piophenone (III), with mp 123° [1], and 0.03 g (15%) of 2,2'-dipropionyl-5,5'-dinitroazoxybenzene (VIII), with mp 138°. No melting-point depression was observed for mixtures of both compounds with samples previously obtained.

Reduction of 6-Nitro-3-ethylanthranil (II). A solution of 0.75 g (0.004 mole) of anthranil II in 5 ml of ethanol was added to 1 g of reduced iron in 10 ml of glacial acetic acid, and the mixture was heated with stirring to 60°. It was maintained at this temperature for 10-12 min, after which it was poured into 100 ml of water. The reduction products were extracted with two 30-ml portions of ether, and the extract was washed with water and dried with calcium chloride. The solvent was evaporated, and the residue was chromatographed as described above to give 0.67 g (88%) of 2-amino-4-nitropropiophenone (III) with mp 124°.

Conversion of 2-Nitroso-4-nitropropiophenone (I) in Benzene in the Absence of Hydrogen Chloride. A solution of 0.1 g (0.0005 mole) of nitroso ketone I in 20 ml of dry benzene was allowed to stand in the dark for 4-5 days, after which the solvent was evaporated to a volume of 1 ml. The resulting precipitate [the starting nitroso ketone, 0.065 g (65%), mp 101° [4] was removed by filtration, and the residue was chromatographed with standards in a thin layer of aluminum oxide in an ether–petroleum (40-70°) system (1 : 3). According to the TLC data, the reaction mixture contained 6-nitro-3-ethylanthranil (II), 2-amino-4-nitropropiophenone (III), 2,4-dinitropropiophenone (VII), and 2,2'-dipropionyl-5,5'-dinitroazoxybenzene (VIII).

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SYNTHESIS OF 2-ARYLBENZOXAZOLES FROM COPPER COMPLEXES OF o-NITROSOPHENOLS AND AROMATIC ALDEHYDES

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2-Arylbenzoxazoles were obtained by heating copper complexes of o-nitrosophenols with aromatic aldehydes in tetralin.

In [1] we showed that benzoxazoles can be successfully obtained by heating o-nitrophenols with aromatic aldehydes in tetralin. In this research it was also noted that α-nitroso-β-naphthol also undergoes a similar reaction.

The aim of the present research was to study the reaction of aromatic aldehydes with o-nitrosophenols. The latter are unstable and are isolated primarily in the form of copper complexes [2]. We established that the corresponding 2-arylbenzoxazoles are formed in up to 56% yields (Table 1) when these complexes are heated with aromatic aldehydes in tetralin with simultaneous removal of the liberated water by distillation. Since benzoic acids are detected in the reaction products, it may be assumed that the reaction proceeds via the following scheme:

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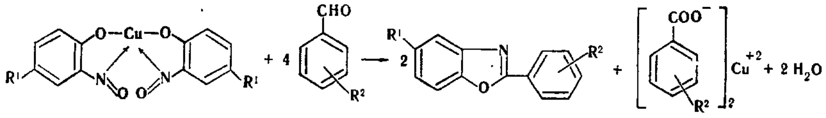

TABLE 1. Benzoxazoles

Compound	R^1	R^2	mp, °C	Literature mp, °C	Empirical formula	N, %		Yield, %
						found	calc.	
I	Cl	4-OCH_3	150,5	152[3]	$C_{14}H_{10}ClNO_2$	5,5	5,4	52
II	Cl	4-OH	140	144[1]	$C_{13}H_8ClNO_2$	5,6	5,7	29
III	CH_3	4-OCH_3	97	98—100[1]	$C_{15}H_{13}NO_2$	6,0	5,8	32
IV	CH_3	2-OH	134	134—135[1]	$C_{14}H_{11}NO_2$	6,4	6,2	27
V	Cl	3-Br	155	—	$C_{13}H_7BrClNO$	4,8	4,5	44
VI	CH_3	3-Br	132	—	$C_{14}H_{10}BrNO$	4,9	4,9	48
VII	Br	3-Br	147	—	$C_{13}H_7Br_2NO$	4,3	4,0	30

EXPERIMENTAL

3-Arylbenzoxazoles (I-VII, Table 1). A 0.01-mole sample of the copper complex of o-nitrosophenol, 15 ml of tetralin, and 0.03 mole of aromatic aldehyde were placed in a round-bottom flask equipped with a Dean—Stark trap, and the mixture was refluxed for 2-3 h. The end of the reaction was determined from the amount of water liberated during the reaction and also by thin-layer chromatography. At the end of the reaction, the Dean—Stark trap was replaced by a Wurtz adapter, and the tetralin and excess aldehyde were removed by distillation to dryness. The resulting solid mass was pulverized and extracted several times with boiling alcohol or acetic acid. The extract was diluted with water, and the precipitated benzoxazole was removed by filtration and crystallized from alcohol with activated charcoal.

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