SYNTHESIS OF 2-(5-HALOGENO-2-FURYL)-2,3-DIHYDROPERIMIDINES

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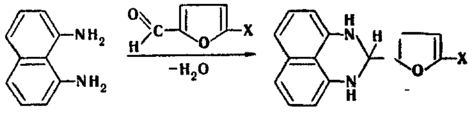
By boiling naphthylene-1,8-diamine with 5-halogeno- and 5-nitrofurfural in benzene or xylene, 90-95% yields of the corresponding 2-(5-halogeno-2-furyl)- and 2-(5-nitro-2-furyl)-2,3-dihydroperimidines have been obtained. The dehydrogenation of 2-(5-bromo-2-furyl)-2,3-dihydroperimidine with palladium on carbon has given 2-(5-bromo-2-furyl)perimidine. The compounds obtained have been characterized by their UV and IR spectra.

The simplest representative of the furylperimidines – 2-(2-furyl)perimidine – was first obtained [1] by boiling a mixture of naphthylene-1,8-diamine (NDA) with furfural in xylene solution in the presence of 10% of palladium on carbon. It was later found [2] that at room temperature NDA and furfural form 2-(2-furyl)-2,3-dihydroperimidine.

It appeared to us to be of interest to investigate the reaction of NDA with 5-halogenofurfurals and 5-nitrofurfural. It was found that when a mixture of NDA with 5-chloro-, 5-bromo-, 5-iodo-, or 5-nitrofurfural was boiled in benzene or xylene, the corresponding 2-(5-halogeno-2-furyl)- or 2-(5-nitro-2-furyl)-2,3-dihydroperimidine (Ia, b, c, or d) was formed (yields in xylene 75-85%, and in benzene 90-95%).

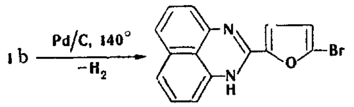


I a-d

a X = Cl; b Br; c I; d NO_2

The high yields of compounds (Ia-d) are obviously a consequence of the stabilizing action of the halogens and of the nitro group on the furan nucleus [3].

When the condensation of NDA with a 5-halogenofurfural was performed in the presence of palladium on carbon as described by Paragamian et al. [1], instead of the expected 2-(5-halogeno-2-furyl)perimidines compounds (Ia-c) were again obtained. Only when (Ib) was subjected to prolonged boiling in xylene solution with 10% of palladium on carbon did dehydrogenation take place, leading to the formation of 2-(5-bromo-2-furyl)perimidine (II).



II

In nitrobenzene, the yield of (II) was 60%. The dehydrogenation of (Ib) by the action of sulfur or selenium [4] in xylene at 125°C gave compound (II) with yields of 25 and 20%, respectively.

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TABLE 1. 2-(2-Furyl)-2,3-dihydroperimidines and 2-(2-Furyl)-perimidines

Compound	Mp, °C*	λ_{max} nm	lg ε	IR spect., cm^{-1}		Empirical formula	Found, %				Calculated, %				Yield, %
				ν_{N-H}	ν_{C-Hal}		C	H	N	halogen	C	H	N	halogen	
Ia	134	270 332 344	3,03 4,17 4,18	3260 3410	550 770	$C_{15}H_{11}ClN_2O$	66,7	4,4	10,7	12,9	66,5	4,2	10,4	13,1	92
Ib	140	270 332 344	3,64 4,17 4,18	3358 3405	550 770	$C_{15}H_{11}BrN_2O$	57,5	3,8	8,9	25,7	57,2	3,5	8,9	25,4	95
Ic	109	270 332 342	3,83 4,09 4,08	3360 3400	550	$C_{15}H_{11}IN_2O$	49,8	3,2	8,0	35,3	49,7	3,0	7,8	35,1	90
Id	165	264 319 380	3,78 4,35 3,47	3260 3355	—	$C_{15}H_{11}N_3O_3$	64,2	4,2	14,6	—	64,1	3,9	14,9	—	67
II	210 (dec.)	268 330 344	4,42 4,17 4,22	1600 † 1640	770	$C_{15}H_9BrN_2O$	57,8	3,0	8,9	25,6	57,5	2,9	8,9	25,5	60
III	146	268 340 346	4,14 4,09 4,13	1590 † 1630	—	$C_{16}H_{13}N_2O$	77,6	5,0	11,4	—	77,4	4,9	11,3	—	56

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* The substances were recrystallized from ethanol.

