SYNTHESIS OF AROMATIC BISBENZOXAZOLES BY REDUCTIVE HETEROCYCLIZATION

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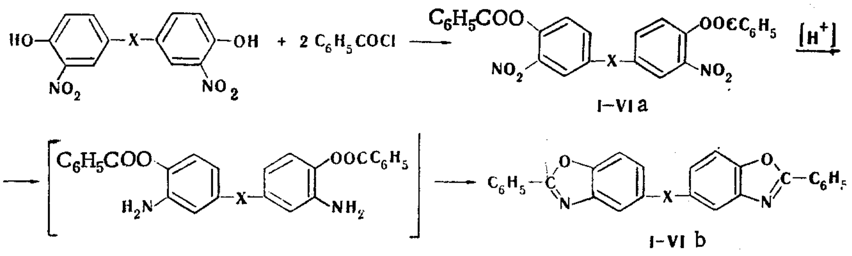
A number of previously described aromatic bisbenzoxazoles were obtained by reductive heterocyclization. The synthesis of bisbenzoxazoles by this method made it possible to select starting compounds that are most acceptable for the synthesis of aromatic polybenzoxazoles by reductive polyheterocyclization.

We have previously developed a new method for the synthesis of polybenzoxazoles that is based on the reductive polyheterocyclization of poly(o-nitro esters) [1] — products of the reaction of bis(o-nitrophenols) with aromatic dicarboxylic acid dichlorides.

To extend this method to other systems we investigated the possibility of the preparation of bisbenzoxazoles from bis(o-nitrophenols) and benzoyl chloride,



I $X=C(CH_3)_2$; II $X=CH_2$; III $X=O$; IV $X=C(C_6H_5)_2$; V $X=SO_2$; VI X = —

as well as from o-nitrophenol and aromatic dicarboxylic acid dichlorides:

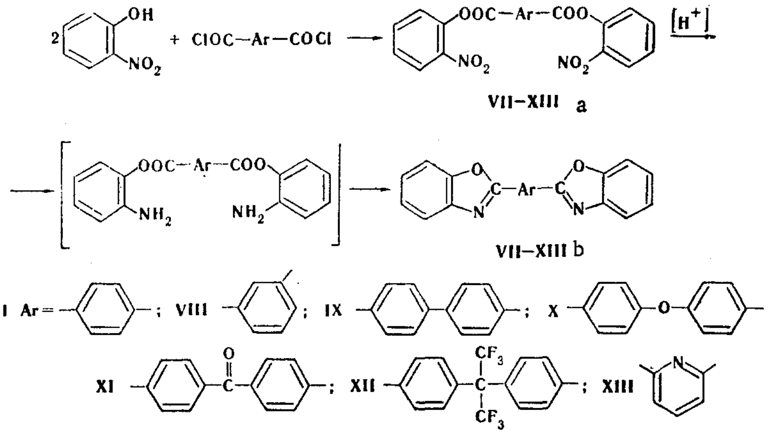


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TABLE 1. Principal Characteristics of the Bis(o-nitro esters) (Ia-XIIIa)

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
I a	152—153	66,8	4,0	5,4	$C_{29}H_{22}O_8N_2$	66,1	4,1	5,3	95
II a	146—147	64,8	3,6	5,7	$C_{27}H_{18}O_8N_2$	65,0	3,6	5,6	95
III a	211—212	62,0	3,0	5,4	$C_{26}H_{16}O_9N_2$	62,4	3,2	5,5	92
IVa	240—242	71,6	3,9	4,3	$C_{39}H_{26}O_8N_2$	71,9	4,0	4,3	90
Va	214—215	56,8	2,9	5,0	$C_{29}H_{16}O_{10}N_2$	56,9	2,9	5,1	93
VIa	163—164	64,2	3,4	5,8	$C_{26}H_{16}O_8N_2$	64,4	3,3	5,7	94
VIIa	203—204	58,2	3,0	6,6	$C_{20}H_{12}O_8N_2$	58,8	2,9	6,8	90
VIIIa	164—165	58,6	3,1	6,7	$C_{20}H_{12}O_8N_2$	58,8	2,9	6,8	92
IXa	244—246	64,2	3,1	5,8	$C_{26}H_{16}O_8N_2$	64,4	3,3	5,7	95
Xa	156—157	62,2	3,4	5,3	$C_{26}H_{16}O_9N_2$	62,4	3,2	5,5	95
XIa	188—190	63,5	2,9	5,0	$C_{27}H_{16}O_9N_2$	63,2	3,1	5,4	86
XIIa	148—150	58,5	2,7	4,7	$C_{29}H_{16}O_8N_2F_6$	58,8	2,5	4,4	89
XIIIa	194—196	55,4	2,3	9,8	$C_{19}H_{11}O_8N_3$	55,7	2,7	10,2	85

