloroethane, the final reaction product should have been N-benzoyl-5-nitroanthranilic acid rather than N-(3-nitrobenzoyl)anthranilic acid.

The entry of the nitro group into the phenyl ring of 2-phenyl-4H-3,1-benzoxazin-4-one indicates that the electron density in the phenyl ring is higher than in the benzoxazinone portion of the molecule. In this case, the latter acts as an orienting group of the II type.

We accomplished the nitration of 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-one only in dichloroethane, inasmuch as detosylation is possible in sulfuric acid [1]. 2-(2-Tosylamino-5-nitrophenyl)-4H-3,1-benzoxazin-4-one is formed in the nitration. In addition. N-(2-tosylamino-5-nitrobenzoyl)anthranilic acid is detected in the reaction mixture.

The presence of nitrated benzoxazinone in the reaction products indicates that hydrolysis in the case of o-tosylamino-substituted 2-phenyl-4H-3,1-benzoxazin-4-one is hindered and that there is time for nitration of the nonhydrolyzed benzoxazinone. In this case, the 5' position of the phenyl ring undergoes attack, which is promoted by the coordinated orientation of the tosylamine group – an orienting group of the I type – and the benzoxazinone ring, which as we noted above is an orienting group of the II type.

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EXPERIMENTAL

2-(3-Nitrophenyl)-4H-3,1-benzoxazin-4-one. A 0.5-cm^3 (0.012 mole) sample of fuming nitric acid was added at 15-20° with vigorous stirring in the course of 15 min to a solution of 2.23 g (0.01 mole) of 2-phenyl-4H-3,1-benzoxazin-4-one [2] in 7.5 cm^3 of concentrated sulfuric acid, after which the mixture was stirred at the same temperature for another hour. It was then poured into 150 g of crushed ice, and the resulting precipitate was removed by filtration, washed to neutrality with water, dried, and recrystallized from acetic anhydride (with decolorization by charcoal) to give 1.25 g (46%) of a product with mp 164.5-166°. The product was identical to a sample of 2-(3-nitrophenyl)-4H-3,1-benzoxazin-4-one synthesized by the method in [3].

2-(2-Tosylamino-5-nitrophenyl)-4H-3,1-benzoxazin-4-one. A 3.75-cm^3 (0.09 mole) sample of fuming nitric acid (sp. gr. 1.5) was added in the course of an hour with vigorous stirring at 70° to a solution of 3.95 g (0.01 mole) of 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-one [4] in 50 cm^3 of dichloroethane, after which the mixture was stirred for another 15 min. It was then poured into 300 cm^3 of ice water, and the organic layer was separated, washed with water, and dried over calcium chloride. The dichloroethane was removed in vacuo, and the residual solid product was crystallized from acetic anhydride to give 1.5 g (34%) of a product with mp 247-248°. The product was identical to a sample of 2-(2-tosylamino-5-nitrophenyl-4H-3,1-benzoxazin-4-one synthesized by the method in [5].

LITERATURE CITED

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