RESEARCH ON PERINONE COMPOUNDS

IV.* SYNTHESIS OF 10-SUBSTITUTED NAPHTHALOPERINONES

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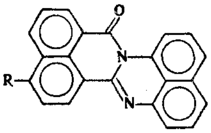
10-Substituted 14H-benz[4,5]isoquinolino[2,1-*a*]perimidin-14-ones were synthesized, and their spectra were studied. In contrast to electron-acceptor substituents, electron-donor substituents have little effect on the shift of the absorption maxima.

To study the chromaticity of perinone compounds we obtained a number of new perinone compounds from the previously described [1] 10-amino-14H-benz[4,5]isoquinolino[2,1-*a*]perimidin-14-one (I) via the Sandmeyer reaction. In contrast to 10-bromonaphthaloperinone, 10-cyanonaphthaloperinone (II) is obtained in low yield because of the formation of a large number of side products. We were able to isolate II by chromatography with a column filled with aluminum oxide. Compound II was hydrolyzed to 10-carboxynaphthaloperinone (III) with subsequent conversion to the methyl ester (IV).



I–VIII

I $R=NH_2$; II $R=CN$; III $R=COOH$; IV $R=COOCH_3$; V $R=Br$; VI $R=OH$; VII $R=OCH_3$; VIII $R=NHCOCH_3$

10-Hydroxynaphthaloperinone (VI) was obtained by refluxing the diazonium salt in dilute sulfuric acid. Methylation of VI with dimethyl sulfate in alkaline media gives methoxy derivative VII and is accompanied by the formation of a considerable number of side products; this can be explained by cleavage of the perinone ring [2].

The introduction of both electron-donor and electron-acceptor substituents leads to a bathochromic shift of the absorption maxima of 10-substituted naphthaloperinones as compared with unsubstituted naphthaloperinone (Table 1). The deepening in color increases in the following order: $OCH_3 < OH < NHCOCH_3 < Br < COOH < COOCH_3 < CN$.

The introduction of electron-acceptor substituents into the 10 position of naphthaloperinone causes a bathochromic effect; this attests to appreciable conjugation of substituent R in II-V with the heterocyclic ring of naphthaloperinone, which consequently displays electron-donor character. The introduction of electron-donor substituents has little effect on the position of the long-wave absorption band. It is well known that the presence of two substituents of the same sort in the benzene ring has practically no reflection in the absorption spectrum as compared with the monosubstituted compound. In other words, the heterocyclic ring of naphthaloperinone in I and VI-VIII manifests itself as an electron donor.

The correlation coefficients were calculated by the method of least squares [3] by comparison of the various types of σ substituent constants with the wave numbers of the absorption maxima of the 10-substituted naphthaloperinones (Table 2). The best correlations are achieved when nucleophilic and electro-

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*See [1] for communication III.

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TABLE 1. 10-R-Naphthaloperinones

Comp.	R	mp, °C (crystalliz. solvent)	Empirical formula	N(Br), %		λ_{max}, nm	lg ε	Yield, %
				found	calc.			
I	NH_2	—	—	—	—	486	3,86	—
II	CN	241—242 (chlorobenz.)	$C_{23}H_{11}N_3O$	12,3	12,2	508	3,57	34
III	COOH	>350 (pyridine)	$C_{23}H_{12}N_2O_3$	7,4	7,7	500	3,68	34
IV	$COOCH_3$	209—210 (benzene)	$C_{24}H_{14}N_2O_3$	7,5	7,4	504	3,70	39
V	Br	238—239 (chlorobenz.)	$C_{22}H_{11}BrN_2O$	(20,2)	(20,0)	495	3,69	63
VI	OH	350 (pyridine)	$C_{22}H_{12}N_2O_2$	8,0	8,3	482	3,71	44
VII	OCH_3	231—232 (benzene)	$C_{23}H_{14}N_2O_2$	8,3	8,0	474	3,74	17
VIII	$NHCOCH_3$	249—251 (chlorobenz.)	$C_{24}H_{15}N_3O_2$	11,0	11,2	480	3,64	43

TABLE 2. Correlation of the Shifts of the Absorption Maxima of 10-R-Naphthaloperinones with Different Types of Substituent Constants

R	σ	r*	P
NH_2; $NHCOCH_3$; OH; OCH_3; H	σ	0,751	−13,159
	σ^+	0,891	− 8,502
	σ_c^+	0,843	− 7,257
	σ_I	—	—
NO_2; CN; $COOCH_3$; COOH; Br; H	σ	0,938	46,334
	σ^-	0,936	28,332
	σ_c^-	0,998	34,234
	σ_I	0,903	59,265

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*The symbol r is the correlation coefficient and P is the sensitivity coefficient. The Student coefficient (t_α) corresponds to reliability $\alpha = 0.999$.

philic constants are used; this reflects the dominating influence of the mesomeric effect of substituents on the change in the absrotpion maxima as compared with unsubstituted naphthaloperinone (λ_{max} 472 nm, log ε 3.65).

