DIRECT NITRATION AND ACETYLATION OF THE FURAN NUCLEUS OF 1-ALKYL-2-[β-(2'-FURYL)VINYL]-BENZIMIDAZOLES

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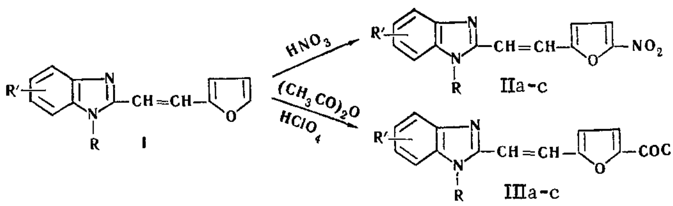
The direct nitration and acetylation of 1-methyl-, 1-ethyl-, and 1-benzyl-2-[β-(2'-furyl)vinyl]benzimidazoles has given the corresponding 1-alkyl- and 1-benzyl-2-[β-(5'-nitro-2'-furyl)vinyl]benzimidazoles and 1-alkyl- and 1-benzyl-2-[β-(5'-acetyl-2'-furyl)vinyl]benzimidazoles. The UV spectra of these compounds have been recorded and their ionization constants have been determined.

A furan nucleus directly attached to a vinyl group readily takes part in electrophilic substitution reactions [1, 3]. In view of this, it appeared of interest to study the direct nitration and acetylation of the 1-alkyl-2-[β-(2'-furyl)vinyl]benzimidazoles I described previously [4].

It was found that when compounds I were added to a mixture of acetic anhydride and nitric acid (d 1.5) cooled to −15°C, 1-alkyl-2-[β-(5'-nitro-2'-furyl)vinyl]benzimidazoles II, identical with the compounds synthesized by the condensation of 1-alkyl-2-methylbenzimidazoles with 5-nitrofurfural [5] were obtained with yields of 65-70%.

The action of acetic anhydride on compounds I in the presence of perchloric acid [6, 7] gave the 1-alkyl-2-[β-(5'-acetyl-2'-furyl)vinyl]benzimidazoles III.



II a $R=C_2H_5$, $R'=H$; b $R=CH_2C_6H_5$, $R'=H$; c $R=CH_3$, $R'=NO_2$
III a $R=CH_3$, $R'=H$; b $R=CH_2C_6H_5$, $R'=H$; c $R=C_2H_5$, $R'=NO_2$

Compounds II and III, unlike compounds I, do not undergo quaternization under the action of methyl iodide or of methyl benzenesulfonate. This is due to the fact that in compounds II and III the nucleophilicity of the nitrogen of the imidazole nucleus is lowered because of the electron-accepting effect of the $-COCH_3$ and $-NO_2$ groups transmitted through the system of conjugated double bonds (see the pK values in Table 1).

A consideration of the UV spectra of the compounds obtained (Table 1) has shown that the introduction of nitro and acetyl groups into the furan nucleus of compounds I causes a bathochromic absorption effect.

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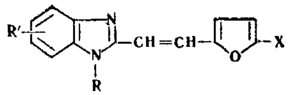
TABLE 1



Compound	Mp, °C (from ethanol)	pK*	λ_{max}, nm	log ε	Empirical formula	Found, %			Calculated, %			Yield, %
						C	H	N	C	H	N	
IIa	165	4,06	304; 388	3,88; 4,08	$C_{15}H_{13}N_3O_3$	63,35	4,80	15,03	63,38	4,57	14,84	70
IIb	191—192	3,77	308; 386	4,18; 4,44	$C_{20}H_{15}N_3O_3$	69,28	4,54	12,12	69,55	4,38	12,16	68
IIc	290	2,74	—	—	$C_{14}H_{10}N_4O_5$	55,03	3,51	15,26	55,26	3,31	15,13	63
IIIa	164—165	—	286; 370	3,88; 4,32	$C_{16}H_{14}N_2O_2$	72,00	5,45	10,02	72,16	5,21	10,50	62
2,4-Dinitrophenylhydrazone of IIIa	250	—	—	—	$C_{22}H_{18}N_6O_5$	—	—	18,27	—	—	18,50	Quant.
Methyl acetate derivative of IIIa	250 (from water)	—	280; 368	4,00; 4,22	$C_{19}H_{20}N_2O_4$	66,83	5,96	8,52	67,05	5,88	8,22	56
IIIb	154—155	4,12	286; 374	3,98; 4,56	$C_{22}H_{18}N_2O_2$	76,62	5,90	8,29	77,16	5,29	8,18	90
2,4-Dinitrophenylhydrazone of IIIb	256—257	—	—	—	$C_{23}H_{22}N_6O_5$	58,38	4,72	19,18	58,33	4,84	19,40	Quant.
Semicarbazone of IIIb	170—171	—	—	—	$C_{23}H_{21}N_5O_2$	—	—	17,82	—	—	17,53	Quant.
Methyl acetate derivative of IIIb	250 (from water)	—	—	—	$C_{25}H_{24}N_2O_4$	71,94	5,95	6,91	72,11	5,78	6,73	50
IIIc	205—206	3,49	—	—	$C_{17}H_{15}N_3O_4$	62,97	4,55	12,76	62,77	4,33	12,91	84
2,4-Dinitrophenylhydrazone of IIIc	300	—	—	—	$C_{23}H_{19}N_7O_7$	54,22	4,41	19,29	54,66	3,78	19,40	Quant.

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*pK values of the initial 2-[β-(2′-furyl)vinyl]benzimidazole and its 1-benzyl derivative, respectively, 5.14 and 4.85.

EXPERIMENTAL

1-Alkyl-2-[β-(5'-nitro-2'-furyl)vinyl]benzimidazoles (IIa-c). Nitric acid (19 g) d 1.5, was added to 30 g of freshly distilled acetic anhydride cooled to −5°C. With vigorous stirring at −15°C, 0.02 mole of I was added in small portions to the resulting nitrating mixture. The mixture was stirred at −15°C for another 2-3 h, after which it was poured onto 150 g of crushed ice. The bright yellow nitration product that deposited was filtered off, carefully washed with water, and recrystallized from ethanol.

1-Alkyl-2-[β-(5'-acetyl-2'-furyl)vinyl]benzimidazoles (IIIa-c). A solution of 0.01 mole of a compound I in 0.1 mole of freshly distilled acetic anhydride was treated with 2-3 drops of 42% perchloric acid and the mixture was stirred for 30 min, care being taken that the temperature did not exceed 25-30°C. Then it was poured into cold water and neutralized with sodium carbonate to pH 7, and the methyl ketone that had deposited was filtered off and recrystallized from ethanol.

The methyl acetate derivatives of compounds IIIa and b were obtained by acetylating the methiodides of compounds I with acetic anhydride in the presence of perchloric acid under the conditions for the synthesis of compounds IIIa and b. Under these conditions, an acetyl group entered the furan nucleus and the iodide ion was replaced by an acetate ion. Bright yellow crystals readily soluble in water.

The UV spectra were taken in methanol on an SF-4 spectrophotometer.

The ionization constants of the compounds obtained were determined in 50% ethanol at 25°C.

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