STUDIES ON QUINONES

IX. Chlorination of Anthraquinoneoxa-, -Thia-, and -Selenadiazoles*

M. V. Gorelik, S. B. Lantsman, and T. P. Kononova

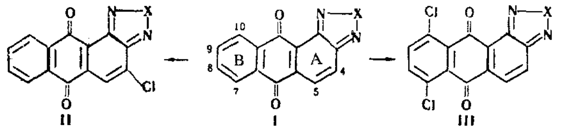
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 5, pp. 808–811, 1968

UDC 547.673'547.794.3

Anthra[1,2-c]-[1,2,5]-oxa-, -thia-, and -selenadiazole-6,11-diones (I) chlorinate in acetic acid in position 4, giving the 4-chloroanthraquinonediazoles (II) and in sulfuric acid or oleum in the benzene ring remote from the heterocycle with the formation of the 7,10-dichloro derivatives III.

As reported in previous communications [1–4], the reaction of anthraquinonediazoles (I) with nucleophilic agents bears an anomalous character. It was of interest to study the behavior of the anthraquinonediaazoles under the conditions of electropilic substitution reactions.

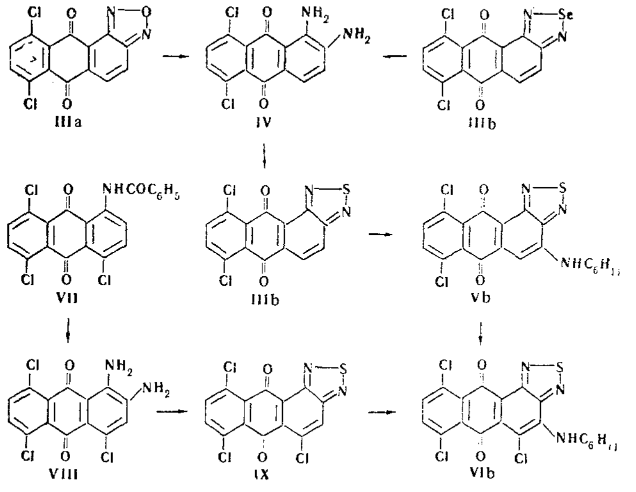
It is known [5] that the 1,2,5-oxa-, -thia-, and -selenadiazole rings lower the electron density in a benzene ring condensed with them, particularly in positions 5 and 6. It was to be expected that in the quinonediazoles I ring A, adjacent to the heterocycle, would be deactivated to a greater extent by the influence of the heterocycle than the remote ring B. However, on chlorination in boiling acetic acid in the presence of ferric chloride, under conditions in which anthraquinone itself does not react, the anthraquinonediazoles were smoothly converted into the 4-chloro derivatives II. The structure of the latter was confirmed by comparison with the quinonediazoles synthesized from 1,2-diamino-3-chloroanthraquinone (IIb, c) [2, 4] and anthraquinoneoxadiazole-4-sulfonic acid (IIa) [3].



a X = O; b X = S; c X = Se

In sulfuric acid or oleum, where the protonation of the nitrogen atom greatly increases the electron-accepting influence of the heterocycle, substitution in the presence of iodine as catalyst takes place predominantly in the α-position of the ring remote from the heterocycle, giving high yields of the dichloro derivatives III.

The entry of the chlorine into the same positions in the case of the oxa-, thia-, and selenadiazoles (Ia–c) is shown by the reduction of IIIa with hydrosulfite and the opening of the selenadiazole ring in IIIc by the action of caustic soda [7] with the formation of a 1,2-diaminodichloroanthraquinone (IV) which was converted into the thiadiazole (IIIb) on being heated with thionyl chloride. The fact that the chlorine atoms in III are present in the benzene ring remote from the heterocycle is shown by the capacity of the quinones IIIa and IIIb for being converted, without displacement of substituents, into the 4-cyclohexylamine derivatives V on treatment with cyclohexylamine and of then undergoing chlorination in position 5 with sulfuryl chloride with the formation of the trichloro derivatives VI. The direction of these reactions in the positions of the anthraquinonediazole nucleus stated has been established previously [1, 2, 4]. Since under the same conditions anthraquinone chlorinates in the α-position, it appeared likely that compounds III have the structure of 7,10-dichloro derivatives. For proof, we performed the independent synthesis of 4-cyclohexylamino-5,7,10-trichloroanthra[1, 2-c]-[1, 2, 5]-thiadiazole-6, 11-dione (IVb) starting from 1-benzoylamino-4, 5, 8-trichloroanthraquinone (VII) [8]. By nitration in concentrated nitric acid with subsequent hydrolysis of the acyl group and reduction with sodium sulfide we obtained 1,2-diamino-4,5,8-trichloroanthraquinone (VIII) the cyclohexylamine led to compound VIb, identical with that obtained from the product of the chlorination of IIIb.

