OXAZOLES FROM 8-HYDROXY-9-AMINOFLUORANTHENE

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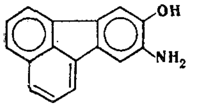
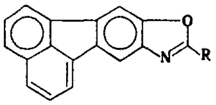
A number of fluoranthenoxazoles were synthesized from 8-hydroxy-9-aminofluoranthene, and their UV and IR spectra were studied.

The possibility of the cyclization of 8-hydroxy-9-aminofluoranthene (I) [1] and a number of its derivatives was studied in the present research with the idea of obtaining new fluoranthene derivatives – fluoroanthenoxazoles – the UV spectra of which contain absorption maxima at 298 and 322 nm; this makes them of interest as possible optical bleaches.

Inhibition of the interaction of two alternating portions (naphthalene and phenylene) through a five-membered ring in a nonalternating hydrocarbon – fluoranthene [2] – provides a basis for assignment of the properties of benzene and its derivatives to the phenylene portion of the molecule. We have found that 8-hydroxy-9-aminofluoranthene and some of its derivatives display a somewhat higher tendency for cyclization than o-aminophenol and substituted o-aminophenols [3]. Fluoranthen[8,9-d]oxazole (IIa) was obtained in good yield under relatively mild conditions by heating I with formamide. Under conditions close to those in the synthesis of 2-methylbenzoxazole [4], the N,O-diacetyl derivative of I cyclizes to 2-methylfluoranthen[8,9-d]oxazole (IIb). Alkaline hydrolysis of the diacetyl derivative of 8-hydroxy-9-aminofluoranthene and IIb leads to the same product – 8-hydroxy-9-acetamidofluoranthene; this is evidence for the two-step character of the formation of the oxazole. The synthesis of 2-phenylfluoranthene[8,9-d]oxazole (IIc) was accomplished from 8-hydroxy-9-(N-benzoyl)aminofluoranthene, which was obtained by alkaline hydrolysis of the N,O-dibenzoyl derivative of 8-hydroxy-9-aminofluoranthene.



I



II

II a R=H; b $R=CH_3$; c $R=C_6H_5$

An attempt to synthesize a fluoranthenoxazole containing a stilbene residue in the oxazole portion of the molecule under the conditions used to obtain benzoxazoles via a known method [5] was unsuccessful because of resinification.

The IR spectra of IIa-c contain absorption bands at 1615-1625 and 1555-1580 cm^{-1}, which are characteristic for the benzoxazole ring [6], and a band at 925 cm^{-1}. The presence of a benzoxazole ring in the compounds obtained is also confirmed by the presence of bands at 1220 and 1040 cm^{-1}, which are related to the C–O–C stretching vibrations [7]. The UV spectra of IIa-b give absorption maxima to 298 nm, while a bathochromic shift of the absorption maximum to λ 322 nm (Fig. 1) is observed for IIc; this is explained by conjugation between the phenyl residue of the oxazole portion of the fluoranthene molecule and the fluoranthene molecule itself.

In contrast to the starting compounds, which have green fluorescence, all of the fluoranthenoxazoles in organic solvents (chloroform, acetone, etc.) have light-blue fluorescence in UV beams.

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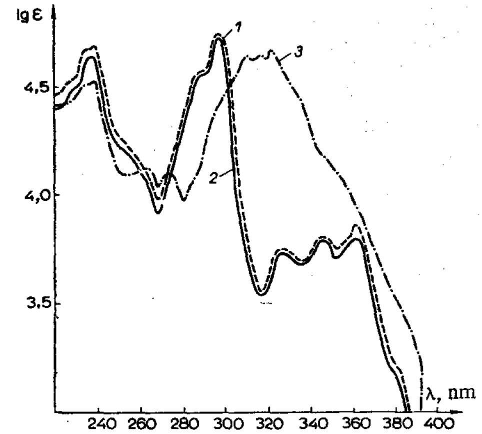

Fig. 1. UV spectra: 1) fluoranthen[8,9-d]-oxazole (IIa); 2) 2-methylfluoranthen[8,-9-d] oxazole (IIb); 3) 2-phenylfluoranthen-[8,9-d]oxazole (IIc).

