Anal. Calcd. for $C_{12}H_8O_3NCl$: Cl, 14.20; N, 5.61. Found: Cl, 13.70; N, 5.73.

3,5-Dichloro-4'-nitro-4-hydroxydiphenyl.—Two grams of 3,5-dichloro-4-hydroxydiphenyl (b. p. 188.7° at 5 mm.) was dissolved in 10 cc. of acetic acid, and 5 cc. of acetic acid containing one molar proportion of nitric acid was added to the solution over a period of several hours. The long thin needles which formed by the conclusion of the nitration were filtered. Evaporation of the filtrate to dryness even at room temperature left only a tarry mass. Recrystallization of the first crystalline fraction from carbon tetrachloride yielded only 6.5% of the desired product of m. p. 214–215° corr. A mixed melting point with the isomeric phenol of m. p. 191° gave 170°.

Anal. Calcd. for $C_{12}H_7O_3NCl_2$: Cl, 24.97; N, 4.93. Found: Cl, 25.15; N, 5.28.

Chlorination of 4-Hydroxydiphenyl Using Acetic Acid as Solvent.—Chlorine gas was bubbled through solutions of 20-g. portions of 4-hydroxydiphenyl dissolved in 300 cc. of glacial acetic acid. The yields after thirty minutes, one and one-half hours, two and one-half hours, four hours and five hours were, respectively: 95% recovery of starting material, 38% yield of monochloro derivative, 25% yield of dichloro, 10% yield of trichloro and 12.5% yield of trichloro-4-hydroxydiphenyl. It was not found possible to isolate other products than those named.

Ten grams of 4-hydroxydiphenyl was dissolved in 150 cc. of acetic acid and chlorine gas bubbled through the solution for ten hours. A red solution formed and when the evaporation of excess acetic acid was attempted a deep red oil settled to the bottom. After two days evaporation at room temperature well-developed, colorless crystals formed in the oil. When treated with acetone the oil dissolved leaving crystals behind. A second crop of crystals separated from the oil which remained when the acetone was removed from the mother liquor by evaporation. The first and second crystal fractions melted at 142–145°. Soluble in hot acetone, in carbon tetrachloride and in alcohol but insoluble in mineral acids and in alkali with which a black, gummy oil was formed.

Anal. Calcd. for $C_{12}H_3OCl_7$: Cl, 60.36. Found: Cl, 59.43.

Two more crops of crystals separated from the red oil remaining from the preparation already described. The m. p. of the last two fractions was 115–118°. A mixed melting point with the supposed heptachloro derivative gave 115° or a drop of about 30° from the higher melting point. The analysis for chlorine indicated that the pentachloro derivative was contaminated by a small percentage of the heptachloro compound. This substance like the heptachloro is insoluble in alkali.

Anal. Calcd. for $C_{12}H_5OCl_5$: Cl, 51.87. Found: Cl, 52.87.

Derivatives of the Phenols Mentioned in this Paper.—A large number of derivatives of the chloro and nitro phenols already mentioned were obtained in connection with this work. Since the methods used are either self evident or will be found by reference to the preceding paper,[5] this portion of the investigation has been summarized in the table.

Summary

1. The orientation of chlorine atoms in mono and dichloro-4-hydroxydiphenyl has been partially substantiated by the preparation of isomeric dichloronitro derivatives of 4-hydroxydiphenyl.
2. Penta- and heptachloro derivatives of 4-hydroxydiphenyl are described. Investigation into the structure of these polychlorinated hydroxydiphenyls is proceeding in this Laboratory.
3. Numerous new derivatives of 4-hydroxydiphenyl have been reported.

