RESEARCHES ON QUINONES

III. Reaction of Anthra[1, 2-c][1, 2, 5]Oxadiazole-6, 11-Dione with Bisulfite*

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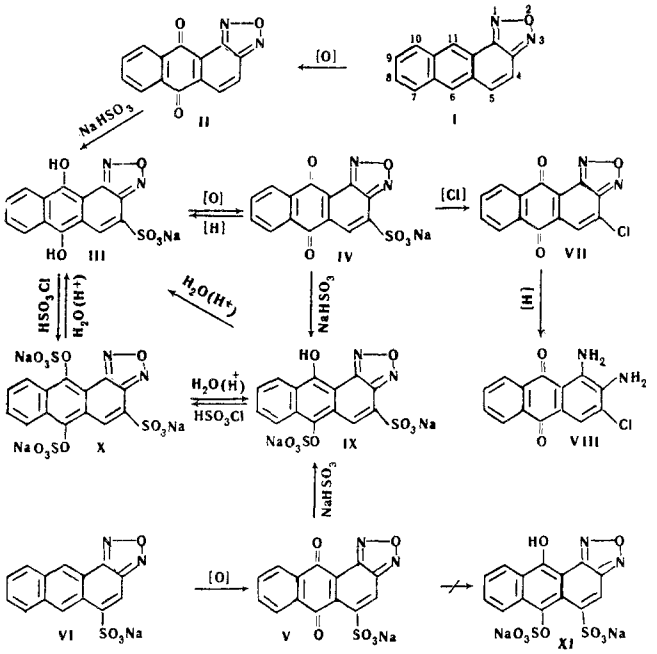
When anthra[1, 2, 5]oxadiazole-6, 11-dione reacts with sodium bisulfite, the sulfonic group enters at position 4 in the ring, giving 6, 11-dihydroxyanthra[1, 2-c][1, 2, 5]oxadiazole-4-sulfonic acid. The latter compound is also formed by treating with bisulfite anthra[1, 2-c]-[1, 2, 5]oxadiazole-6, 11-dione-5-sulfonic acid, obviously initially converted to the 4-sulfonic acid by addition-elimination of a molecule of bisulfite. The formation of sulfuric monoester observed in the course of the work in the reaction of quinone with bisulfite, is an example of an addition of a type unusual for carbonyl compounds, where a nucleophilic reagent, the sulfite ion, adds to carbonyl oxygen.

By oxidizing anthra[1, 2-c][1, 2, 5]oxadiazole (1, 2-anthrafurazan, I), M. V. Gorelik and S. V. Bogdanov synthesized anthra[1, 2-c][1, 2, 5]oxadiazole-6, 11-dione (1, 2-anthraquinonefurazan, II) [2]. It was of interest to study the properties of this ketone in greater detail.



It was found that anthra[1, 2-c][1, 2, 5]oxadiazole-6,-11-dione (II) reacts readily with sodium bisulfite [3]. The resultant compound III is not decomposed by nitrous or chromic acid, but converted into compounds not differing greatly in composition, and is resistant to further oxidation. This shows that bisulfite does not add to quinone II at a carbonyl group, since as a rule α-hydroxysulfonic acids are readily decomposed in acid solution [4]. The sulfonic acid IV, prepared by oxidation of the bisulfite compound, contains the C=O group, its electronic and IR spectra resemble those of the starting anthraquinonoxadiazole II (see Figs. 1 and 2), and obviously it is a derivative of the latter. It is improbable that the sulfonic acid group enters a ring of the anthraquinone ring system, not joined to a heterocyclic ring, since anthraquinone itself does not react with sodium bisulfite. Consequently the sulfonic acid group could be assumed to be at position 4 or 5 on molecule II. The corresponding 5-sulfonic acid (V), synthesized by oxidizing anthraoxadiazole-5-sulfonic acid (VI) [5] with sodium dichromate, differs from the compound under investigation both in respect of the melting point of the sulfochloride and IR spectrum (Fig. 1), so it was considered to be anthra[1, 2-c][1, 2, 5]oxadiazole-6, 11-dione-4-sulfonic acid (IV). For proof regarding the sulfonic acid group in the latter, this group was replaced by chlorine by treatment with potassium chlorate in hydrochloric acid solution, and the resultant 4-chloro derivative (VII), by treatment with stannous chloride and sodium hydrosulfite, was reduced to 3-chloro-1, 2-diaminoanthraquinone (VIII), identified by comparison with a specimen prepared by an independent method.

