INVESTIGATION OF QUINONES

XXVI.* PREPARATION OF INDANTHRONE DERIVATIVES BY NUCLEOPHILIC ADDITION TO ANTHRAQUINONAZINE

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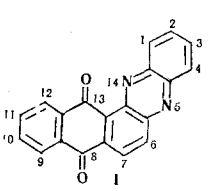
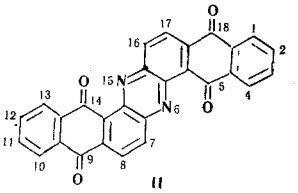
The addition of hydrogen halides, sulfinic acids, and mercaptans to dinaphtho[2,3-a : 2,3-h]-phenazine-5,9,14,18-tetraone (anthraquinonazine) leads to the corresponding 7-substituted indanthrones. Subsequent oxidation and treatment of these products with nucleophilic agents make it possible to obtain 7,16-disubstituted indanthrones that contain both identical and different substituents.

In [1, 2], it was demonstrated that the anthraquinone ring of naphtho[2,3-a]phenazine-8,13-dione (I) undergoes attack at the closest-to-the-heteroring β position (6 position) in the reaction of I with nucleophilic agents. Acid catalysis caused by protonation of the nitrogen atom in the 14 position to form an intramolecular hydrogen bond plays a decisive role in this reaction The formation of the intramolecular hydrogen bond intensifies the coordinated electron-acceptor effect of the peri-situated nitrogen and oxygen atoms and thereby promotes nucleophilic attack. The same effect should be displayed in the protonated dinaphtho-[2,3-a : 2,3-h]phenazine-5,9,14,18-tetraone (II) (anthraquinonazine) molecule, of which I is a structural fragment. The energetic favorability of H-chelate formation during protonation of anthraquinonazine II is a consequence of the presence of a very strong intramolecular hydrogen bond in indanthrone (III) [3].



I



II

Anthraquinonazine II is readily formed by the oxidation of indanthrone III with nitric acid. Scholl, who first obtained this compound [4], noted its ability to add hydrogen chloride, ammonia, and aniline and, in analogy with phenazine, assigned the 8-chloro- and 8-aminoindanthrone structures [4, 6] to the resulting products. However, considering the properties of naphthophenazinedione I that we studied, it might have been expected that the nucleophilic agent would have entered the β-position of the anthraquinone ring of azine II to form 7-substituted indanthrones. The similarity of the dichloro derivative, obtained by the addition of hydrogen chloride, to 7,16-dichloroindanthrone was established in [7] in a comparison of the various haloindanthrones, but unambiguous proof was not presented.

The difficulties in carrying out reactions of anthraquinonazine are caused by its extremely low solubility in organic solvents. It was necessary to carry out the reaction with hydrogen chloride by heating anthraquinonazine with hydrochloric acid for many hours in sealed tubes. We found that 70-80% phosphoric acid, in which the reaction of anthraquinonazine with nucleophilic agents proceeds very rapidly, even on slight heating, can be successfully used as a reaction medium.

*See [2] for communication XXV.

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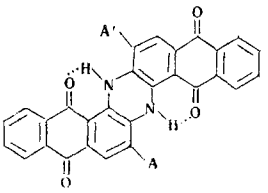
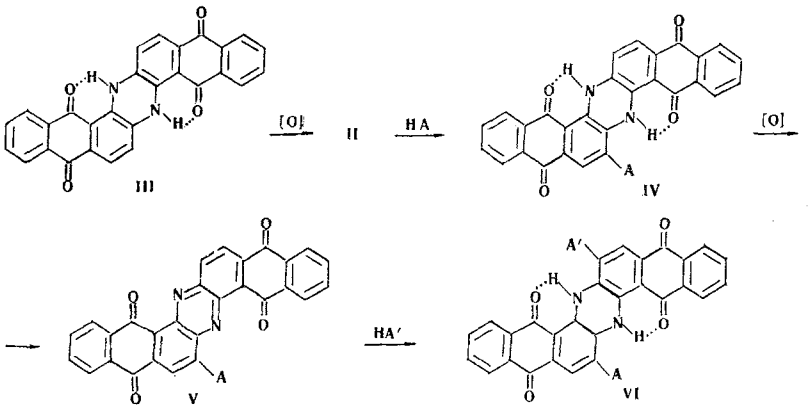
TABLE 1. Indanthrone Derivatives