[5] Colbert and others, THIS JOURNAL, **56**, 202 (1934).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

The Photolysis of Halogenated Anthrahydroquinones

BY ALBERT E. GOLDSTEIN WITH JOHN H. GARDNER

It was observed by Weber[1] that when textiles which had been dipped in solutions of the leuco vats of certain halogen-containing anthraquinone and indigoid dyes were exposed to sunlight before oxidation, the resulting dyes were off-color. He regarded this as due to a dehalogenation since the color produced in each case corresponded to that of the corresponding halogen-free dye. Assuming Weber's explanation to be correct, this suggests a method for the removal of halogen from compounds of the anthraquinone series. The results of this investigation show that this method is practical in a number of cases and give some idea of the relation between the position of the halogen and its rate of removal. The compounds studied were 1- and 2-chloro-, 1- and 2-bromo and 1-chloro-4-hydroxyanthraquinone.

Preliminary experiments on solutions of 1-chloroanthrahydroquinone using a small mercury arc lamp with quartz and glass vessels indicated that the effect is due to visible light rather than to ultraviolet. Consequently, the mercury arc was replaced with an Eastman "Floodlight" (500-watt) to provide an intense source of white light. Solutions of the anthrahydroquinones in

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[1] Weber, *Dyestuffs*, **33**, 1 (1933).

alkaline sodium hydrosulfite were exposed to the light for varying periods of time, with exclusion of air. The anthrahydroquinones were oxidized to the corresponding anthraquinones with air and the amount of dehalogenation calculated from the halogen content of the crude product. The final product from each of the halogenoanthraquinones was identified as anthraquinone and that from 1-chloro-4-hydroxyanthraquinone, as α-hydroxyanthraquinone.

It was found that an α-halogen is much more readily removed by this method than a β-halogen, and bromine more readily than chlorine. Since the temperature of the illuminated solutions rose to 60–65°, a solution of 1-chloroanthrahydroquinone was heated at that temperature for twelve hours. No dehalogenation was detected.

Experimental

General Procedure.—To 0.15 g. of the halogenoanthraquinone moistened with a little alcohol there was added 100 cc. of 20% sodium hydroxide and the mixture was heated on the steam-bath. The minimum amount of solid sodium hydrosulfite required to reduce the anthraquinone was added and the solution was placed in a Pyrex flask provided with a Bunsen valve to exclude air. The flask was supported 10 cm. from a 500-watt "Floodlight" lamp provided with a reflector and was exposed for the desired length of time. The anthrahydroquinone was then oxidized with air and the crude product filtered out. In the case of the products from 1-chloro-4-hydroxyanthrahydroquinone, the solution was saturated with carbon dioxide after oxidation. The crude products were analyzed for halogen and were purified by crystallization and, in some cases, sublimation. The results are given in Table I.

TABLE I

Anthraquinone	Exposure, hours	% Halogen	% Unchanged	M. p., °C., purified product
1-Chloro-	0.0	14.70 Cl	100	
	0.5	3.97	27.2	
	1.0	1.13	7.7	285.5[a]
	1.5	0.85	5.8	
	3.0	0.26	1.8	
2-Chloro-	0.0	14.69 Cl	100	
	14	0.84	5.7	284–285[a]
	16	0.66	4.5	
	20	0.52	3.6	
1-Bromo-	0.0	27.73 Br	100	
	0.25	1.94	7.0	285–286[a]
	0.5	0.51	1.9	
	1.0	0.36	1.3	
2-Bromo-	0.0	27.72 Br	100	
	1.0	1.01	3.6	285–286[a]
	2.0	0.89	3.2	
	4.0	0.64	2.3	
1-Chloro-4-hydroxy-	0.0	13.68 Cl	100	
	4	1.18	8.6	195–196[b]
	5	0.85	6.2	

[a] Mixed m. p. with anthraquinone (m. p. 285–285.5°) gave no depression.

[b] Mixed m. p. with α-hydroxyanthraquinone (m. p. 199–199.5°), 199–199.5°. Acetate, m. p. 183.5–184°, no depression with acetate of α-hydroxyanthraquinone, same m. p.

Summary

1. A method has been developed for the removal of halogen atoms from substituted anthraquinones by the photolysis of the sodium salts of their corresponding anthrahydroquinones.

2. A preliminary study has been made of the scope of applicability of the method.

3. The relationship between velocity of dehalogenation and the position of the halogen in the anthraquinone molecule, and also the kind of halogen atom, has been investigated.

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