RESEARCHES ON QUINONES

II. Reaction of Anthra[1, 2-c][1, 2, 5]Selenadiazole-6, 11-Dione With Amines*

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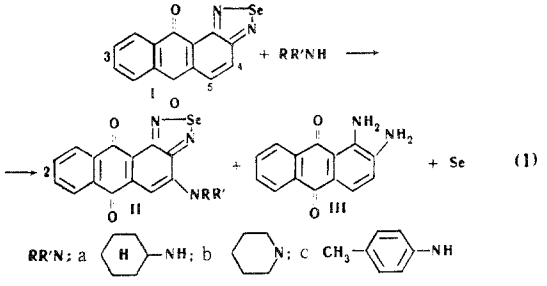
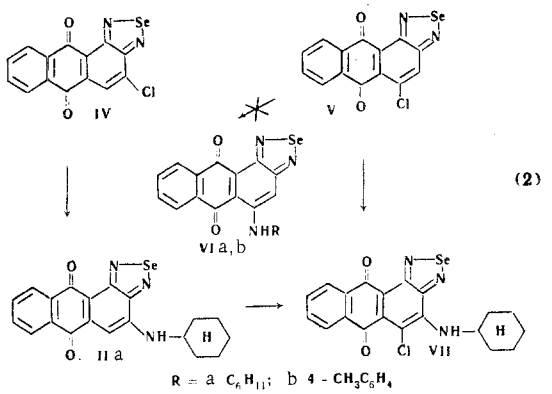
When anthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione is heated with primary and secondary amines, a hydrogen atom at position 4 is replaced by an amino group, and part of the starting quinone, functioning as an oxidizing agent, forms 1, 2-diaminoanthraquinone, with separation of elemental selenium. 5-Chloroanthra[1, 2-c][1, 2, 5]-anthraselenadiazole-6, 11-dione reacts similarly, but with the 4-chloro derivative, the chlorine atom is replaced. The corresponding 5-amino derivatives of anthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione, synthesized for comparison, are anomalously deeply colored. The enhanced reactivity of anthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione, due to the mutual effects of the hetero ring and the quinone group, since neither anthra [1, 2-c][1, 2, 5]selenadiazole nor anthraquinone undergo reaction under similar circumstances.

Anthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione (I) was previously prepared by S. V. Bogdanov and the present author, by treating 1, 2-diaminoanthraquinone with selenium dioxide, and by chromic acid oxidation of anthra[1, 2-c][1, 2, 5]selenadiazole [2].

Continuing this work it was shown that quinone I reacts readily with primary and secondary amines, e.g. cyclohexylamine, piperidine, p-toluidine, etc. Thus boiling pale-yellow quinone I with cyclohexylamine for a short time gives a mixture of deeply-colored reaction products, the main one of which is cyclohexylaminoanthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione (IIa). In addition to the amino derivative IIa (yield 62–63%), 25–27% 1, 2-diaminoanthraquinone (III) and over 30% selenium were isolated. Reaction with aromatic amines is considerably slower, but can be accelerated by adding copper salts. Heating quinone I with p-toluidine at 150° C, in the presence of copper acetate, gives the p-toluidino derivative IIc.



The ratios of the compounds isolated make it possible to draw certain conclusions regarding the nature of the reaction. Probably there is initially addition of amine to the anthraquinoneselenadiazole I, followed by oxidation of the resultant adduct by the starting quinone, which is thereby reduced, mainly to 1, 2-diaminoanthraquinone, with separation of elemental selenium. In that case, as equation 1 indicates, two thirds of the quinoneselenadiazole I are converted into amino derivative II, and one third to 1, 2-diaminoanthraquinone (III), in agreement with the amounts found experimentally.



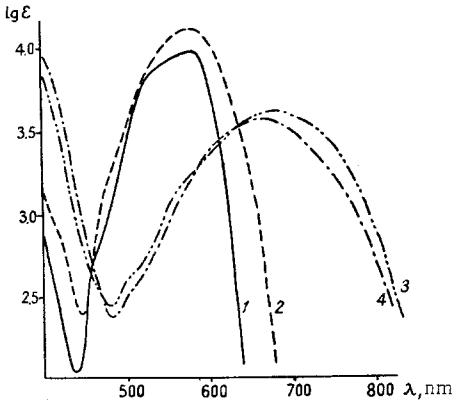
To determine where the amino group enters the molecule I, the reaction of cyclohexylamine with 4- and 5-chloroanthraquinoeselenadiazoles (IV and V) was investigated. These latter compounds were prepared from, respectively, 3- and 4-chloro-1, 2-diaminoanthraquinone.