Compound			Empirical formula	Found, %				Calc., %				Yield, %
№	A	A′		Br	Cl	N	S	Br	Cl	N	S	
IVa	Cl	H	$C_{28}H_{13}ClN_2O_4$	—	7,35 7,21	6,08 5,97	—	—	7,43	5,88	—	96
IVb	Br	H	$C_{28}H_{13}BrN_2O_4$	15,03 15,40	—	5,34 5,12	—	15,33	—	5,37	—	96
IVc	$SO_2C_6H_5$	H	$C_{34}H_{18}N_2O_6S$	—	—	4,91 5,07	5,63 5,70	—	—	4,80	5,50	90
IVd	SC_6H_5	H	$C_{34}H_{18}N_2O_4S$	—	—	5,29 5,36	5,73 5,87	—	—	5,08	5,82	70
VIa	$SO_2C_6H_5$	$SO_2C_6H_5$	$C_{34}H_{22}N_2O_8S_2$	—	—	3,71 3,61	8,73 8,65	—	—	3,87	8,87	88
VIb	$SO_2C_6H_5$	Cl	$C_{34}H_{17}ClN_2O_6S$	—	5,88 5,80	4,34 4,60	4,81 4,93	—	5,74	4,54	5,19	94 92
VIc	SCH_2COOH	Cl	$C_{30}H_{15}ClN_2O_6S$	—	6,13 6,21	4,87 4,69	5,47 5,58	—	6,25	4,94	5,65	57
VId	$SO_2C_6H_5$	SC_6H_5	$C_{40}H_{22}N_2O_6S_2$	—	—	4,21 4,17	9,13 9,07	—	—	4,05	9,28	68
VIe	Cl	Br	$C_{28}H_{12}BrClN_2O_4$	14,12 14,18	6,15 6,33	5,07 5,10	—	14,38	6,37	5,04	—	86 90
VIf	Cl	Cl	$C_{28}H_{12}Cl_2N_2O_4$	—	13,40 13,68	5,65 5,67	—	—	13,87	5,47	—	92

* From chloroanthraquinonazine (V, A = Cl).

Monosubstituted indanthrones (IV) are formed in high yields by the reaction of anthraquinonazine II with sulfinic acids, mercaptans, and hydrogen chloride or bromide. Oxidation of IV with nitric acid gives substituted azines (V), which in turn add nucleophilic agents and are converted to disubstituted indanthrones (VI).



The position of the sulfonyl groupings was proved by alternative synthesis of diphenylsulfonyl derivative VIa (see Table 1) from 1-bromo-3-phenylsulfonyl-2-aminoanthraquinone. The conversion of phenylmercaptoindanthrone IVd by hydrogen peroxide oxidation to sulfone IVc, which is identical to the compound obtained by the reaction of anthraquinonazine II with benzenesulfinic acid, is evidence for the position of the sulfide groups. The position of the halogen atoms was proved by the coincidence of the IR spectra of dichloro derivative VIf and 7,16-dichloroindanthrone obtained from 2-amino-3-chloroanthraquinone. Consequently, the nucleophilic agent residue enters the 7(16)-position of the anthraquinonazine molecule in all cases.

It is interesting that the nucleophilic addition to anthraquinonazine proceeds more readily than nucleophilic substitution of labile substituents such as halogen or an arylsulfonyl group. Thus the treatment of 7-chloroanthraquinonazine with benzensulfinic or thiogycolic acid does not result in displacement of chlorine but leads to incorporation of a sulfonyl or sulfide grouping in the 16 position to form disubstituted indanthrones VIb and VIc, respectively (see Table 1). Compound VIb was also obtained by the action of hydrogen

chloride on phenylsulfonylanthraquinonazine (V, A = $C_6H_5SO_2$). The reaction of the latter with thiophenol leads to unsymmetrical derivative VId, the structure of which was confirmed by hydrogen peroxide oxidation to diphenylsulfonylindanthrone VIa. The same chlorobromo derivative (VIe) is formed by the action of both hydrogen chloride on 7-bromoanthraquinonazine (V, A = Br) and of hydrogen bromide on 7-chloroanthraquinonazine (V, A = Cl).

Thus the addition of nucleophilic agents to anthraquinonazine makes it possible to obtain not only monosubstituted indanthrones but also disubstituted indanthrones that contain different substituents. These sorts of compounds cannot be synthesized by other known methods and therefore were not accessible until now. Since compounds of the indanthrone series find broad application as dyes and pigments, the reaction may apparently be of practical significance.

EXPERIMENTAL

7-Substituted Indanthrones (IV). A 0.01-mole quantity of sodium benzenesulfinate, thiophenol, thioglycolic acid or (at 110-115°C) 0.03 mole of sodium chloride or bromide was added at 70°C to a suspension of 2.20 g (0.005 mole) of anthraquinonazine II in 70 ml of 74% phosphoric acid. After 2-3 min, the mixture was cooled and diluted with water, and the appropriate 7-substituted indanthrone (IVa-d, see Table 1) separated as dark-blue needles (from quinoline). Addition of 3 ml of 30% hydrogen peroxide at 70°C to a suspension of 0.5 g of sulfide IVd and 20 ml of phosphoric acid give 71% of the phenylsulfonyl derivative, which was identical (from the IR spectrum) to IVc obtained by the reaction of azine II with benzenesulfinic acid, IR spectrum (cm^{-1}): 720 strong (s), 735 medium (m), 755 m, 850 m, 1030 s, 1050 weak (w), 1070 m, 1093 m, 1115 w, 1160 s, 1195 m, 1270 s, 1335 m, 1350 m, 1490 s, 1593 m, 1668 s, and 3070 w.