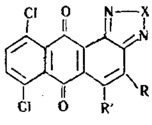


EXPERIMENTAL

4-Chloro-anthra[1,2-c]-[1, 2, 5]-X-diazole-6,11-diones (II). To a boiling solution of 0.01 mole of Ia in 80 ml of acetic acid was added 0.3 g of ground iron turnings or ferric chloride, and chlorine was passed in for 8 hr at the rate of ~150 ml/min, after which the hot solution was filtered and diluted with water. The yellow precipitate was separated off, washed with water, dried, filtered in the form of chloroform solution through a layer of alumina, and crystallized from acetic acid. This gave 2.31 g (81%) of IIa, mp 246.5°–247° C; mixture with a sample synthesized from anthraquinoneoxadiazole-4-sulfonic acid [3], mp 246.5°–246.8° C.

---

*For part VIII, see [9].



Compound	X	R	R′	Mp, °C	Empirical formula	Found, %				Calculated, %			
						C	H	N	Cl	C	H	N	Cl
IIIa	O	H	H	250.5—251	$C_{14}H_4Cl_2N_2O_3$	52.53 52.59	1.50 1.37	8.98 8.65	21.96 22.15	52.67	1.26	8.78	22.21
IIIb	S	H	H	299—300	$C_{14}H_4Cl_2N_2O_2S$	50.41 50.38	1.12 1.18	8.47 8.60	21.24 21.33	50.17	1.20	8.36	21.15
IIIc	Se	H	H	327—328 (decomp.)	$C_{14}H_4Cl_2N_2O_2Se$	—	—	7.30 7.42	18.38 18.24	—	—	7.33	18.56
Va	O	NHC_6H_{11}	H	232.5—233	$C_{20}H_{15}Cl_2N_3O_3$	57.78 57.93	3.78 3.67	10.02 9.87	16.99 16.90	57.69	3.63	10.09	17.03
Vb	S	NHC_6H_{11}	H	270—271	$C_{20}H_{15}Cl_2N_3O_2S$	55.80	3.55	9.71 9.73	16.24	55.55	3.50	9.72	16.40
VIa	O	NHC_6H_{11}	Cl	230—230,5	$C_{20}H_{14}Cl_3N_3O_3$	—	—	9.14 9.29	23.46 23.28	—	—	9.32	23.59
VIb	S	NHC_6H_{11}	Cl	222—223	$C_{20}H_{14}Cl_3N_3O_2S$	51.15 51.21	3.08 3.06	8.88 8.84	23.03 22.89	51.45	3.02	9.00	22.78
IX	S	H	Cl	298—299	$C_{14}H_3Cl_3N_2O_2S$	45.74 45.70	0.71 0.80	7.64 7.80	28.98 29.11	45.48	0.82	7.58	28.77

Similarly, but using larger amounts of acetic acid, the 4-chloro derivatives IIb and IIc were obtained with mp 284°–285° C and 346°–347° C, respectively (yields 60–65%); they gave no depression of the melting point in admixture with sample prepared from 1,2-diamino-3-chloroanthraquinone [2,4] and were identical with them in their properties and IR spectra.

7,10-Dichloroanthra[1,2-c]-[1,2,5]-X-diazole-6,11-diones (III). Chlorine was passed into a solution of 0.01 mole of I and 0.06 g of iodine in 30 ml of 3% oleum at 40° C for 3–4 hr, after which the reaction mixture was poured onto ice. The precipitate was separated off, filtered in the form of a solution in dioxane through a layer of alumina and crystallized from acetic acid. The yield of III was 83–87% (table).

7,10-Dichloro-4-cyclohexylaminoanthra[1,2-c]-[1,2,5]-oxa- and -thiadiazole-6,11-diones (Va,b). To a solution of 0.002 mole of IIIa or b in dimethylformamide at 20° C was added 4.8 ml (0.04 mole) of cyclohexylamine, and after 15 hr the solution was poured into dilute hydrochloric acid. The precipitate was filtered off, washed, dried, and chromatographed on alumina, the violet-red band being eluted with chloroform or benzene. Red needles, from dioxane. Yield 75–83% (table).

5,7,10-Trichloro-4-cyclohexylaminoanthra[1,2-c]-[1,2,5]-oxa- and -thiadiazole-6,11-diones (VIa,b). a) The cyclohexylamine derivatives Va and b were chlorinated with sulfuryl chloride in chloroform under the conditions described previously [1,4]. Red needles (from aqueous dioxane) (table).

b) The thiazole IX was treated with cyclohexylamine as shown above for compounds IIIa and b. After chromatography in benzene on alumina and crystallization, a substance was isolated which was identical from its IR and UV spectra with that obtained by method (a), mp 222°–223° C; a mixture of the substances gave no depression of the melting point.

