STUDIES ON QUINONES

X. Addition to Phenanthrene Quinone Furazan*

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 6, pp. 970–971, 1968

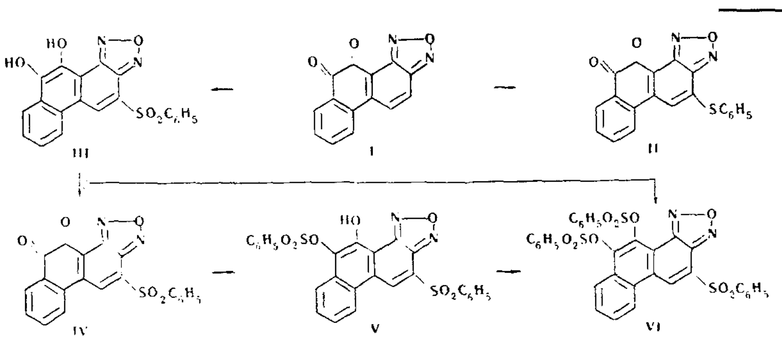
UDC 547.677.6'547:793.6

Phenanthro[1, 2-c][1, 2, 5]oxadiazole-10, 11-dione (phenanthrene quinone furazan, I), like anthraquinone furazan, is capable of adding nucleophilic agents to carbon atom 4 of the carbon skeleton or to the oxygen of the carbonyl group. Thus, its reactions with thiophenol and benzenesulfinic acid, with subsequent oxidation lead, respectively, to the substituted quinones II and IV, the latter of which is converted by the action of benzenesulfinic acid into the benzenesulfonic ester V.

It was found previously that some derivatives of anthraquinone containing an angularly condensed heterocycle possess unexpected activity in nucleophilic addition reactions [2–4]. The nucleophilic agent combines with the carbon atom of the nucleus conjugated with the carbonyl group closest to the heterocycle or with the oxygen of the carbonyl remote from the heterocycle. It was of interest to study whether this reactivity is a specific feature of anthraquinone derivatives alone.

As the subject of investigation we selected phenanthro[1,2-c][1,2,5]oxadiazole-10,11-dione (phenanthrene quinone furazan, I) [5]. It was found that I, like anthraquinone furazan, readily reacts with mercaptans, sulfinic acids, and amines.

Its reaction with thiophenol in dimethylformamide, with subsequent oxidation by ferric chloride, led to the phenylthio-substituted quinone II, very similar in its properties and IR and UV spectra to 4-phenylthioanthra[1,2-c][1,2,5]oxadiazole-6,11-dione [4]. When I was heated with benzenesulfinic acid in acetic acid solution, the benzenesulfonyl-substituted phenanthrene hydroquinone III was formed, which was converted on treatment with $FeCl_3$ into the quinone IV. These reactions are similar to those studied for anthraquinone furazan [4] and it may be assumed that here, also, the nucleophilic agent attacks at position 4.



The analogy also extends to addition to the oxygen of a CO group. Under the action of benzenesulfinic acid, the quinone IV gives the ester V, which by acylation with benzenesulfonyl chloride is converted into the diester VI, identical with that obtained from the hydroquinone III. In the IR spectrum of the monoester V, as in the corresponding anthracene derivative [4], the ν_{OH} band is displaced in the direction of lower frequencies, which permits the assumption of the existence of an intramolecular hydrogen bond and, consequently, in this case also, the presence of an ester grouping bound to the oxygen atom remote from the heterocycle.

Thus, the introduction of the furazan ring in the 1,2-position of phenanthrenequinone leads, as in the anthraquinone series, to a high reactivity to nucleophilic agents which is not a characteristic of phenanthrene quinone and its derivatives.

EXPERIMENTAL

4-Phenylthiophenanthro[1, 2-c][1, 2, 5]oxadiazole-10, 11-dione (II). A mixture of 0.25 g (0.001 mole) of I, 10 ml of dimethylformamide, and 0.5 g of thiophenol was heated to boiling. Then, 6 ml of 35% $FeCl_3$ solution was added and the mixture was boiled for another 2–3 min. After cooling, crystals of II were filtered off and washed with dimethylformamide and ethanol; yield 0.33 g (92%). Orange-red needles (from acetic acid) not melting below 350° C; λ_{max}, nm (log ε): 265 (4.40), 355 (3.66, shoulder), 410 (4.06), 475 (3.95). Found, %: S 8.68, 8.72. Calculated for $C_{20}H_{10}N_2O_3S$, %: S 8.95.

