SYNTHESIS AND TRANSFORMATIONS OF 2-(2-FURYL)- AND 2-[β-(2-FURYL)VINYL] PHENANTHR[9,10]IMIDAZOLES

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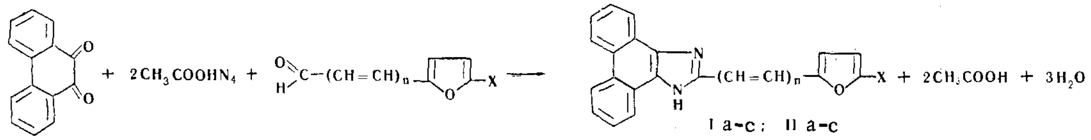
The corresponding 2-(2-furyl)- and 2-[β-(2-furyl)vinyl] phenanthr[9,10]imidazoles were obtained by the condensation of 9,10 phenanthrenequinone with furfural, β-(2-furyl)acrolein, and their 5-bromo and 5-nitro derivatives in the presence of ammonium acetate in glacial acetic acid. Their metallation, acetylation, nitration, and replacement of halogen by a nitro group were studied.

Continuing our investigations of 2-substituted imidazoles that contain a furan ring [1-3], we set out to study methods for the synthesis and the reactions of 2-(2-furyl)phenanthr[9,10]imidazoles (I) and 2-[β-(2-furyl)vinyl]phenanthr[9,10]imidazoles (II). It seemed of interest to ascertain the effect of the polynuclear aromatic phenanthrene system in these compounds on the reactivity of the imidazole and furan rings.

Attempts to obtain I and II from 9,10-diaminophenanthrene by the Weidenhagen [4] and Phillips [5] methods were unsuccessful. They were synthesized in high yields by the condensation of 9,10-phenanthrenequinone with the appropriate aldehyde of the furan series and ammonium acetate in glacial acetic acid [6].



I a–c; II a–c

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

The alternative synthesis of IIa–c was accomplished by the condensation of 2-methylphenanthr[9,10] imidazole with furfural and with 5-bromo- and 5-nitrofurfurals, respectively, in the presence of boric acid [2] or in acetic anhydride [8].

Compounds Ia–c and IIa–c, in contrast to the corresponding furyl- and furylvinylbenzimidazoles [1,2], do not form N-methyl derivatives (Id and IId) readily, and the latter quaternize weakly. This is a consequence of the reduction in the basicity of the imidazole ring of the indicated compounds induced by the phenanthrene system (the pK_a values for Ia,b and IIa,b are, respectively, 4.26, 4.27 and 4.23, 4.05) and also by the apparent steric hindrance.

The reaction of Ib and IIb with excess sodium nitrite in glacial acetic acid proceeds, in contrast to 2-(5-halo-2-furyl)benzimidazoles [7], to form two reaction products, of which the major products are mononitroso compounds (Ic and IIc). We did not elucidate the structures of the side products. In contrast to 2-[β-(2-furyl)vinyl]benzimidazoles, which are smoothly nitrated in the free α-position of the furan ring by a mixture of nitric acid and acetic anhydride [3], under these conditions Ia forms a mononitro product that contains a nitro group in the phenanthrene ring, while IIa gives IIc (70%) and IIe (15%).

Like 2-(2-furyl)benzimidazole [3], Ia is not acetylated by acetic anhydride in the presence of catalytic amounts of perchloric acid. Compound IIa, on the other hand, forms 2-[β-(5-acetyl-2-furyl)vinyl]phenanthr–

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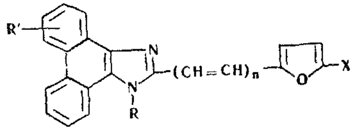
TABLE 1