1,2-Diamino-5,8-dichloroanthraquinone (IV). a) A mixture of 3.06 g (0.008 mole) of IIIc, 100 ml of dioxane, 65 ml of water, and 5 ml of 40% caustic soda solution was boiled for 2 hr and diluted with 200 ml of water. The precipitate (2.4 g) was filtered off, washed with water, and dried. Elongated prisms (from chlorobenzene) mp 274°–275° C (decomp.). When 0.005 mole of IV was heated with 0.03 mole of thionyl chloride in dioxane [4], after chromatography on alumina in chloroform solution a 64% yield was obtained of a yellow substance with mp 299°–300° C, giving no depression of the melting point in admixture with the IIIb obtained by the chlorination of the anthraquinonethiadiazole Ib.

b) A solution of 4 g of sodium hydrosulfite in 20 ml of water was added to a suspension of 0.638 g (0.002 mole) of IIIa in 90 ml of 4% caustic soda solution at 50° C. After the mixture had been stirred for 20 minutes at the same temperature, it was cooled and air was passed through it until it was decolorized. The precipitate was separated off, washed with water, dried, and chromatographed on alumina, the violet band being eluted with a mixture of chlorobenzene and pyridine (8:1). After crystallization from chlorobenzene, a substance was obtained with mp 275° C (decomp.). showing no depression of the melting point in admixture with the sample obtained by method (a). Found, %: Cl 22.91, 22.70; N 9.10, 9.28. Calculated for $C_{14}H_8Cl_2N_2O_2$, %: Cl 23.09; N 9.12.

1-Amino-4,5,8-trichloro-2-nitroanthraquinone. A solution of 2.15 g (0.005 mole) of VII [8] in 5 ml of 96% nitric acid was stirred at 20° C for 1 hr 30 min and poured into ice water. The yellow precipitate (2.50 g) was filtered off, washed with water, dried, and heated in 20 ml of concentrated sulfuric acid at 95° C for 1 hr. Then 11 ml of water was added at a temperature not exceeding 10° C, and the precipitate was separated off and treated with hot water. This yielded 1.45 g (78%) of the nitro compound. Orange-red plates (from chlorobenzene), mp 317°–318° C. Found, %: C 45.34, 45.44; H 1.39, 1.51; Cl 28.64, 28.34; N 7.37, 7.29. Calculated for $C_{14}H_5Cl_3N_2O_4$, %: C 45.25; H 1.36; Cl 28.63; N 7.54.

1,2-Diamino-4,5,8-trichloroanthraquinone (VIII). A mixture of 1.86 g (0.005 mole) of 1-amino-4,5,8-trichloro-2-nitroanthraquinone, 30 ml of water, and 4.8 g of sodium sulfide was heated in the boiling water bath for 1 hr. The precipitate (1.43 g) was filtered off, washed with hot water, and dried. For analysis, the product was chromatographed on alumina and eluted with a mixture of chlorobenzene and pyridine. Elongated prisms (from chlorobenzene), mp 294°–295° C (decomp.). Found, %: C 49.35, 49.34; H 2.05, 1.99; Cl 30.91, 30.79; N 7.95, 7.85. Calculated for $C_{14}H_7Cl_3N_2O_2$, %: C 49.28; H 2.07; Cl 31.13; N 8.10.

The action of thionyl chloride [4] on VIII gave a 70% yield of 5,7,10-trichloroanthra[1,2-c]-[1,2,5]-thiadiazole-6,11-dione (IX) (table).

REFERENCES

1. M. V. Gorelik, T. P. Kononova, and N. S. Dokunikhin, KhGS [Chemistry of Heterocyclic Compounds], 4, 463, 1968.

2. M. V. Gorelik, KhGS [Chemistry of Heterocyclic Compounds], 3, 541, 1967.

3. M. V. Gorelik, T. P. Kononova, and N. S. Dokunikhin, KhGS [Chemistry of Heterocyclic Compounds], 3, 545, 1967.

4. M. V. Gorelik and S. B. Lantsman, KhGS [Chemistry of Heterocyclic Compounds], 4, 453, 1968.

5. L. S. Efros, Usp. khim., 29, 162, 1960.
6. E. Sawicki and A. Carr, J. Org. Chem., 22, 503, 1957.
7. M. V. Gorelik, V. V. Puchkova, and I. Ya. Koshcheeva, Authors' Certificate 184878, 1966; Byull. izobr., 16, 1966.
8. H. Volmann, W. Hohmann, and F. Baumann, German Federal Republic Patent 1154490, 1963; C. A., 60, 4283, 1964.
9. M. V. Gorelik, B. E. Zaitsev, T. P. Kononova, and N. S. Dokunikhin, KhGS [Chemistry of Heterocyclic Compounds], 4, 780, 1968.

18 July 1966

Scientific-Research Institute
for Organic Intermediates
and Dyes, Moscow