THERMAL CYCLIZATION OF α-NITROSO-β-NAPHTHOL, o-NITRONAPHTHOLS, AND o-NITROPHENOLS WITH AROMATIC ALDEHYDES*

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The possibility of obtaining 2-aryl-substituted benzoxazoles and naphthoxazoles by heating o-nitrophenols, o-nitronaphthols, and α-nitroso-β-naphthol with aromatic aldehydes in high-boiling solvents with simultaneous removal of the water formed by distillation is demonstrated.

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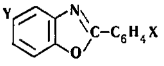
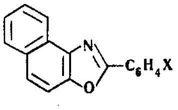
*Communication VI of the series "Structure and Properties of Nitroso Compounds." See [1] for communication V.

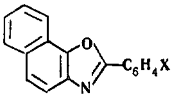
TABLE 1.



I–XV



XVI–XVIII, XXI, XXII



XIX–XX

Compound	X	Y	Reaction time, h	Mp, °C	Yield, %*
I	4-OCH_3	H	3,0	100—101[4]	53
II	4-CH_3	H	4,5	115—116[4]	55
III	4-NO_2	H	2,0	268—269[4]	30
IV	4-Cl	H	3,0	149—150[4]	64
V	2-OH	H	4,0	122—123[4]	62
VI	4-OCH_3	5-CH_3	1,0	98—100	82
VII	4-CH_3	5-CH_3	5,0	125	71
VIII	4-NO_2	5-CH_3	1,5	208—209[5]	40
IX	4-Cl	5-CH_3	3,0	147—148	67
X	2-OH	5-CH_3	7,0	134—135	52
XI	4-OCH_3	5-Cl	1,5	150—152[4]	51
XII	4-CH_3	5-Cl	4,0	138—139	37
XIII	4-NO_2	5-Cl	2,0	242—243[4]	9
XIV	4-Cl	5-Cl	2,5	191—192[4]	19
XV	2-OH	5-Cl	8,0	144	12
XVI	H	—	3,5	134[6]	20
XVII	4-CH_3	—	4,0	169—170[6]	22
XVIII	4-Cl	—	5,0	188—189[6]	16
XIX	4-CH_3	—	3,5	144	14
XX	4-Cl	—	4,0	173—174[6]	11
XXI	4-CH_3	—	2,5	169—170[6]	13
XXII	4-Cl	—	4,5	188—189[6]	12

*The preparation of XVI was carried out in mesitylene, while the other compounds were prepared in tetralin (10-20 ml of solvent per 0.03 mole of the hydroxy compound). In the preparation of III, VIII, XIII, and XVI-XVIII, 3 moles of aldehyde were introduced into the reaction per mole of hydroxy compound, while 5 moles of the aldehyde per mole of hydroxy compound were used in the remaining cases. Compounds XVI-XVIII were obtained from α-nitroso-β-naphthol, XXI-XXII were obtained from α-nitro-β-naphthol, and XIX-XX were obtained from β-nitro-α-naphthol.

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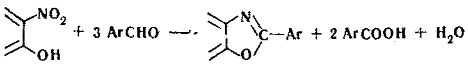
TABLE 2. Results of the Analysis of the New Compounds

Compound	Empirical formula	N, %	
		found	calc.
VI	$C_{15}H_{13}NO_2$	5,9	5,8
VII	$C_{15}H_{13}NO$	6,5	6,3
IX	$C_{14}H_{10}ClNO$	5,9	5,7
X	$C_{14}H_{11}NO_2$	6,5	6,2
XII	$C_{14}H_{10}ClNO$	6,0	5,7
XV	$C_{13}H_8ClNO_2$	6,0	5,7
XIX	$C_{18}H_{13}NO$	5,5	5,4

It has been reported [2] that 2-phenylbenzimidazole was isolated in 20% yield from the reaction of o-nitroaniline with benzaldehyde. We have subsequently demonstrated that the cyclization proceeds with various o-nitroanilines and aromatic aldehydes [3]. In the present paper, we have studied the possibility of the formation of an oxazole ring during the reaction of aromatic aldehydes with o-nitro derivatives of phenols, α- and β-naphthols, and also with α-nitroso-β-naphthol. In fact, we have found that when the compounds enumerated above are heated in high-boiling solvents (tetraline and mesitylene) with 3-5 moles of aldehydes, the corresponding benzoxazoles and naphthoxazoles (Tables 1 and 2) are formed. In this reaction, the aldehyde is apparently the reducing agent and the cyclizing agent.



A confirmation of this is the fact that the amount of water liberated as a result of the reaction in experiments with the highest yields of benzoxazole was close to the amount calculated in conformity with the above equation, and the corresponding aromatic acid was always found in the reaction products. The reaction with p-nitrobenzaldehyde is accompanied by side reactions of the aldehyde itself, which is confirmed by the liberation of water when a tetralin solution of this aldehyde is heated. The reaction was monitored from the amount of reaction water isolated in a Dean–Stark trap and by thin-layer chromatography. At the end of the reaction, the solvent and excess aldehyde were removed by distillation, and the oxazoles were repeatedly extracted from the resinous mass with hot concentrated HCl. The acid solutions were decolorized with activated charcoal and diluted with water. The naphthoxazoles were isolated only when the solutions were allowed to stand. They were purified by crystallization from alcohol–water (3:1), alcohol–benzene (1:1), and heptane–benzene (1:2). The benzoxazoles were crystallized from aqueous alcohol. Attempts to carry out the cyclization of β-nitroso-α-naphthol with p-tolualdehyde or anisaldehyde were unsuccessful.

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