Reduction of sulfonic acid IV with stannous chloride gives the same compound as reaction of quinone II with sodium bisulfite. Its IR spectrum (Fig. 1) lacks the carbonyl vibration band, in alkaline solution, like anthraquinoxadiazole, it gives a blue color, while acetic anhydride converts it to a diacetyl derivative, so that it is the hydroquinone III corresponding to quinone IV.

The IR spectra of quinoxadiazoles II, IV, and V (Fig. 1) closely resemble the spectrum of anthraquinone. Bands connected with heterocyclic ring vibrations, and lying in the range 1610–1450 cm^{-1} [6], are overlapped by the more intense bands of the aromatic rings of the anthraquinone. Introduction of a sulfonic acid group into molecule II, results in rise of carbonyl group vibration frequency, particular with V, to appearance of a band in the range 1636–1620 cm^{-1}, evidently connected with disturbance of aromatic rings, and also intense sulfonic acid group bands in the regions 1240–1210 and 1080–1070 cm^{-1}. Due to superposition of sulfonic acid group vibrations and OH deformation vibrations, the spectra of III and IX are found to exhibit one wide intense band at 1200–1300 cm^{-1}.

*For Part II see [1].

Anthra[1, 2-c][1, 2, 5]oxadiazole-6, 11-dione-4-sulfonic acid (IV) in its turn rapidly adds a molecule of bisulfite on heating with sodium bisulfite solution. The IR spectrum of the resultant "bisulfite compound" lacks the carbonyl group band (Fig. 1), while its electronic spectrum differs from that of the starting quinonesulfonic acid by the appearance of an absorption maximum in the visible region, near 410 mμ (Fig. 3). Such peculiarities poorly accord with the formula of a product of addition of bisulfite to one of the carbonyl groups of the quinone IV. Such a structure is also wholly contradicted by the stability to alkalies, quite unusual for bisulfite compounds of ketones and quinones; the compound withstands boiling in sodium hydroxide solution. It is decomposed by mineral acids, but neither sulfurous acid, nor the starting quinonesulfonic acid IV is thereby formed, instead the product is the hydroquinonesulfonic acid III. Controls showed that under similar conditions the quinonesulfonic acid is not reduced by the amount of sulfurous acid which can be split off from the "bisulfite compound," and that hydroquinonesulfonic acid III does not react with sodium bisulfite. It must also be considered that the product of addition of bisulfite to quinonesulfonic acid IV is decomposed in acid solution with immediate formation of sulfurous acid and hydroquinonesulfonic acid III, so that the compound in question is the monosulfuric ester of the latter, i.e. it is IX. Such a structure fully explains the stability of the compound to alkali, and the lack of CO group vibration bands in the IR spectra, as well as other properties.

The correctness of the assumption is confirmed by formation of sulfuric acid diester when hydroquinonesulfonic acid III, and compound IX are treated with chlorosulfonic acid in pyridine. The diester X fluoresces strongly in ultraviolet light, and its electronic spectra closely resembles that of the diacetyl derivative of sulfonic acid III (Fig. 3). Heating diester X with aqueous mineral acid gives hydroquinonesulfonic acid III, but at 20° C only one ester group is hydrolyzed, and compound IX results, identical in properties, IR, and UV spectra with that obtained from quinonesulfonic acid IV and bisulfite. Thus it can be taken as proved that the compound IX is the monoester of 6, 11-dihydroxyanthra[1, 2-c][1, 2, 5]oxadiazole-4-sulfonic acid.

