STUDIES ON QUINONES

VIII. Addition Reactions to Anthraquinonefurazans*

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 5, pp. 780–784, 1968

UDC 547.673'547.793.6:543.422.4

Anthra[1,2-c][1,2,5]oxadiazole-6,11-dione (I) was added to benzenesulfinic acid and thiophenol with the formation of 4-phenylsulfonyl- and 4-phenylmercapto-substituted hydroquinones, which on oxidation were converted into the corresponding quinones III and VII. 4-Phenylsulfonylanthra[1,2-c][1,2,5]oxadiazole-6,11-dione (III), in turn, reacted readily with benzenesulfinic acid, adding a molecule of the latter to the carbonyl oxygen atom and was converted into the O-benzenesulfonic monoester [6] (IV). Using compounds IV and hydroxynaphtho[1,2-c][1,2,5]oxadiazole (XId) the capability of the nitrogen atom of the furazan ring of participating in the formation of intramolecular hydrogen bonds was shown.

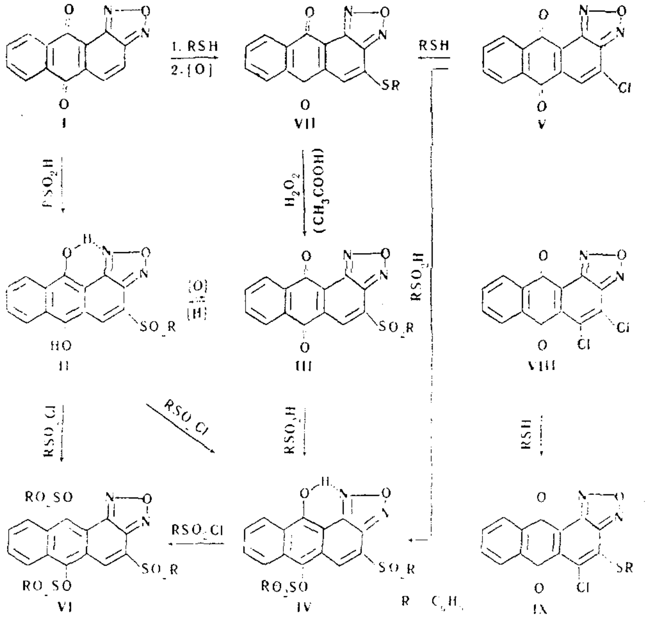
It has previously been shown that anthra[1,2-c]-[1,2,5]oxadiazole-6,11-dione (anthraquinonefurazan, I) adds bisulfite to carbon atom 4 of the ring, or, if position 4 is occupied by a sulfo group, anomolously to the oxygen atom of one of its carbonyl groups [2]. The present work shows that the reaction with sulfinic acids proceeds in the same way.

On being heated with benzenesulfinic acid in the presence of acetic acid, anthraquinonefurazan (I) is rapidly converted into the anthraquinone II, which is then oxidized to 4-phenylsulfonylanthra[1,2-c][1,2,5]oxadiazole-6,11-dione (III). The latter in turn easily adds a molecule of benzenesulfinic acid, giving the benzenesulfonic ester IV. In the reaction of benzenesulfinic acid with 4-chloroanthraquinonefurazan (V), substitution of the chlorine atom and addition to the oxygen occur simultaneously, as a result of which the monoester IV is formed in a single step.

Proof of the presence of the ester group is the synthesis of the monoester IV by the treatment of the hydroquinone II with an equivalent amount of benzenesulfonyl chloride, and that of the diester VI by the acylation with benzenesulfonyl chloride of the hydroquinone II and the monoester IV.

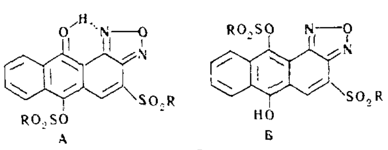
The reaction of the quinone I with thiophenol in dimethylformamide followed by subsequent oxidation with ferric chloride produces the 4-phenylmercapto-substituted VII. The same compound is obtained by heating the 4-chloro-substituted V with thiophenol, while in the case of 4,5-dichloroanthraquinonefurazan (VIII), the chlorine-containing sulfide IX is obtained. These conversions show that there is at carbon atom 4 a phenylmercapto group in the quinones VII and IX, and a phenylsulfonyl group in the quinone III, which is formed by the oxidation of the sulfide VII with peracetic acid.