EXPERIMENTAL

The IR spectra of IIa-c were recorded with a UR-20 spectrometer. The UV spectra of 10^{-4}-10^{-5} mole/liter solutions in 95% ethanol were recorded with an SF-4 spectrometer.

Fluoranthen[8,9-d] oxazole (IIa). A mixture of 2.33 g (10 mmole) of I and 11.4 g (254 mmole) of formamide was heated at 180-185° for 2 h and worked up to give 1.62 g (67%) of long colorless neeldes of IIa with mp 193-194° (from aqueous dimethylformamide). Found: C 84.0; H 4.1; N 5.6%. $C_{17}H_9NO$. Calculated: C 83.9; H 3.9; N 5.8%.

8-Acetoxy-9-acetamidofluoranthene. A mixture of 1.75 g (7.5 mmole) of I and 71.4 g (700 mmole) of acetic anhydride was stirred and heated to 100°. Cooling of the resulting light-brown solution gave 1.78 g (74%) of white needles with mp 244-245° (from aqueous acetic acid). Found: C 76.0; H 4.9; N 4.3%. $C_{20}H_{15}NO_3$. Calculated: C 75.8; H 4.8; N 4.4%.

2-Methylfluoranthen[8,9-d]oxazole (IIb). A 1.19-g (3.8 mmole) sample of the diacetyl derivative of I was heated to 245°, after which the temperature was lowered to 215-220° and held there for 40 min; workup of the mixture gave 0.94 g (98%) of long light-yellow needles of IIb with mp 196-197° (from benzene-petroleum ether). Found: C 84.0; H 4.2; N 5.3%. $C_{18}H_{11}NO$. Calculated: C 84.1; H 4.3; N 5.4%.

8-Hydroxy-9-acetamidofluoranthene. A 1.6-g (5 mmole) sample of the diacetyl derivative of I was heated in 2% sodium hydroxide solution at 75°, after which the mixture was worked up to give gray crystals with mp 240-241° (from benzene). Found: C 78.9; H 4.0; N 5.0%. $C_{18}H_{11}NO_2$. Calculated: C 79.1; H 4.05; N 5.1%.

An identical product was obtained from IIb by alkaline hydrolysis.

N,O-Dibenzoyl Derivative of 8-Hydroxy-9-aminofluoranthene. A total of 105 ml of 10% sodium hydroxide solution was added dropwise with vigorous stirring to a suspension of 1.15 g (5 mmole) of I in 15.2 g (108 mmole) of benzoyl chloride, after which the mixture was worked up to give 1.54 g (73%) of light-green needles with mp 208-209° (from toluene). Found: C 81.9; H 4.3; N 3.3%. $C_{30}H_{19}NO_3$. Calculated: C 81.7; H 4.3; N 3.2%.

8-Hydroxy-9-(N-benzamido)fluoranthene. A suspension of 0.88 g (2 mmole) of the N,O-dibenzoyl derivative of I and 0.1 g (2.5 mmole) of sodium hydroxide in 50 ml of ethanol was heated to the boiling point, and the resulting red solution was diluted with water and acidified with 10% hydrochloric acid to give 0.62 g (94%) of light-green needles with mp 247-248° (from glacial acetic acid). Found: C 81.9; H 4.7; N 4.0%. $C_{23}H_{15}NO_2$. Calculated %: C 81.8; H 4.5; N 4.1%.

2-Phenylfluoranthen[8,9-d]oxazole (IIc). A 2.25-g (6.6 mmole) sample of 8-hydroxy-9-(N-benzamido)-fluoranthene was heated with stirring to 250°, after which the temperature was lowered to 230-235° and held there for 12 min. The melt was cooled to give 1.9 g (89%) of IIc with mp 228-229° (from toluene). Found: C 86.5; H 3.9; N 4.5%. $C_{23}H_{13}NO$. Calculated: C 86.6; H 4.1; N 4.4%.

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