Anthra[1, 2-c][1, 2, 5]oxadiazole-6, 11-dione-5-sulfonic acid (V) reacts just as easily as sulfonic acid IV with sodium bisulfite. It is unexpectedly found that this reaction did not give compound XI, but monoester IX; acid hydrolysis gave the quinonesulfonic acid III, and oxidation gave quinonoxadiazole-4-sulfonic acid IV. Obviously treatment of quinone-5-sulfonic acid with sodium bisulfite leads to its conversion to sulfonic acid IV, evidently through simultaneous addition-splitting out of a bisulfite molecule. The resultant quinonesulfonic acid IV reacts further with bisulfite, giving sulfuric acid monoester IX.

Addition of a nucleophilic reagent, sodium bisulfite, to oxygen of a carbonyl group is unusual. As far as can be seen, the literature does not describe any case of formation of sulfuric esters by reaction of bisulfite with carbonyl compounds. In this connection the transformations of anthra[1, 2-c][1, 2, 5]oxadiazole-6, 11-dione and its derivatives merit further study.

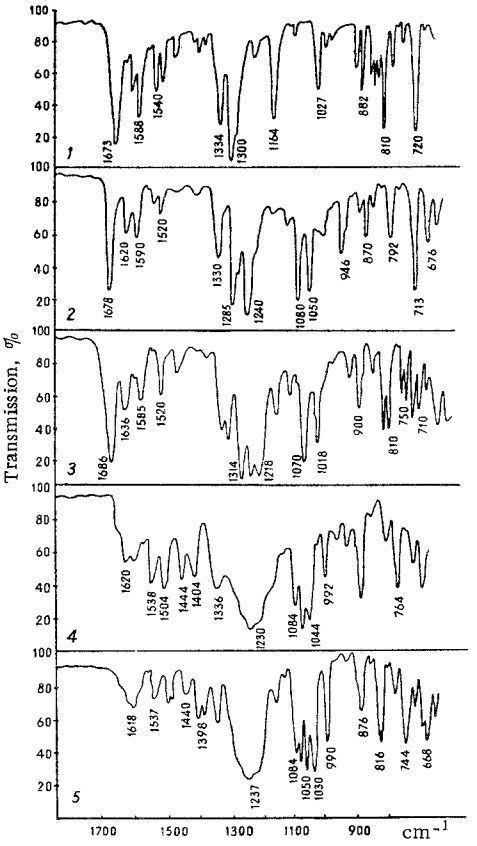


Fig. 1. IR spectra (tabletted with KBr). 1) Anthra[1,2-c][1,2,5]oxadiazole-6, 11-dione (II); 2) anthra[1,2-c][1,2,5]oxadizole-6, 11-dione-4-sulfonic acid (IV); 3) anthra[1,2-c][1,2,5]oxadiazole-6, 11-dione-5-sulfonic acid (V); 4) 6, 11-dihydroxyanthra[1,2-c][1,2,5]oxadiazole-4-sulfonic acid (III); 5) sulfuric acid monoester of 6,11-dihydroxyanthra[1,2-c][1,2,5]oxadiazole-4-sulfonic acid (IX).

The question of to which oxygen atom of quinone IV the bisulfite group adds is so far an open one though the position indicated in formula IX seems more likely.

EXPERIMENT

6, 11-Dihydroxyanthra[1, 2-c][1, 2, 5]oxadiazole-4-sulfonic acid (III). a) A suspension of 5 g (0.02 mole) quinone II in a mixture of 50 ml water, 29 ml 5 M $NaHSO_3$, and 1 ml pyridine, were refluxed together for 2 hr, under N. After cooling, crystals of Na salt III were filtered off, washed with NaCl solution, then with EtOH, and finally with ether, yield 6.50 g (87%, somewhat less in the presence of air). The

compound is stable in the crystalline state, but its aqueous solutions darken on heating, and on adding NaOH turn blue or violet, blue flocs separating later.