All of the syntheses of the bisbenzoxazoles were accomplished under the conditions of the synthesis of polymers [1, 2], viz., by reaction of the starting compounds in N-methyl-2-pyrrolidone (N-MP) with subsequent saturation of the solutions with dry HCl, addition of reduced iron, and heating to 140-150°C.

The structures of the bis(o-nitro esters) (Ia-XIIIa) and bisbenzoxazoles (I-IIb, IV-XIIb) were confirmed by the results of elementary analysis (Tables 1 and 2) and IR spectroscopic data. The IR spectra of Ia-XIIIa contain absorption maxima at 1350, 1540 (NO_2), and 1740 cm^{-1} (ester C=O bond) [3].

These results, in conjunction with the high yields, constitute evidence for the possibility of the use of all of the monomers, regardless of their structures, for the preparation of bis(o-nitro esters).

A different pattern is observed in the case of the reductive heterocyclization of the bis(o-nitro esters) obtained. The structures of both the nitrophenols and the acid chlorides affect the formation and yields of the bisbenzoxazoles. The principal process that competes with cyclization of the bis(o-amino esters) is hydrolysis of the ester bond, and all of the principles that are characteristic of acid hydrolysis [4] are manifested here.

When 3,3'-dinitro-4,4'-dihydroxydiphenyl ether is used as the starting monomer, the positive effect of the conjugation of the bridging oxygen atom increases the density of the electron charge on the oxygen atom of the carboxy group. This in turn increases the rate of the rate-determining step (tying up of a proton) in the acid hydrolysis.

The electron-charge density on the oxygen atom of the protonated ester group increases during the reduction, since the electron-acceptor nitro group is replaced by the less effective electron-acceptor nitroso group and subsequently by the electron-donor hydroxylamino and amino groups. With respect to their effect on the rate of the rate-determining step in the hydrolysis, ortho substituents can be arranged in the order [5] $NO_2 < NO < NHOH < NH_2$.

A different type of regularity is displayed in the case of bisphenols with electron-acceptor "hinged groups" (IV, V). The amino groups that are formed when their benzoates are reduced are less reactive because of their low nucleophilicities [6], and they undergo cyclization at higher temperatures, i.e., at temperatures at which the rate of hydrolysis of the ester bond increases. An analysis of the effect of the activities of the starting acid chlorides on the yields of the bisbenzoxazoles showed that, since the second step in the hydrolysis is attack by a water molecule on the positively charged carbon atom of the carboxy group, the magnitude of this charge affects both the rate of hydrolysis and the rate of cyclization. A decrease in the yields of the bisbenzoxazoles is observed when acid chlorides with high activities due to the relatively high positive charge on the carbon atom of the carboxy group are used; this can be explained by the prevailing increase in the rate of hydrolysis. The best results are obtained when acid chlorides with medium activities (IX, X) are used; this in turn can be explained by a decrease in the contribution of the hydrolysis reaction, which competes with the formation of a benzoxazole ring (Table 2). Thus, the best results in the preparation of bisbenzoxazoles by the reductive heterocycliza-

TABLE 2. Principal Characteristics of the Bisbenzoxazoles (Ia-IIb, IVa-XIIb)

