SYNTHESIS OF 2-PHENYL-3-(2-FURYL)- AND 2-PHENYL-3-[β-(2-FURYL)VINYL]-1,2-DIHYDRO-NAPHTHO[1,2-d]-1,2,4-TRIAZINES

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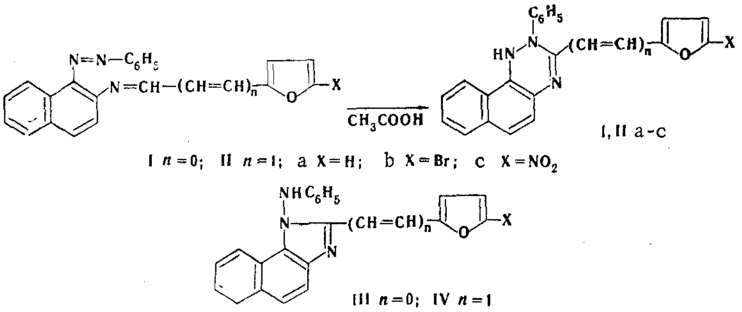
The corresponding 2-phenyl-3-(2-furyl)- and 2-phenyl-3-[β-(2-furyl)vinyl]-1,2-dihydronaphtho-[1,2-d]-1,2,4-triazines were obtained by heating Schiff bases [prepared by reaction of 1-(phenylazo)-2-aminonaphthalene with furfural, β-(2-furyl)acrolein, and their 5-bromo and 5-nitro derivatives] in glacial acetic acid.

Continuing our investigations of the synthesis of 2-(2-furyl)naphth[1,2-d]imidazoles [1], we turned to the method developed for the preparation of 1-arylamino-2-(2-furyl)benzimidazoles [2], which consists in the condensation of 2-aminoazobenzenes with furfural. However, unexpected results were obtained.



I,II a-c

I $n=0$; II $n=1$; a $X=H$; b $X=Br$; c $X=NO_2$

III $n=0$; IV $n=1$

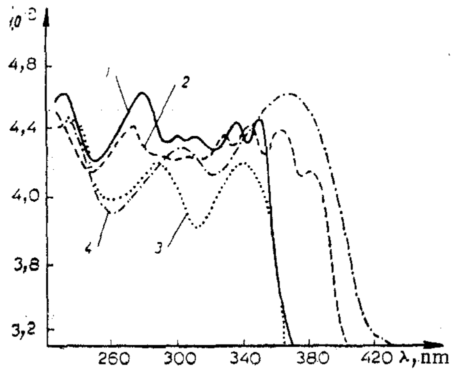


Fig. 1. UV spectra. 1) 2-Phenyl-3-(5-bromo-2-furyl)-1,2,-dihydronaphtho[1,2-d]-1,2,4-triazine; 2) 2-phenyl-3-[β-(5-bromo-2-furyl)-vinyl]-1,2-dihydronaphtho[1,2-d]-1,2,4-triazine; 3) 2-(5-bromo-2-furyl)naphth[1,2-d]-imidazole; 4) 2-[β-(5-bromo-2-furyl)vinyl]-naphth[1,2-d]imidazole.

When Schiff bases obtained by the reaction of 1-(phenylazo)-2-aminonaphthalene with furfural, β-(2-furyl)acrolein, and their 5-bromo and 5-nitro derivatives are heated in glacial acetic acid, 2-phenyl-3-(2-furyl)-1,2-dihydronaphtho[1,2-d]-1,2,4-triazines (Ia-c) and 2-phenyl-3-[β-(2-furyl)vinyl]-1,2-dihydronaphtho-[1,2-d]-1,2,4-triazines (IIa-c), respectively, are formed instead of the expected (according to [2]) 1-phenylamino-2-(2-furyl)naphth[1,2-d]imidazoles (III) and 1-phenylamino-2-[β-(2-furyl)vinyl]naphth[1,2-d]imidazoles (IV).

The compounds that we obtained (I and II) do not change during the action of Raney nickel in refluxing methanol, while III and IV, which are unusual trisubstituted hydrazines, should have been reduced with cleavage of the N—N bond under these conditions [3].

