SYNTHESIS AND TRANSFORMATIONS OF 2-(2-FURYL)- AND 2-[β-(2-FURYL)VINYL]NAPHTH[1,2-d]IMIDAZOLES

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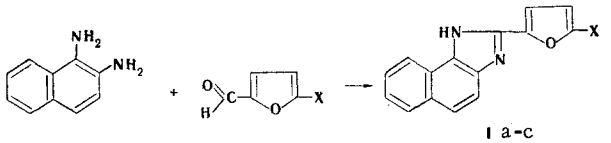
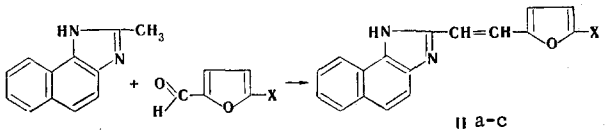
The corresponding 2-(2-furyl)naphth[1,2-d]imidazoles were obtained by heating Schiff bases, prepared from 1,2-naphthalenediamine and furfural and 5-bromo- and 5-nitrofurfurals, in nitrobenzene. 2-[β-(2-Furyl)vinyl]naphth[1,2-d]imidazoles were synthesized by condensation of 2-methylnaphth[1,2-d]imidazole with furfural and 5-bromo- and 5-nitrofurfural. The methylation, nitration, and acetylation of the compounds obtained were studied, and the replacement of the bromine atom in the furan ring by a nitro group was also investigated.

In our previous papers [1-3] we demonstrated that the nature of the aromatic system condensed with the imidazole ring has a substantial effect on the reactivities of the imidazole and furan rings in 2-furylimidazoles. Continuing these studies, we have synthesized 2-(2-furyl)- and 2-[β-(2-furyl)vinyl]naphth[1,2-d]imidazoles (Ia-c and IIa-c) and have studied their typical reactions in the imidazole and furan rings. Compounds Ia-c were obtained by heating Schiff bases, prepared by the reaction of 1,2-naphthalenediamine with furfural and 5-bromo- and 5-nitrofurfural, in nitrobenzene [4]. We were unable to obtain II by a similar method because of the pronounced resinification of the Schiff bases formed from 1,2-naphthalenediamine and the corresponding 2-furylacroleins. Compound IIa was synthesized by fusing 2-methylnaphth[1,2-d]imidazole with furfural at 195-200°C, while IIb and IIc were obtained by refluxing a mixture of equimolecular amounts of 2-methylnaphth[1,2-d]imidazole with 5-bromo- and 5-nitrofurfural in acetic anhydride [1].



I a-c



II a-c

a X=H; b X=Br; c X=NO_2

The methylation of I and II proceeds with greater difficulty than in the case of other furylimidazoles [1-3]. 3-Methyl-2-(2-furyl)naphth[1,2-d]imidazole methiodide (Id) was obtained by refluxing a mixture of Ia with methyl iodide in alcoholic alkali solution for 6 h. Under similar conditions, IIa gives a mixture of 1- and 3-methyl derivatives, the chromatographic separation of which gave 3-methyl-2-[β-(2-furyl)vinyl]-naphth[1,2-d]imidazole (IId).

The replacement of the bromine atom in Ib and IIb by a nitro group under the conditions in [2,3,5] proceeds smoothly and gives Ic and IIc (Table 1) in high yields.

The free α position of the furan ring in Ia does not react with electrophilic reagents. On the other hand, IIa, like other furylvinylimidazoles [1-3], is readily acetylated in the α position of the furan ring by acetic anhydride in the presence of perchloric acid to give a methyl ketone (IIe). The nitration of IIa with

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TABLE 1. 2-(2-Furyl)naphth[1,2-d]imidazoles (I) and 2-[β-(2-Furyl)vinyl]naphth[1,2-d]imidazoles (II)

Comp.	mp, °C (ethanol)	λ_{max}, nm	lg ε	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	N	C	H	N	
Ia	121—122	272, 284, 342	4,56; 4,29; 4,25	$C_{15}H_{10}N_2O$	76,6	4,5	11,6	76,9	4,3	11,9	49
Ib	145—146	236, 292, 340	4,47; 4,21; 4,22	$C_{15}H_9BrN_2O$	—	—	8,6	—	—	8,9	52
Ic	253—254	233, 271, 404	4,56; 4,30; 4,28	$C_{15}H_9N_3O_3$	—	—	14,7	—	—	15,0	43
Id	172—173	286, 334, 350	4,29; 4,24; 4,18	$C_{17}H_{15}IN_2O$	—	—	6,7	—	—	7,1	22
IIa	195—196	302, 365	4,33; 4,64	$C_{17}H_{12}N_2O$	78,2	4,8	11,0	78,4	4,6	10,8	31
IIb	208—209	—	—	$C_{17}H_{11}BrN_2O$	58,4	3,5	8,1	58,8	3,2	8,2	26
IIc	226—227	290, 425	4,14; 4,50	$C_{17}H_{11}N_3O_3$	64,5	3,8	13,5	65,4	3,6	13,7	36
IId	175—176	304, 370	4,30; 4,45	$C_{18}H_{14}N_2O$	79,2	5,2	10,1	78,8	5,1	10,2	28
IIe*	216—217	302, 390	4,02; 4,44	$C_{19}H_{11}N_2O_2$	75,6	4,4	9,1	75,5	4,6	9,2	71
IIf	300 dec.	286, 385	4,30; 4,31	$C_{21}H_{10}N_4O_8$	55,5	3,4	12,3	55,7	3,5	12,4	57

*The 2,4-dinitrophenylhydrazone of IIe melted above 350° (dec.).

nitric acid in acetic anhydride proceeds with greater difficulty than in the case of other similarly constructed furylvinylimidazoles [2,3,6] and gives the acetate of the dinitro derivative containing a nitro group in the furan ring and a nitro and acetyl group in the naphthalene ring (IIf).

EXPERIMENTAL

2-(2-Furyl)naphth[1,2-d]imidazoles (Ia-c). A mixture of 0.01 mole of 1,2-naphthalenediamine, 0.01 mole of the appropriate furfural, and 2 ml of ethanol was held at room temperature for 2 h. Nitrobenzene (4 ml) was added to the resulting Schiff base, and the mixture was heated to 170-180° and held at this temperature for 1 h. It was then cooled, and 2 ml of 20% hydrochloric acid was added. This mixture was then stirred thoroughly, and the resulting hydrochloride of the reaction product was washed out from the nitrobenzene with ether. The hydrochloride was recrystallized from alcohol and converted to the base by treatment with 2 ml of saturated sodium carbonate solution.

2-[β-(2-Furyl)vinyl]naphth[1,2-d]imidazole (IIa). A mixture of 0.01 mole of 2-methylnaphth[1,2-d]-imidazole, 0.015 mole of furfural, and 0.01 g of boric acid was heated at 195-200° for 10 h. The solidified melt was treated with chloroform, and the reaction product was isolated by passing the chloroform extract through a chromatographic column filled with aluminum oxide.

2-[β-(5-Bromo-2-furyl)vinyl]naphth[1,2-d]imidazole (IIb). A mixture of 0.01 mole of 2-methylnaphth-[1,2-d]imidazole, 0.01 mole of 5-bromofurfural, and 8 ml of acetic anhydride was refluxed for 8-10 h. The solvent was removed by distillation, and the residue was extracted with chloroform. The reaction product was isolated as in the case of IIa. Compound IIc was similarly obtained.

The UV spectra of methanol solutions of the compounds were recorded with an SF-4a spectrophotometer.

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