Compound	mp, °C (literature mp)	Found, %			Empirical formula	Calculated %			UV spectrum ($c \cdot 10^{-5}$), moles/liter		Yield, %
		C	H	N		C	H	N	λ_{max}	lg ε	
Ib	136—137 (85)[12]	80,4	5,0	6,1	$C_{29}H_{22}O_2N_2$	80,9	5,1	6,5	227 342	4,12 3,84	70
IIb	215—216	80,1	4,9	7,4	$C_{27}H_{18}O_2N_2$	80,5	4,5	6,9	218 320	4,06 3,80	73
IVb	115—116	84,4	4,3	6,4	$C_{39}H_{26}O_2N_2$	84,4	4,7	6,0	205 278	4,44 3,67	41
Vb	250—252 (253—254)[13]	68,3	3,1	5,8	$C_{26}H_{16}O_4N_2S$	68,9	3,6	6,1	208 265	4,78 3,89	33
VIb	242—244 (240—241)[14]	80,7	4,5	7,6	$C_{25}H_{16}O_2N_2$	80,4	4,8	7,2	261 346	4,46 3,92	62
VIIb	351—353 (355—356)[15]	76,9	3,6	8,6	$C_{20}H_{12}O_2N_2$	76,9	3,8	8,9	205 400	4,70 3,90	72
VIIIb	237—238 (233—234)[16]	76,4	3,3	8,2	$C_{20}H_{12}O_2N_2$	76,9	3,8	8,9	205 388	4,70 3,80	73
IXb	349—350 (350)[17]	80,0	3,9	7,7	$C_{26}H_{16}O_2N_2$	80,3	4,1	7,2	207 390	4,72 3,94	80
Xb	246—247 (245)[18]	77,5	4,2	7,3	$C_{26}H_{16}O_3N_2$	77,2	3,9	6,9	200 345	4,32 3,84	82
XIb	347—348	77,2	4,1	7,0	$C_{27}H_{16}O_3N_2$	77,8	3,8	6,7	206 390	4,74 3,82	69
XIIb	251—253	64,9	3,2	5,6	$C_{29}H_{16}O_2N_2F_6$	64,6	2,9	5,2	202 312	3,92 3,73	80

tion method are obtained when one selects starting compounds with medium activities — both the bis(o-nitrophenols) and dicarboxylic acid dichlorides [7].

The structures of the bisbenzoxazoles were confirmed by the results of elementary analysis (Table 2) and the IR spectra. The IR spectra of the bisbenzoxazoles do not contain the absorption bands characteristic for NO_2 and $O-C=O$ groups, but new absorption bands that are characteristic for benzoxazole rings [8] appear at 930, 1420, 1480, 1555, 1595, and 1620 cm^{-1}.

The principal characteristics of the benzoxazoles are presented in Table 2.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with an IK-20 spectrometer. The UV spectra of solutions of the compounds in sulfuric acid were recorded with a Specord UV-vis spectrophotometer.

Starting Compounds. 2,2-Bis(3-nitro-4-hydroxyphenyl)propane was obtained and purified by the method in [9] and had mp 135-136°C (mp 136°C [9]). Bis(3-nitro-4-hydroxyphenyl) sulfone was purified by recrystallization from acetic acid and had mp 235-236°C (mp 238-240 °C [10]). Bis(3-nitro-4-hydroxyphenyl)methane (mp 226-228°C), bis(3-nitro-4-hydroxyphenyl) ether (mp 156-157°C), 3,3'-dinitro-4,4'-dihydroxytetraphenylmethane (mp 226-228°C), and 3,3'-dinitro-4,4'-dihydroxybiphenyl (mp 278°C) were obtained by the method in [11]. The aromatic dicarboxylic acid dichlorides were obtained and purified by the method in [11].

Prior to its use, N-methyl-2-pyrrolidone was distilled in a stream of nitrogen over CaH_2 and had bp 94-95°C (18 mm) and n_D 1.466.

Bisbenzoxazoles (I-IIb and IV-XIIb). A 0.02-mole sample of triethylamine was added to a solution of 0.01 mole of bis(o-nitrophenol) (or 0.02 mole of o-nitrophenol) in 25 ml of N-MP, 0.02 mole of benzoyl chloride (or 0.01 mole of the aromatic dicarboxylic acid dichloride), and the mixture was stirred at 25°C for 15 min. The resulting bis(o-nitro esters) were poured into ether, and the precipitated products were removed by filtration, washed with distilled water, and recrystallized from dioxane.

For the preparation of the bisbenzoxazoles, dry HCl was passed through the reaction solutions for 30 min, after which a twofold (as compared with the calculated value) amount of reduced iron was added, and the temperature was raised to 140-150°C and maintained at this level in a stream of HCl for another 30 min. The resulting light-colored homogeneous solutions were cooled to 30°C and poured into water, and the precipitated bisbenzoxazoles were purified by recrystallization and sublimation.

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