Halogen at the α position in anthraquinone is known to be more mobile than that at the β position. In its turn the selenadiazole ring, because of its electrophilic character, facilitates nucleophilic replacement of halogen, in the case of benzoselenadiazole, at position 5 in particular [2]. Hence it would be expected that chlorine in compound V would be more easily exchanged for the cyclohexylamino group, than that in compound IV. Actually however it is only the chlorine of derivative IV which is replaced, to give an 84% yield of the same compound, IIa, as is obtained from the unsubstituted quinone I. In the case of the 5-chloro derivative what takes place is not replacement of chlorine and formation of VIa, but nucleophilic addition followed by oxidation, in accordance with equation 1, to give compound VII, identical with the product obtained by chlorinating IIa with sulfuryl chloride. Hence in the reactions of quinones I, IV, and V, the amino group enters the ring at one and the same position, viz. position 4.

5-Amino derivatives of anthraquinoneselenadiazole (VIa, b) are synthesized by a roundabout method: action of the appropriate amine on 4-chloro-1, 2-diaminoanthraquinone, followed by treatment with selenium dioxide. They are bluish-green, absorbing

*For Part I see [1].

over a wide region of the spectrum, with a maximum at about 680 nm, distinctly different from that (see fig.) of the violet 4-amino derivatives IIa (λmax 580 nm). The much deeper color of 5-amino substituted compounds VI compared with red α-alkylamino- and α-arylaminoanthraquinones, indicates the considerable effect of the selenadiazole ring on the π electron system of the anthraquinone.



Absorption spectra in chloroform. 1) 4-Cyclohexylaminoanthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione (IIa); 2) 4-(p-toluidino)anthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione (IIc); 3) 5-cyclohexylaminoanthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione (VIa); 4) 5-(p-toluidino)-anthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione (VIb).

The unusual reactivity of anthra[1, 2-c][1, 2, 5]-selenadiazole-6, 11-dione compared with the amines is evidently due to reciprocal interaction between heterocyclic ring and quinone group, since neither anthraquinone nor anthra[1, 2-c][1, 2, 5]selendiazole is appreciably altered under the conditions of conversion of quinone I.

EXPERIMENTAL

4- and 5-Chloroanthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione (IV and V). A solution of 2.72 g (0.01 mole) 3- or 4-chloro-1, 2-diaminoanthraquinone in 40 ml dimethylformamide was mixed, at 100° C, with a solution of 2 g (0.018 mole) SeO_2 in 10 ml water, and the whole boiled for 2–3 min. The selenadiazoles were obtained in almost quantitative yield. Pale yellow needles (ex benzene trichloride), slightly soluble in organic solvents. **Quinone IV:** mp 346°–347° C. Found: C 48.32; 48.42; H 1.18; 1.39; Cl 10.53; 10.41; N 8.20; 8.25%. Calculated for $C_{14}H_5ClN_2O_2Se$: C 48.38; H 1.44; Cl 10.20; N 8.06%. **Quinone VI:** mp 309.5°–310° C. Found: C 48.39; 48.57; H 1.46; 1.42; Cl 10.28; 10.37; N 8.14; 8.00%. Calculated for $C_{14}H_5ClN_2O_2Se$: C 48.38; H 1.44; Cl 10.20; N 8.06%.

4-Cyclohexylaminoanthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione (IIa). a) A mixture of 1.566 g (0.005 mole) I and 16 ml dicyclohexylamine was refluxed for 3 min, and poured into dilute HCl. The reaction product (1.89 g) was separated off, dried, and dissolved in $CHCl_3$, the insoluble residue being washed with hot acetone. This residue, 0.134 g (43%) was the yellow crystalline modification of Se. After oxidizing it with HNO_3 and reacting the product with o-phenylenediamine, benzoselenadiazole mp 75.4°–75.8° C, was obtained (the literature [4] gives mp 76°). A $CHCl_3$ solution was chromatographed on alumina (For Chromatography, Activity II), when elution of the red band with acetone gave 0.320 g (27%) 1, 2-diaminoanthraquinone, brown prisms, mp 297°–298° C (ex chlorobenzene) (the literature [5] gives mp 301° C). Elution of the blue band with pyridine led to the isolation of 1.292 g (63%) amino derivative IIa, forming bluish-red hexahedral plates (ex chlorobenzene), or violet-blue needles (ex aqueous pyridine), mp 273.4°–273.7° C; $\nu_{C=O}$ 1680 cm^{-1}, ν_{N-H} 3390 cm^{-1}. Found: C 58.34; 58.53; H 4.15; 4.10; N 10.10; 10.29%. Calculated for $C_{20}H_{17}N_3O_2Se$: C 58.52; H 4.17; N 10.24%.

b) 1.738 g (0.005 mole) VI was refluxed for 5 min with 16 ml cyclohexylamine. The base obtained by pouring into dilute HCl was worked up in the way described in a) above. Neither Se nor diaminoanthraquinone was found. Pyridine eluted 1.724 g (84%) compound IIa, undepressed mixed mp with a specimen prepared as in a) above, and with an identical IR spectrum.