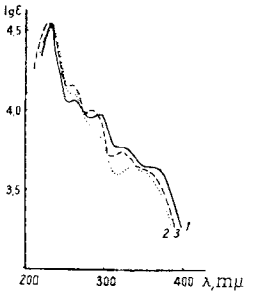


Fig. 2. UV spectra. 1) Anthra[1,2-c][1,2,5]oxadiazole-6,11-dione-4-sulfonic acid (IV) (in water); 2) Anthra[1,2-c][1,2,5]oxadiazole-6,11-dione-5-sulfonic acid (V) (in water); 3) Anthra-[1,2-c][1,2,5]oxadiazole-6,11-dione (II) (in EtOH).

b) A solution of 1 g Na salt IV in 50 ml water was boiled for a few minutes after adding 3 g $SnCl_2$ in 5 ml concentrated acid. Addition of NaCl gave 0.82 g Na salt III. Yellow needles, (ex aqueous EtOH containing $SnCl_2$). Found: C 45.37; 45.06; H 2.71; 2.85; N 7.71; 7.72; Na 6.22; 6.29; H_2O 4.64% (vacuum-dried at 110° C, over P_2O_5). Calculated for $C_{14}H_7N_2O_8SNa \cdot H_2O$: C 45.17; H 2.42; N 7.53; Na 6.18; H_2O 4.84%.

6,11-Diacetoxyanthra[1,2-c][1,2,5]oxadiazole-4-sulfonic acid. A solution of 3.72 g (0.01 mole) Na salt III in a mixture of 40 ml Ac_2O and 50 ml dimethylformamide was heated to boiling, and evaporated under vacuum to small volume, yield 3.52 g (80%). Minute colorless needles. Found: Na 5.33; 5.41%. Calculated for $C_{18}H_{11}N_2O_8SNa$: Na 5.25%.

S-Benzylthiuronium salt. Colorless elongated plates, mp 238° C (decomp, ex 50% EtOH). Specimens of S-benzylthiuronium salt obtained from III and by hydrolyzing monoester IX, gave an undepressed mixed mp. Found: C 53.92; 54.00; H 3.85; 4.05; S 10.80; 10.76%. Calculated for $C_{26}H_{22}N_4O_8S_2$: C 53.62; H 3.78; S 11.01%.

Anthra[1,2-c][1,2,5]oxadiazole-6,11-dione-4-sulfonic acid (IV). 5 ml Concentrated HCl and 4 ml 30% $NaNO_2$ solution were added to a suspension of 3.72 g (0.01 mole) sodium salt III in 100 ml water, the whole heated to boiling, and 20 ml saturated NaCl solution added, yield of Na salt IV 3.66 g (96%). Rhombic or hexahedral pale yellow plates, (ex water), very slightly soluble in alcohol. Addition of sodium hydroxide to a solution of the compound gave a brown color, then a green amorphous precipitate separated. Found: C 45.18; 44.91; H 2.02; 2.17; N 7.50; 7.43; S 8.52; 8.38; H_2O 4.97; 4.48% (dried at 100° C). Calculated for $C_{14}H_5N_2O_6SNa \cdot H_2O$: C 45.41; H 1.89; N 7.57; S 8.66; H_2O 4.87%. Sulfonyl chloride: long pale-yellow plates, mp 224°–225° C (ex benzene–n-hexane). Found: Cl 10.35; 10.22; N 8.19; 8.16%. Calculated for $C_{14}H_5ClN_2O_5S$: Cl 10.18; N 8.03%.

Anthra[1,2-c][1,2,5]oxadiazole-6,11-dione-5-sulfonic acid (V). A solution of 8 g (0.026 mole) $Na_2Cr_2O_7$ in 30 ml water was added to a solution of 7.00 g (0.02 mole) Na salt VI [5] in 100 ml water containing 10 ml concentrated H_2SO_4, the whole stirred for 20 min at 80° C, and 15 Na_2SO_4 added. The precipitate was filtered off, and recrystallized from water. Yield 4.05 g (52%), elongated prisms Na salt V, giving a violet-red solution with alkalies, from which blue flocs separated. Found: N 7.11; 7.13; S 8.12; 7.98; H_2O 9.07% (dried at 120° C). Calculated for $C_{14}H_5N_2O_6SNa \cdot 2H_2O$: N 7.22; S 8.26; H_2O 9.27%. Sulfonyl chloride, yellow rhombic prisms, mp 179°–180° C (decomp, ex benzene–n-hexane). Found: Cl 9.92; 9.98; N 7.75; 7.95%. Calculated for $C_{14}H_5ClN_2O_5S$: Cl 10.18; N 8.03%.