Compound	n	R	R'	X	mp*	λ_{max}, nm	lg ε	Empirical formula	Found, %			Calc., %			Yield, %
									C	H	N	C	H	N	
I a	0	H	H	H	181—182	256, 312, 355	4,74; 4,40; 3,95	$C_{19}H_{12}N_2O$	79,8	4,6	9,8	80,1	4,2	9,8	88
I b	0	H	H	Br	255—257	260, 330, 362	4,80; 4,50; 4,41	$C_{19}H_{11}N_2OBr$	62,7	3,4	7,6	62,9	3,0	7,7	88
I c	0	H	H	NO_2	296—298	256, 280, 415	4,77; 4,35; 4,28	$C_{19}H_{11}N_3O_3$	69,4	3,3	12,7	69,3	3,3	12,8	90
I d	0	CH_3	H	Br	199—200	259, 308, 358	4,85; 4,45; 4,17	$C_{20}H_{13}N_2OBr$	—	—	7,3	—	—	7,4	20
I e	0	H	NO_2	H	323—325	256, 268, 400	4,85; 4,52; 4,42	$C_{19}H_{11}N_3O_3$	69,2	3,5	12,5	69,3	3,3	12,8	90
II a	1	H	H	H	224—226	236, 261, 375	4,28; 4,43; 4,41	$C_{21}H_{14}N_2O$	81,1	5,0	9,3	81,2	4,4	9,0	84**
II b	1	H	H	Br	240—242	362, 330, 362	4,82; 4,55; 4,45	$C_{21}H_{13}N_2OBr$	65,0	3,7	7,2	64,8	3,4	7,2	69**
II c	1	H	H	NO_2	290—292	259, 305, 435	4,61; 4,25; 4,48	$C_{21}H_{13}N_3O_3$	70,5	3,5	12,0	70,8	3,7	11,8	75**
II d	1	CH_3	H	Br	198—199	260, 310, 358	4,79; 4,39; 4,10	$C_{22}H_{15}N_2OBr$	—	—	7,0	—	—	7,0	20
II e	1	H	NO_2	H	253—255	256, 308, 432	4,60; 4,19; 4,36	$C_{21}H_{13}N_3O_3$	—	—	12,0	—	—	11,8	15
II f	1	H	H	$COCH_3$	262—264	260, 302, 392	4,43; 4,09; 4,42	$C_{23}H_{17}N_3O_5$	78,7	4,8	7,7	78,4	4,6	8,0	90
Acetate IIc					302—304	—	—	$C_{23}H_{17}N_3O_5$	66,1	3,6	9,9	66,0	4,0	10,1	73
2,4-Dinitrophenylhydrazone of IIf					400	—	—	$C_{29}H_{20}N_6O_5$	—	—	15,6	—	—	15,8	100

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*Compounds Ic and IId were recrystallized from chloroform; Ie, acetate IIc, IIf, and its dinitrophenylhydrazone were crystallized from alcohol; and the remaining compounds were recrystallized from benzene.

†These are the yields via method A. The yields via method B were as follows: IIa 21%, IIb 19%, and IIc 70%.

[9,10]imidazole acetate under the same conditions [3], which is converted to a base (IIf) on treatment with ammonia in alcohol.

EXPERIMENTAL

2-(2-Furyl)phenanthr[9,10]imidazole (Ia). Ammonium acetate (0.2 mole) and 0.014 mole of furfural in 10 ml of glacial acetic acid were added rapidly to a solution of 0.01 mole of 9,10-phenanthrenequinone in 30 ml of hot glacial acetic acid. The mixture was refluxed for 1 h and allowed to stand at room temperature for 2-3 h. The precipitate of side product was removed by filtration and washed with 10 ml of acetic acid. The filtrate was poured into 100 g of crushed ice and neutralized with ammonium hydroxide to pH 7 at 0-5 deg. The crystals of Ia were filtered, dried, and purified by recrystallization or separation with a chromatographic column filled with aluminum oxide with chloroform as the solvent. Compounds Ib and Ic were similarly obtained (Table 1).

2-[β-(2-Furyl)vinyl]phenanthr[9,10]imidazoles (IIa-c). A) The compounds were obtained by the method used to synthesize Ia-c.

B) A mixture of 0.01 mole of 2-methylphenanthr[9,10]imidazole, 0.01 mole of furfural, and 0.05 g of boric acid was heated for 4-5 h at 190-195 deg. IIa was leached from the melt with boiling alcohol.

C) A mixture of 0.01 mole of 2-methylphenanthr[9,10]imidazole and 0.01 mole of 5-bromo- or 5-nitrofurfural was refluxed in acetic anhydride for 4 h. The acetic anhydride was removed by distillation, and the residue was treated with 1 N hydrochloric acid.

1-Methyl-2-(5-bromo-2-furyl)- (Id) and 1-Methyl-2-[β-(5-bromo-2-furyl)vinyl]phenanthr[9,10] imidazoles (IId). A solution of 0.005 mole of Ib or IIb, 0.56 g (0.01 mole) of potassium hydroxide, and 1.42 g (0.01 mole) of methyl iodide in 25 ml of methanol was refluxed for 6 h and allowed to stand overnight. The solvent was removed by distillation, and the residue was extracted with chloroform. The extract was washed with water, dried with anhydrous potassium carbonate, and passed through a column filled with aluminum oxide. The reaction products were crystallized from chloroform or benzene.

The nitration and acetylation of Ia and IIa were carried out by the methods described in [3]. The halogen atom in Ib and IIb was replaced by a nitro group via the method in [7]. The reaction products were separated with a chromatographic column filled with aluminum oxide. Chloroform was used as the solvent.

The UV spectra of methanol solutions of the compounds were recorded with an SF-4A spectrophotometer. The ionization constants of the compounds were determined in 50% ethanol at 21 deg.

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