4-Piperidinanthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione (IIb). This compound was synthesized similarly to IIa, by refluxing 0.002 mole selenadiazole I in 5 ml piperidine. Solution of the reaction products in $CHCl_3$ led to the separation of 0.050 g Se. Chromatographing on alumina gave 0.057 g 1, 2-diaminoanthraquinone and 0.548 g amino derivative IIb, elongated plates and prisms, mp 243° C (decomp, ex dioxane). Found: N 10.66; 10.59%. Calculated for $C_{19}H_{15}N_3O_2Se$: N 10.85%.

4-(p-Toluidin)anthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione (IIc). A mixture of 0.005 mole selenadiazole I, 15 g p-toluidine, and 0.2 g $Cu(OAc)_2$ was heated at 150° C for 3 hr. The p-toluidine was washed out with dilute HCl, and the product recrystallized from trichlorobenzene. 0.16 g insoluble yellow precipitate was obtained, consisting mainly of Se, and 0.96 g chromatographically pure compound IIc, violet needles, mp 313°–314° C (decomb, ex chlorobenzene). Found: N 9.86; 9.91%. Calculated for $C_{21}H_{13}N_3O_2Se$: N 10.04%.

5-Chloro-4-cyclohexylaminoanthra[1, 2-c][1, 2, 5]-selenadiazole-6, 11-dione (VI). a) 0.869 g (0.0025 mole) V was boiled for 5 min with 8 ml cyclohexylamine, and the product worked up as described for IIa. 0.057 g (29%) Se was isolated. Acetone elution of the red band gave 0.158 g (23%) 4-chloro-1, 2-diaminoanthraquinone, converted by SeO_2 to the selenadiazole V. Acetone elution of the second, blue band, gave 0.154 g VI. Bluish-violet minute needles, mp 239° C (decomp, ex chlorobenzene). MeOH eluted a further 0.125 g material, apparently a mixture of amine derivatives IIa and VI.

b) 0.16 g SO_2Cl_2 was added to a boiling solution of 0.41 g IIa in 30 ml $CHCl_3$. A chromatographic check showed chlorination to be complete in a few minutes. The precipitate was filtered off, washed with EtOH and water, dried, and recrystallized from chloro-

benzene. Yield 0.28 g bluish-violet needles, mp 40° C (decomp), undepressed mixed mp with a specimen prepared as in a) above, and having the same IR spectrum. Found: C 54.33; 54.31; H 3.51; 3.71; Cl 17.69; 17.86; N 9.49; 9.60%. Calculated for $C_{20}H_{16}ClN_3O_2Se$: C 54.01; H 3.38; Cl 17.99; N 9.45%.

4-Cyclohexylamino-1, 2-diaminoanthraquinone (VIIIa). A mixture of 2.73 g (0.01 mole) 4-chloro-1,-2-diaminoanthraquinone, 35 g cyclohexylamine, 1.5 g fused KOAc, and 0.15 g $Cu(OAc)_2$ was refluxed for 5 hr, cooled, and poured into dilute HCl. The solid (3.25 g) was filtered off, dissolved in $CHCl_3$, and chromatographed on alumina, eluant $CHCl_3$ (blue band). Yield 1.08 g brown prisms, mp 227°–229° C (ex $CHCl_3$). Found: C 71.68; 71.66; H 6.35; 6.54; N 12.32; 12.29%. Calculated for $C_{20}H_{21}N_3O_2$: C 71.60; H 6.27; N 12.53%.

4-(p-Toluidino-1, 2-diaminoanthraquinone (VIIIb). Prepared similarly to the above, at 140°–150°. Chromatographic purification gave 1.58 g bluish-violet minute prisms, mp about 210° C (decomp, ex benzene-n-hexane). Found: C 73.25; 72.97; H 5.11; 5.25; N 12.12; 12.23%. Calculated for $C_{12}H_{17}N_3O_2$: C 73.43; H 4.99; N 12.24%.

5-Cyclohexylamino- and 5-(p-toluidin)anthra[1, 2-c][1, 2, 5]selenadiazole-6, 11-dione (VIa, b). A solution of 0.4 g (0.0036 mole) SeO_2 in 2 ml water was poured into a suspension of 0.001 mole VIIIa or VIIIb in 14 ml AcOH. On heating to boiling, the color of the solution rapidly changed from violet to greenish-blue. After cooling, crystals of V were filtered off and recrystallized from benzene–n-hexane, yield 70–75%. The compounds formed dark green prisms, forming greenish-blue solutions in benzene and $CHCl_3$, in which they were readily soluble, or in EtOH and AcOH, in which they were slightly soluble.

Compound VIa. Mp about 195° C (decomp). Found: C 58.63; 58.60; H 4.10; 4.05; N 9.95; 10.06%. Calculated for $C_{20}H_{17}N_3O_2Se$: C 58.52; H 4.17; N 10.24%.

Compound VIb. Mp about 232° C (decomp). Found: C 59.93; 60.05; H 3.29; 3.20; N 9.96%. Calculated for $C_{21}H_{13}N_3O_2Se$: C 60.29; H 3.13; N 10.04%.

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