4-Chloroanthra[1,2-c][1,2,5]oxadiazole-6,11-dione (VII). 40 ml saturated $NaClO_3$ was added, over a period of 5 hr, to a boiling solution of 3.70 g (0.01 mole) Na salt IV in 100 ml water and 10 ml concentrated HCl. Yield of quinone VII 2.62 g (92%). Long yellow needles, soluble in alcohols, and benzene, more soluble in dioxane and $CHCl_3$, mp 246.7°–247° C (ex AcOH). Found: Cl 12.45; 12.46%. Calculated for $C_{14}H_5ClN_2O$: Cl 12.46%.

6,11-Dihydroxyanthra[1,2-c][1,2,5]oxadiazole. A solution of 1.25 g (0.005 mole) quinone II in 20 ml AcOH was mixed with a solution of 4 g (0.018 mole) $SnCl_2$ in 5 ml concentrated HCl, and boiled for 5 min.

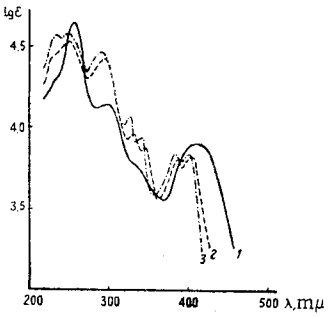


Fig. 3. UV spectra (in water). 1) Sulfuric monoester of 6,11-dihydroxy[1,2-][1,2,5]anthraoxadiazole-4-sulfonic acid (IX); 2) sulfuric acid diester of 6,11-dihydroxyanthra[1,2-c][1,2,5]-oxadiazole-4-sulfonic acid (X); 3) 6,11-diacetoxyanthra[1,2-c][1,2,5]-oxadiazole-4-sulfonic acid.

After cooling the precipitate was filtered off and washed. Yellow needles, giving a blue color with aqueous alkalies, mp 182° C (ex AcOH). Found: C

66.89; 66.99; H 3.36; 3.40; N 11.13; 11.40%. Calculated for $C_{14}H_8N_2O_2$: C 66.68; H 3.20; N 11.11%. Diacetyl derivative, colorless needles mp 255° C (ex AcOH). Found: N 8.33; 8.47%. Calculated for $C_{18}H_{12}N_2O_5$: N 8.33%.

4-Chloro-6, 11-dihydroxyanthra[1, 2-c][1, 2, 5]-oxadiazole. This was prepared similarly to 6, 11-dihydroxyanthraoxadiazole, and its properties were similar. Orange-yellow needles, mp 204°–205° C. Found: C 58.66; 58.88; H 2.53; 2.45; Cl 12.27; 12.26%. Calculated for $C_{14}H_7ClN_2O_3$: C 58.64; H 2.44; Cl 12.38%.

3-Chloro-1, 2-diaminoanthraquinone (VIII). A mixture of 0.3 g (0.001 mole) 4-chloro-6, 11-dihydroxyanthraoxadiazole, 50 ml water, 3 g (0.014 mole) Na hydrosulfite, and 4 ml 30% NaOH was stirred for 20 min at 60° C, when the color turned from bluish-violet to yellowish-red. Air was passed through the cold mixture for 1 hr, the precipitate filtered off, and recrystallized from chlorobenzene. Yield 0.16 g (55%) golden-brown prisms VIII mp 307°–308° C. For comparison the diamine VIII was prepared from 1-bromo-3-chloro-2-aminoanthraquinone, similarly to 3-bromo-1, 2-diaminoanthraquinone [7], mp 307.5°–308.5° C; undepressed mixed mp. Found: Cl 13.05; 12.93; N 10.08; 10.30%. Calculated for $C_{14}H_{10}ClN_2O_2$: Cl 13.03; N 10.28%.