7,16-Disubstituted Indanthrones (VI). A total of 0.9 ml (0.008 mole) of 58% nitric acid was added at 0°C to a solution of 0.002 mole of substituted indanthrone IVa, b in 20 ml of sulfuric acid, and, after 30 min, ice was added until a yellow-brown precipitate of the azine formed. In the oxidation of phenylsulfonyl derivative IVc, the solution obtained after the mixture had stood for 90 min was poured into 70 ml of acetic acid and diluted with water. The reaction of substituted azines V with nucleophilic agents was carried out as described for azine II to obtain disubstituted indanthrones VI (see Table 1). The product of the reaction of the 7-phenylsulfonyl-substituted azine (V, A = $C_6H_5SO_2$) with benzenesulfinic acid was identical (with respect to the IR spectrum) to indanthrone derivative VIa, synthesized from 1-bromo-3-phenylsulfonyl-2-aminoanthraquinone in the same way as bis(n-butylsulfonyl)indanthrone [8]. IR spectrum (cm^{-1}): 720 s, 732 m, 745 m, 760 m, 772 w, 850 w, 880 w, 970 m, 1035 m, 1063 m, 1090 m, 1155 w, 1275 w, 1335 m, 1357 w, 1454 m, 1495 w, 1570 w, 1600 w, 1640 m (shoulder), 1685 s, and 3070 w. The same compound (VIa) was obtained by treatment of derivative VId with hydrogen peroxide in phosphoric acid. The product of the reaction of chloroanthraquinonazine (V, A = Cl) with hydrogen chloride was identical (with respect to the IR spectra) to dichloroindanthrone VIf obtained from 1-bromo-3-chloro-2-aminoanthraquinone [9]. IR spectrum: 715 s, 755 m, 842 w, 920 w, 963 w, 1035 m, 1062 m, 1165 w, 1280 s, 1330 w, 1350 s, 1495 s, 1587 m, 1645 m, 1670 s, and 3080 w cm^{-1}. Compounds VIb and VIe were synthesized, respectively, by the addition of sulfinic acid or hydrogen bromide to chloroanthraquinonazine (V, A = Cl) and by the addition of hydrogen chloride to phenylsulfonylanthraquinonazine (V, A = $SO_2C_6H_5$) or to bromoanthraquinonazine (V, A = Br). The IR spectra of the substances obtained by one or another path coincided. IR spectrum of VIb (cm^{-1}): 720 s, 755 m, 845 m, 950 w, 1032 m, 1065 m, 1095 m, 1160 s, 1195 s, 1195 w, 1225 w, 1275 s, 1332 s, 1350 m, 1490 s, 1595 m, 1668 s, 3070 w. IR spectrum of VIe (cm^{-1}): 720 s, 755 m, 840 w, 950 w, 1033 m, 1062 m, 1165 w, 1270 s, 1330 m, 1350 m, 1490 s, 1585 m, 1595 m, 1640 w (shoulder), 1665 s, 3080 w.

3-Phenylsulfonyl-2-aminoanthraquinone. A mixture of 5.15 g (0.02 mole) of 3-chloro-2-aminoanthraquinone, 12 g (0.06 mole) of sodium benzenesulfinate, and 4.2 g (0.03 mole) of anhydrous potassium carbonate in 100 ml of dimethylformamide was refluxed for 6-7 h and filtered. The hot filtrate was diluted with water until it became turbid and was then cooled to give 4.36 g of a dark-yellow precipitate, which was chromatographed on anhydrous aluminum oxide in 6% pyridine in chlorobenzene to give 3.87 g (53%) of yellow prisms (from chlorobenzene) of 3-phenylsulfonyl-2-aminoanthraquinone with mp 210-211°C (sublimation). Found: N 3.95; 3.70; S 8.67; 8.94%. $C_{20}H_{13}NO_4S$. Calculated: N 3.85; S 8.82%.

1-Bromo-3-phenylsulfonyl-2-aminoanthraquinone. A 1.45-g (0.004 mole) sample of 3-phenylsulfonyl-2-aminoanthraquinone was dissolved in 7 ml of concentrated sulfuric acid, and the solution was poured into 40 ml of water. Bromine [1 ml (~0.02 mole)] was poured into the suspension at 10°C, and the mixture was stirred at 25°C for 1.5 h, heated to 75°C, and a solution of 2.45 g (0.02 mole) of potassium chlorate in 32 ml of water was added in the course of 2 h. A solution of sodium sulfite was then added, and the resulting pre-

cipitate was separated and dissolved in chloroform. The chloroform solution was passed through a layer of anhydrous aluminum oxide and crystallized from acetic acid to give small, yellow needles with mp 263-264.5°C. Found: Br 18.17; 18.28; N 3.07; 3.09; S 7.12; 7.26%. $C_{20}H_{12}BrNO_4S$. Calculated: Br 18.07; N 3.17; S 7.25%.

The IR spectra of KBr pellets were measured with a UR-10 spectrometer.

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