10, 11-Dihydroxy-4-phenylsulfonylphenanthro[1, 2-c][1, 2, 5]oxadiazole (III). A solution of 0.004 mole of sodium benzenesulfinate in 6 ml of water was added to a boiling solution of 0.75 g (0.0015 mole) of I in 120 ml of acetic acid. Crystals began to separate out after 2–3 minutes. After 80 ml of acetic acid had been distilled off and the residual solution had been cooled, 1.03 g (87%) of the hydroquinone III was obtained. Long yellow-orange needles (from acetic acid), sparingly soluble in organic solvents, decomposing without melting on being heated to 350° C. In aqueous dioxane, the addition of caustic soda led to an intense blue coloration. No ν_{CO} band was present in the IR spectrum. Found, %: C 61.25, 61.18; H 3.03, 3.09; N 7.13, 7.36; S 8.14, 8.20. Calculated for $C_{20}H_{12}N_2O_5S$, %: C 61.21; H 3.06; N 7.14; S 8.17.

4-Phenylsulfonylphenanthro[1, 2-c][1, 2, 5]oxadiazole-10, 11-dione (IV). To a suspension of 0.78 g (0.002 mole) of III in 25 ml of acetic acide at 100° C was added to 10 ml of a 35% solution of $FeCl_3$. The solid matter dissolved and, after 5 min boiling, crystals of the quinone separated out. Yield of IV 0.58 g (74.3%). Long orange prisms (from acetic acid), mp 250–251° C (decomp.); ν_{CO} 1670 cm^{-1},

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*For part IX, see [1]

ν_{SO_2} 1148 cm^{-1}; λ_{max}, nm (log ε): 245 (4.92), 298 (3.97), 345 (3.98), 436 (3.52), 450 (3.48). Found, %: C 61.58, 61.61; H 2.54, 2.75; N 7.22, 7.16; S 8.19, 8.30. Calculated for $C_{20}H_{10}N_2O_5S$, %: C 61.55; H 2.58; N 7.18; S 8.21.

Monobenzenesulfonate of 10,11-dihydroxy-4-phenylsulfonylphenanthro[1,2-c][1,2,5]oxadiazole (V). A solution of 0.003 mole of sodium benzenesulfinate in 4 ml of water was added to a boiling solution of 0.001 mole of IV in 40 ml of acetic acid. After 40 min boiling with the distillation of half the acetic acid, followed by cooling, 0.42 g (78%) of the ester V was filtered off. Light yellow needles (from dioxane), not melting on being heated to 350° C. In aqueous dioxane with the addition of ether, the substance gave a red coloration changing to blue on heating. The IR spectrum of the substance lacked the band of carbonyl vibrations and had ν_{SO_2} 1182, 1159 cm^{-1} and ν_{OH} 3380 cm^{-1}; λ_{max}, nm (log ε): 290 (4.52), 338 (3.70), 355 (3.72), 408 (4.07). Found, %: C 58.32, 58.54; H 2.83, 3.09; N 5.18, 5.21; S 12.12, 11.98. Calculated for $C_{26}H_{16}N_2O_7S_2$, %: C 58.64; H 3.03; N 5.26; S 12.04.

Dibenzenesulfonate of 10,11-dihydroxy-4-phenylsulfonylphenanthro[1,2-c][1,2,5]oxadiazole (VI). A solution of 0.15 g of the ester V or the hydroquinone III in 5 ml of pyridine was mixed with 1 ml of benzenesulfonyl chloride, and after 12 hr standing at 18–20° C, the mixture was poured into water. The precipitate was separated off, washed with water, and crystallized from acetic acid, mp 247.5–248° C. A mixture of the substances obtained from V and from II showed no depression of the melting point. Found, %: C 57.21, 57.09; H 3.07, 3.15; N 4.26, 4.17; S 14.37, 14.08. Calculated for $C_{32}H_{20}N_2O_9S_3$, %: C 57.11; H 2.97; N 4.16; S 14.30.

The UV spectra were measured in an SF-4 spectrophotometer in chloroform and the IR spectra on an IKS-14 instrument in tablets of KBr.

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11 August 1966

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