Sulfuric acid monoester of 6, 11-dihydroxyanthra-[1, 2-c][1, 2, 5]oxadiazole-4-sulfonic acid (IX). a) A mixture of 3.70 g (0.01 mole) Na salt IV, 3 ml 4.5 M $NaHSO_3$ and 2 ml water was refluxed for 5–10 min until the solid completely dissolved, then 10 ml saturated solution of NaCl was added. After 12 hr the precipitate which formed (3.52 g) was separated off, and recrystallized from aqueous EtOH. Yield 2.35 g (44.4%) Na salt IX. The bulked filtrates were acidified with HCl, $NaNO_2$ added, the mixture boiled for a few minutes, and cooled. 1.50 g (about 40%) of the starting Na salt IV was obtained.

Na salt IX formed straw-yellow needles, very readily soluble in water, and insoluble in EtOH. It gave a bottle-green color with $FeCl_3$ solution, was completely resistant to boiling with 1 N NaOH, and could be recovered as the orange trisodium salt by adding EtOH.

b) 0.01 mole Na salt V was treated with $NaHSO_3$, as described for IV. Crystallization from water gave 2.46 g (46.5%) compound, identical in properties, IR and UV spectra, with that obtained by method a). Boiling with aqueous HCl converted it to the hydroxyquinonesulfonic acid III (yield 85%), identified as the S-benzylthiuronium salt of the diacetyl derivative. Treatment with HCl and $NaNO_2$ converted the compound to a quinonesulfonic acid, giving a sulfonyl chloride (mp 223.5°–225° C) whose mp was undepressed by a mixture with the sulfonyl chloride from IV.

c) A solution of 0.5 g Na salt X in 2 ml N HCl was kept at 20° for 5 days, until a test portion of the solution, diluted with EtOH, no longer fluoresced blue in UV light. The solution was filtered, and EtOH added, to precipitate a compound which was recrystallized a few times from aqueous EtOH. The properties, IR and UV spectra of the compound were identical with those of that obtained by method a). Found: Na 8.56; N_2O 14.20% (dried at 110° C). Calculated for $C_{14}H_6N_2O_9S_2Na_2 \cdot 4H_2O$: Na 8.71; H_2O 13.63%. After drying at 100° C. Found: C 36.52; 36.67; H 1.61; 1.78; N 6.16; 6.19; S 14.23%. Calculated for $C_{14}H_6N_2O_9S_2Na_2$: C 36.84; H 1.31; N 6.13; S 14.06%.

Sulfuric diester of 6, 11-dihydroxyanthra[1, 2-c]-[1, 2, 5]oxadiazole-5-sulfonic acid (X). 1 g dried Na salt III or IX was added to a mixture of 14 ml pyridine and 1 ml chlorosulfonic acid at 40° C. The resultant orange solution was held at 50° C for 30 min, and then poured into 50 ml 5% NaOAc. The pyridine and water were vacuum-distilled off until a solid began to separate; this was then filtered off, and recrystallized from aqueous EtOH. Both routes gave a compound with the same chemical and spectroscopic properties. Pale yellow needles, slightly soluble in water, and dimethylformamide, insoluble in EtOH and most organic solvents. On boiling with dilute HCl, the Na salt III separated. Found: C 30.11; 30.11; H 1.12; 1.23; N 5.05; 5.33; S 17.33; 17.58%. Calculated for $C_{14}H_5N_2O_{12}S_3Na_3$: C 30.11; H 0.90; N 5.02; S 17.23%.

The UV spectra were determined with a SF-4 instrument, using solutions which were 10^{-4} and $0.25 \cdot 10^{-4}$ M; the IR spectra were determined with an IKS-14 spectrometer, tabletting with KBr. The authors thank B. E. Zaitsev for assistance in determining and analyzing the IR spectra.

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