The presence of a correlation in the case of electron-acceptor substituents and the absence of a correlation for electron-donor substituents also attest to the fact that perinones have an electron-donor effect with respect to substituents in the naphthalic acid residue.

We thank G. A. Yugai for his assistance in performing the calculations.

EXPERIMENTAL

The absorption spectra of chlorobenzene solutions were recorded with an SF-14 spectrophotometer. Chromatography was carried out with anhydrous aluminum oxide.

10-Bromonaphthaloperinone (V). A 1.14-g (3.3 mmole) sample of I was refluxed for 30 min in 50 ml of 15% sulfuric acid, after which the mixture was cooled to 0° and treated with a solution of 0.28 g of sodium nitrite in 2 ml of water. The mixture was stirred at 0° for 30 min and then poured slowly into a solution of 0.76 g of cuprous bromide, 1.14 g of potassium bromide, and 7 ml of 48% hydrobromic acid in 25 ml of water. The aqueous mixture was stirred for 1 h and heated to 80°. After 30 min, it was filtered, and the solid was washed with water and dried. Chromatography with a column filled with aluminum oxide (the solvent and eluent were chlorobenzene) gave V as brown needles.

10-Cyanonaphthaloperinone (II). A 1.68-g (5.5 mmole) sample of I was refluxed for 30 min in 50 ml of 15% sulfuric acid, after which the mixture was cooled to 0° and treated (dropwise) with a solution of 0.38 g of sodium nitrite in 2 ml of water. The mixture was stirred for 1 h, after which the excess sodium nitrite was removed with urea, and the mixture was neutralized to pH 5.5-6.0 with potassium carbonate. The suspension was poured into a solution of 4 g of sodium cyanide and 5.9 g of cuprous cyanide in 60 ml of water, and the mixture was stirred at room temperature for 1 h and at 70° for 1 h. The precipitate was removed by filtration, washed with water, and dried. The product was dissolved in chloroform and chromatographed twice with a column filled with aluminum oxide [the eluent was cyclohexane–chloroform (1 : 1)]. The first fraction (blue) was collected, and the solvents were removed by distillation to give II as blue needles (Table 1).

Methyl Naphthaloperinone-10-carboxylate (IV). A 0.2-g sample of III was refluxed for 2 h in 10 ml of chlorobenzene containing 0.5 ml of thionyl chloride, after which the excess thionyl chloride was removed by distillation, 5 ml of methanol was added to the residue, and the mixture was refluxed for 8 h. It was then cooled, and the precipitate was removed by filtration, dissolved in benzene, and chromatographed with a column filled with aluminum oxide [elution with benzene–cyclohexane (1 : 1)]. The solvent was removed by distillation to give blue plates of IV.

10-Hydroxynaphthaloperinone (VI). A 0.6-g (1.8 mmole) sample of I was diazotized as in the preparation of II, and the reaction mass was refluxed for 6 h and filtered. The solid was washed with water and dried to give red-brown needles of VI.

10-Methoxynaphthaloperinone (VII). A 0.25-ml sample of 10% sodium hydroxide solution and 0.5 ml of freshly distilled dimethyl sulfate were added to a solution of 0.2 g of VI in 20 ml of acetone, and the mixture was heated to 40°. After 1 h, another 0.25 ml of dimethyl sulfate was added, and the mixture was poured into water after 30 min. The precipitate was removed by filtration, washed with water, and dried. The product was dissolved in benzene and chromatographed with a column filled with aluminum oxide [elution with benzene–ethyl acetate (1 : 1)]. Removal of the solvent by distillation gave red-brown needles of VII.

10-Acetamidonaphthaloperinone (VIII). A 0.2-g sample of I was refluxed for 2 h in 10 ml of acetic anhydride, after which the mixture was cooled and filtered, and the solid was washed with hot water and dried. The product was dissolved in acetone and chromatographed with a column filled with aluminum oxide [elution with cyclohexane–acetone (1 : 1)]. Removal of the solvent by distillation gave brown needles of VIII.

LITERATURE CITED

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3. D. M. Batuner and M. E. Pozin, Mathematical Methods in Chemical Technique [in Russian], Khimizdat (1963).