† Frequency of the perimidine ring.

On the basis of these facts, it can be said that the synthesis of 2-(2-furyl)perimidine by the method of Paragamian et al. [1] takes place in two stages. In the first stage 2-(2-furyl)-2,3-dihydroperimidine is formed, and in the second stage this undergoes catalytic dehydrogenation and is converted into 2-(2-furyl)-perimidine.

We have established that 2-(2-furyl)perimidine, like the condensed 2-(2-furyl)imidazoles [5], does not undergo electrophilic substitution in the free α position of the furan nucleus. Thus, it is not acetylated by acetic anhydride in the presence of perchloric acid [6] and is not nitrated by nitric acid in acetic anhydride [7]. The methylation of 2-(2-furyl)perimidine by method [8] takes place smoothly and gives a high yield of 2-(2-furyl)-1-methylperimidine (III).

The UV spectra of compounds (Ia-c) are extremely complex in relation to the positions of the absorption bands, but the intensity of absorption rises with an increase in the atomic weight of the halogen present in the furan nucleus of these compounds. The IR spectra of the compounds obtained show absorption bands corresponding to stretching vibrations of the N—H, C—Hal, and other groups (Table 1).

EXPERIMENTAL

The UV spectra of compounds (I-III) were taken on an SF-4 spectrophotometer in methanol. The IR spectra were taken on a UR-20 instrument in paraffin oil and in chloroform.

2-(5-Halogeno-2-furyl)-2,3-dihydroperimidines (Ia-c). A mixture of 0.8 g (5 mmoles) of naphthylene-1,8-diamine, 5 mmoles of the appropriate 5-halogenofurfural, and 50 ml of benzene was boiled with mechanical stirring for 1 h. The hot reaction mixture was filtered, the benzene was distilled off from the filtrate, and the residue was crystallized from ethanol. Colorless crystals.

2-(5-Nitro-2-furyl)-2,3-dihydroperimidine (Id). A mixture of 0.8 g (5 mmoles) of naphthylene-1,8-diamine, 0.7 g (5 mmoles) of 5-nitrofurfural, and 30 ml of o-xylene was boiled for 1 h. The solution was filtered while still hot, and the o-xylene was distilled off from the filtrate. The residue was dissolved in chloroform, and the reaction product was isolated by flow chromatography using alumina as adsorbent. Dark red crystals.

2-(5-Bromo-2-furyl)perimidine (II). A mixture of 1.58 g (5 mmoles) of 2-(5-bromo-2-furyl)-2,3-dihydropermidine (Ib), 30 ml of nitrobenzene, and 0.3 g of 10% palladium on carbon was heated with mechanical stirring at 125°C for 2 h. The hot mixture was filtered and the nitrobenzene was distilled off from the filtrate at a pressure of 8-10 mm Hg. The residue was dissolved in benzene and to isolate the reaction product the solution was passed through a column of alumina. Red crystals.

2-(2-Furyl)-1-methylperimidine (III). In a current of nitrogen, with mechanical stirring, a solution of 0.56 g (10 mmoles) of caustic potash in 10 ml of ethanol was added to a solution of 2.34 g (10 mmoles) of 2-(2-furyl)perimidine in 30 ml of ethanol, and then 1.42 g (10 mmoles) of methyl iodide was gradually added. The mixture was boiled in an atmosphere of nitrogen for 3 h and then the ethanol was distilled off in a current of nitrogen. The residue was extracted with chloroform (3 × 30 ml). The chloroform extract was dried with potassium carbonate, and the reaction product was separated by the method of flow chromatography, using alumina as adsorbent. Light-yellow crystals.

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