The structures of the compounds were confirmed by their spectral characteristics. In going from the quinone III to the monoester IV, the carbonyl absorbtion in the IR spectrum disappears, and a band due to the stretching vibrations of the OH group (3383 cm^{-1}) appears, together with a second band (1184 cm^{-1}) due to the symmetrical vibrations of the SO_2 group as is characteristic for sulfonates [3], in the region of higher frequency than ν_{SO_2} of a sulfone (1162 cm^{-1}). The UV spectrum of the compound shows a signifigant displacement to the long-wave region and is similar to the spectrum of the sulfuric monoester of 6,11-dihydroxyanthra[1,2-c][1,2,5]oxdiazole-4-sulfonic acid (X).



When an attempt is made to obtain the bisulfite addition product of the quinone III, displacement of the phenylsulfonyl group takes place with the formation of the ester of the hydroquinonesulfonic acid (X).

In discussing the reaction capabilities of anthraquinonefurazans, it is important to establish which of the two oxygen atoms of the carbonyls adds the bisulfite or sulfinic acid residue. In making a choice between A and B, it must be kept in mind that only in the former is there the possibility for formation of an intramolecular hydrogen bond.



IV R = C_6H_5; X R = ONa

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*For part VII, see [1].

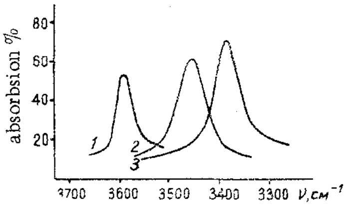
The capability of the nitrogen atom of the 1,2,5-oxadiazole ring of forming chelate rings has not been reported in the literature. Many of the chemical and physical properties of furazans agree with the postulate of the existence in the ring of a closed p, π-election system that does not, as in pyridine, include the unshared pairs of the nitrogen atoms. From data of quantum mechanical calculations, using the Hückel approximation, a charge of -0.27 e should be concentrated on the nitrogens of the furazan ring, which is equal to the charge on the pyridine nitrogen. However, as is well known, the basicity of furazans is so small that they can neither form stable salts nor be oxidized to N-oxides [5]. Since the stability of the hydrogen bond depends on the basicity of the heteroatom, [6, 7] it became necessary to solve this problem experimentally. For this purpose, a study of the IR spectra of the four isomers of hydroxynaphtho[1, 2-c][1, 2, 5]oxadiazole (**XIa–d**), used as model compounds, was made.

9-Hydroxynaphthofurazan (**XIa**) was prepared from 8-acetylamino-1-nitroso-2-naphthol [8] by its reaction with hydroxylamine and sodium hydroxide, with subsequent replacement of the amino group in the 9-aminonaphthofurazan. The remaining hydroxy derivatives were prepared by S. V. Bogdanov and S. F. Petrov [9]*.

In measuring the frequencies and integral intensities of the stretching vibrations of the hydroxy group in chloroform solution, it was established that the parameters cited for each of the compounds (**XIa–c**) in the concentration interval $5 \cdot 10^{-2}$ to $5 \cdot 10^{-3}$ M are practically unchanged. At the same time, the band of the hydroxyl vibrations in the spectrum of 9-hydroxynaphthofurazan is significantly displaced toward a lower frequency in comparison to the ν_{OH} for the 6-, 7- and 8-hydroxy derivatives (figure), and the intensity of the band is significantly greater. This is evidence of the presence of a rather strong hydrogen bond. The absence of a concentration dependence shows its intramolecular nature. The presence of a hydrogen bond in 9-hydroxynaphthofurazan (**XId**) provides the basis for expecting its presence in the compound of structure **A**.

In the IR spectrum of the benzenesulfonic ester IV in the crystalline state and in chloroform solution the symmetrical band of the OH stretching vibrations is of higher intensity and at a lower frequency than that in the spectrum of the 9-hydroxynaphthofurazan (figure). The position and intensity of the band do not change on dilution of the solution.

The production of the proof of the existence of an intramolecular hydrogen bonds shows that compound IV has the structure A and that the ester group is in position 6. Since the additions of bisulfite and of benzenesulfinic acid to quinone I take place analogously, there is every reason for assuming that bisulfite also adds to the oxygen atom of the carbonyl group remote from the heterocycle. What has been said applies equally to the addition of the same reagents to the anthra[1,2-c][1,2,5]thiadiazole-6,11-diones [10].



Absorbtion band of the OH group (in chloroform): 1) 7-hydroxynaphtho[1, 2-c][1, 2, 5]oxadiazole (**XIb**), conc. $1.05 \cdot 10^{-2}$ M, layer thickness, 0.4107 cm; 2) 9-hydroxynaphtho-[1,2-c][1,2,5]oxadiazole (**XId**), conc. $6 \cdot 10^{-3}$, layer thickness, 0.8214 cm; 3) Compound IV, conc. $6.28 \cdot 10^{-3}$, layer thickness, 0.9501.

