INVESTIGATIONS IN THE FIELD OF PERINONE COMPOUNDS

II*. SYNTHESIS OF STRUCTURALLY ISOMERIC NITRONAPHTHALOPERINONES

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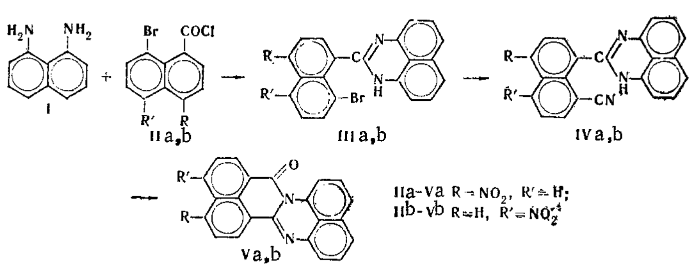
UDC 547.856.7'491.07

The directed synthesis of structurally isomeric nitronaphthaloperinones – 10-nitro- and 11-nitro-14H-benz[4,5]isoquinolino[2,1-a]perinidin-14-ones – has been effected.

As early as 1909, Sachs [2] suggested that the reactions of 1,8-naphthylenediamine with substituted aromatic ortho or peri dicarboxylic acids should form structural isomers of types Va and b. In view of the fact that such isomers have not so far been described and also of the practical usefulness of the perinones [3], we have performed the synthesis of isomeric nitronaphthaloperinones in the following way:



The method of synthesis that we adopted is similar to that described previously for the preparation of structural isomers in the naphthoylenebenzimidazole series [4]. The treatment of 2-(8'-bromo-5'-nitro-1'-naphthyl)perimidine (IIIb) with cuprous cyanide led to the nitrile IVb, which, without further purification, was hydrolyzed with 35% nitric acid, giving 11-nitro-14H-benz[4,5]isoquinolino[2,1-a]perimidin-14-one (Vb). Similarly, IIIa gave 10-nitro-14H-benz[4,5]isoquinolino[2,1-a]perimidine-14-one (Va).

The isomeric nitronaphthaloperinones Va and b obtained have extremely similar physicochemical properties. They do not melt below 360°C, possess approximately the same solubilities in organic solvents, and on thin-layer chromatography in alumina with various eluents have identical R_f values. The absorption spectra of the isomers Va and b in the visible region show appreciable differences: λ_{max} for Va 526 nm, ε 0.48 · 10^3; λ_{max} for Vb 542 nm, ε 0.88 · 10^3. The deepening of the coloration and the higher value for ε for the isomer Vb may be due to the conjugation of the nitro group with the perinone carbonyl, leading to the increased polarization of the molecule.

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*For Communication I, see [1].

Rubezhnoe Branch of the Scientific Research Institute of Organic Intermediate and Dyes. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 6, pp. 842-843, June, 1970. Original article submitted March 17, 1969.

EXPERIMENTAL

2-(8'-Bromo-5'-nitro-1'-naphthyl)perimidine (IIIb). A solution of 4.12 g (26 mmoles) of I in 60 ml of chlorobenzene was added to a solution of 8.2 g (26 mmoles) of 8-bromo-5-nitronaphthoyl chloride [5] in 60 ml of chlorobenzene, and the resulting suspension was stirred at 100°C for 2 h. After cooling, the precipitate was filtered off, washed with 30 ml of methanol, and dried. The product obtained was boiled with 200 ml of 5% sodium carbonate solution for 30 min, filtered off, washed with water, and dried. This gave 4.61 g (42.2%) of IIIb, black needles. After recrystallization from chlorobenzene, mp above 300°C, R_f 0.65 (thin layer of alumina, chlorobenzene). Found, %: Br 19.50; N 10.16. $C_{21}H_{12}BrN_3O_2$. Calculated, %: Br 19.12; N 10.05.

2-(8'-Bromo-4'-nitro-1'-naphthyl)perimidine (IIIa). A mixture of 1.48 g (5 mmoles) of 8-bromo-4-nitro-1-naphthoic acid [6] and 3 ml (~25 mmoles) of thionyl chloride in 20 ml of chlorobenzene was boiled for 1 h 30 min, and then the excess of thionyl chloride was distilled off and a solution of 0.79 g (5 mmoles) of I in 50 ml of chlorobenzene was added to the resulting solution of naphthoyl chloride IIa, giving, as described above, IIIa with a yield of 48.1%,dark crystals. After recrystallization from chlorobenzene, mp above 300°C, R_f 0.65 (thin layer of alumina, chlorobenzene). Found, %: Br 19.40; N 10.21.

11-Nitro-14H-benz[4,5]isoquinolino[2,1-a]perimidin-14-one (Vb). A solution of 0.84 g of IIIb in 15 ml of nitrobenzene and 10 ml of pyridine was treated with 1.04 g of cuprous cyanide, and the mixture was boiled with stirring for 4 h. After cooling, the solid matter was filtered off, washed with 40 ml of methanol, boiled with 200 ml of 35% nitric acid for 2 h, filtered off, washed with water, and dried. This gave 0.41 g (56.2%) of Vb, black needles. After recrystallization from chlorobenzene R_f 0.55 (thin layer of alumina, chlorobenzene). Found, %: C 72.47; H 3.00; N 11.25. $C_{22}H_{11}N_3O_3$. Calculated, %: C 72.33; H 3.03; N 11.50.

10-Nitro-14H-benz[4,5]isoquinolino[2,1-a]perimidin-14-one (Va). This was obtained in a similar manner to IIIa with a yield of 58.3%. After recrystallization from chlorobenzene, R_f 0.54 (thin layer of alumina, chlorobenzene). Found, %: C 71.98; H 3.02; N 10.95.

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