The introduction of substituents into the 1 position of the imidazole ring usually does not cause substantial changes in the character of the UV spectra of con-

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TABLE 1. 1,2-Dihydronaphtho[1,2-d]-1,2,4-triazines (I, II, and V)

Comp.	mp, °C, from alcohol	λ_{max}, nm	lg ε	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	N	C	H	N	
Ia	221—222	231 279 300 311 334 348	4,42 4,53 4,14 4,14 4,22 4,30	$C_{21}H_{15}N_3O$	77,4	4,8	12,9	77,5	4,3	12,9	62
Iб	215—216	231 282 302 314 337 353	4,61 4,64 4,34 4,38 4,47 4,50	$C_{21}H_{14}BrN_3O$	62,7	3,6	10,1	62,4	3,5	10,3	62
Iв	227—228	228 268 392 398	4,62 4,50 4,34 4,36	$C_{21}H_{14}N_4O_3$	68,4	3,9	15,4	68,1	3,8	15,1	70
IIa	226—228 (dec.)	227 314 334 367 386	4,51 4,27 4,34 4,58 4,43	$C_{23}H_{17}N_3O$	78,6	4,6	11,4	78,6	4,8	11,9	60
IIб	180—182 (dec.)	282 314 374 394 356	4,43 4,27 4,34 4,18 4,46	$C_{23}H_{16}BrN_3O$	64,0	3,9	9,9	64,2	3,7	9,8	60
IIв	241—243 (dec.)	286 304 308 404 421	4,27 4,20 4,19 4,40 4,45	$C_{23}H_{16}N_4O_3$	69,3	4,4	14,3	69,6	4,1	14,1	62
V	231—232	242 266 314 326	4,77 3,98 3,74 3,71	$C_{18}H_{15}N_3$	78,9	5,7	15,3	79,1	5,5	15,4	74

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*1,2-Dihydro-2-phenyl-3-methylnaphtho[1,2-d]-1,2,4-triazine.

densed imidazoles [4,5]. However, a comparison of the electronic absorption spectra of I and II with the electronic spectra of 2-(2-furyl)- and 2-[β-(2-furyl)vinyl]naphth[1,2-d]imidazoles [1] demonstrated that they correspond to absolutely different structures (see Fig. 1).

The IR spectra of all of the compounds that we obtained contain an intense band at 3390 cm^{-1}, the assignment of which to the stretching vibrations of the ring imino group seems more correct to us, since there are indications in the literature that the frequencies of the ring imino groups are of much higher intensity than the frequencies of the imino groups of secondary amines [6] and hydrazines [7], to which III and IV may be assigned.

The structures of I and II are in agreement with an earlier study [8], although Fierz-David and Blangey assign a different structure to a similarly obtained compound.

On the basis of all of the facts indicated above, we concluded that the 1,2-dihydro-1,2,4-triazine ring rather than the imidazole ring is closed in the cyclization of the starting Schiff bases, obtained from 1-(phenylazo)-2-aminonaphthalene and furfurals.

When aliphatic aldehydes are used in these syntheses, compounds of similar structure are obtained. Thus, 2-phenyl-3-methyl-1,2-dihydronaphtho[1,2-d]-1,2,4-triazine (V) is formed when acetaldehyde is introduced into the reaction in place of furfural.

EXPERIMENTAL

2-Phenyl-3-methyl-1,2-dihydronaphtho[1,2-d]-1,2,4-triazine (V). A mixture of 2.46 g (0.01 mole) of 1-(phenylazo)-2-aminonaphthalene, 0.5 ml (0.01 mole) of acetaldehyde, and 2 ml of ethanol was heated at 70-80° for 10 min. The alcohol was then removed by distillation, 20 ml of glacial acetic acid was added to the residual Schiff base, and the mixture was refluxed for 1 h. It was then cooled and poured into cold water, and the precipitated product was separated and recrystallized from alcohol.

Compounds Ia-c and IIa-c were similarly obtained.

The UV spectra of methanol solutions were recorded with an SF-4A spectrophotometer. The IR spectra were recorded with a UR-20 spectrometer.

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