EXPERIMENTAL

6,11-Dihydroxy-4-phenylsulfonylanthra[1, 2-c][1, 2, 5]oxadiazole (II). a) To a boiling solution of 2.50 g (0.01 mole) of quinone I in 80 ml acetic acid under nitrogen was added a solution of 4.00 g of sodium benzenesulfinate in 7 ml of water. The crystals which began to separate out after 2–3 min were filtered off after cooling; yield of II, 3.45 g (90%). Yellow needles (from acetic acid), giving a blue coloration in solutions of alkalis, mp 235° C (decomp.).

b) To a solution of 1.45 g (0.005 mole) of III in 200 ml of acetic acid was added a solution of 4 g of stannous chloride in 10 ml of concentrated hydrochloric acid. After boiling for 10 min, and evaporating part of the solvent, 1.33 g of hydroquinone II was obtained. Found, %: N 7.18, 7.22; S 7.98, 8.26. Calculated for $C_{20}H_{12}N_2O_5S$, %: N 7.14; S 8.17.

4-Phenylsulfonylanthra[1, 2-c][1, 2, 5]oxadiazole-6,11-dione (III). a) In the experiment described above (variant a), 60 sec after adding the benzenesulfinate solution, 20 ml of a 40% ferric chloride solution was added and the mixture was boiled for another 5 min. After cooling, along yellow prisms of the quinone III separated, yield 3.36 g (86%); mp 290°–290.5° C (from acetic acid). The oxidation of the hydroquinone II with ferric chloride can also be carried out in dimethylformamide. After heating III with sodium bisulfite under the conditions give previously [2], the sodium salt X was obtained.

b) To a boiling solution of 0.716 g (0.002 mole) of the sulfide VII in 80 ml acetic acid was added over a period of 15 min 10 ml of 30% hydrogen peroxide. After boiling for an additional 10 min, the light yellow precipitate was separated off after cooling and was recrystallized from acetic acid, yield 0.63 g (80%), mp 290°–291° C, a mixed melting point with the material obtained in case (a) showed no depression. Found, %: C 61.76, 61.82; H 2.69, 2.77; N 7.28, 7.22; S 8.33, 8.09. Calculated for $C_{20}H_{10}N_2O_5S$, %: C 61.53; H 2.58; N 7.18; S 8.22.

4-Phenylmercaptoanthra[1, 2-c][1, 2, 5]oxadiazole-6,11-dione (VII). A mixture of 0.50 g (0.002 mole) of quinone I, 15 ml of dimethylformamide, and 0.5 g of thiophenol was heated to boiling and 10 ml of a 40% ferric chloride solution was added. The suspension obtained after boiling for a short time was cooled and filtered, and the precipitate was washed with alcohol and ether.

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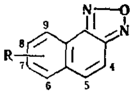
[*] The authors thank S. V. Bogdanov and S. F. Petrov for furnishing samples of these compounds.

Characteristic Stretching Vibrations of the Hydroxy Group



XI

Compound		Concentration, 10^{-3} m	Half band-width, cm^{-1}	Frequency cm^{-1}	Integral intensity, 10^{-4} *l*/mole · cm^2
number	R				
XIa	6-OH	5.4	43	3590	0.65
XIb	7-OH	10.5	41	3594	0.71
XIc	8-OH	13.9	34	3593	0.80
XId	9-OH	6.0	62	3445	1.55
IV		1.3	49	3381	1.70

The yield was 0.69 g (96%) of orange needles of the sulfide VII, mp 247°–247.5° C (from acetic acid or dioxane); λ_{max}nm (lg ε) in alcohol: 270 (4.40), 236 (3.77), 455 (4.00).

b) 0.57 g (0.002 mole) of V, 0.5 g of thiophenol, and 20 ml of ethylene glycol were heated to 150° C for 30 min. The cooled suspension was diluted with 20 ml of alcohol and filtered. Yield of the sulfide VII 0.58 g (81%). Found, %: C 66.88, 67.14; H 2.69, 2.71; S 8.86, 8.82. Calculated for $C_{20}H_{10}N_2O_3S$, %: C 67.03; H 2.81; S 8.95.

5-Chloro-4-phenylmercaptoanthra[1,2-c][1,2,5]oxadiazole-6,11-dione (IX). The compound was obtained analogously to the sulfide VII (variant b) from 4,5-dichloroanthra[1,2-c][1,2,5]oxadiazole-6,11-dione (VIII). After chromatography on aluminum oxide in chloroform solution, and crystallization from chlorobenzene, long orange prisms with a mp 222°–223° C were obtained. Found, %: Cl 8.96, 8.98; S 8.03, 7.96. Calculated for $C_{20}H_9ClN_2O_3S$, %: Cl 9.07; S 8.21.

O-Benzenesulfonic ester [6] of 6,11-dihydroxy-4-phenylsulfonylanthra[1,2-c][1,2,5]oxadiazole (IV). a) To a solution of 0.005 mole of quinone III or V in boiling acetic acid were added, respectively, solutions of 2.5 g and 4.0 g of sodium benzenesulfinate in 10 ml of water. After 45 minutes' boiling with the evoporation of some of the solvent (volume remaining 80 ml), yellow crystals separated. The yields of IV were, respectively, 68% and 82%. Light yellow needles or prisms (from acetic acid or dioxane), mp 200° C (decomp)*, λ_{max}, nm (log ε) in chloroform: 248 (4.53), 306 (4.24) 316 (4.28), 345 (3.86), 360 (3.68), 415 (3.96), 4.33 (3.98) ν_{SO^2} 1186 1162 cm^{-1}. In aqueous dioxane or alcohol with sodium hydroxide, the product gives a red coloration changing to blue on heating.

b) A mixture of 0.392 g (0.001 mole) of the hydroquinone II, 2 ml of pyridine and 0.176 g (0.001 mole) of benzenesulfonyl chloride was stirred at 20° C for 5 min then poured into water. After repeated crystallization from acetic acid and dioxane there was isolated a light yellow product, the properties and IR and UV spectra of which were identical with those of the product obtained in (a). Found, %: C 58.57, 58.46; H 3.02, 2.95; S 11.95, 12.08. Calculated for $C_{26}H_{16}N_2O_7S_2$, %: C 58.64; H 3.03; S 12.04.

Di(benzenesulfonate) of 6,11-dihydroxy-4-phenylsulfonylanthra[1,2-c][1,2,5]oxadiazole (VI). 0.001 mole of the hydroquinone II or the monoester IV in 5 ml of pyridine was treated at 20° C with 1.06 g (0.006 mole) of benzenesulfonyl chloride. The red coloration quickly changed to light yellow. After pouring into water, the precipitated oil quickly hardened; the precipitate was isolated and recrystallized from acetic acid. Pale yellow hexagonal prisms, mp 173.5°–174.5° C. Mixed melting points and a comparison of the IR spectra showed that the products obtained in the two cases were identical. Found, %: C 57.01, 57.21; H 3.17, 3.15; S 13.95, 13.87. Calculated for $C_{32}H_{20}N_2O_9S_3$, %: C 57.13; H 3.00; S 14.30.

9-Aminonaphtho[1,2-c][1,2,5]oxadiazole. 1.00 g (0.004 mole) of 1-nitroso-8-acetylamino-2-naphthol [8] was heated for 30 min at 90° C in 200 ml of an aqueous solution containing 1.5 g (0.022 mole) of hydroxylamine hydrochloride and 3.0 g of crystalline sodium acetate. The solution was filtered hot, and the material which precipitated on cooling was isolated and heated for 30 min with 40 ml of a 0.5 N sodium hydroxide solution. The reaction product was filtered off, washed with water, dried, and passed in chloroform solution through a layer of alumina. Evaporation of the solvent gave 0.21 g of the amino compound. Greenish-yellow prisms (from alcohol) were found, mp 140.7°–141.5° C. Found, %: C 64.67, 64.83; H 3.76, 3.78; N 22.91, 22.76. Calculated for $C_{10}H_7N_3O$, %: C 64.86; H 3.81; N 22.69.

9-Hydroxynaphtho[1,2-c][1,2,5]oxadiazole-6,11-dione (XId). The substance was obtained the same way as the earlier reported hydroxynaphthofurazan [9] from the corresponding amine. Small colorless needles (from aqueous alcohol) with a sharp phenolic odor, easily soluble in aqueous solutions of alkalis and in most organic solvents, were obtained, mp 130°–130.5° C. Found, %: N 16.86, 15.00. Calculated for $C_{10}H_6N_2O_2$, %: N 15.05.

IR spectra was recorded on a IKS-14 spectrophotometer, UV and visible spectra on an SF-4 spectrophotometer. Frequencies and integral intensities of the bands of the stretching vibrations of the OH group were determined in chloroform for compounds XI in the concentration interval $5 \cdot 10^{-2}$–$5 \cdot 10^{-3}$ M, and for compound IV in the interval $6.3 \cdot 10^{-3}$ to $1.3 \cdot 10^{-3}$ M.

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18 August, 1966

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*Depending on the rate of heating.