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PHOTO-NUCLEOPHILIC SUBSTITUTION REACTION OF HALOGENOANTHRAQUINONE IN CONCENTRATED SULFURIC ACID
PHOTO-HYDROXYDEHALOGENATION

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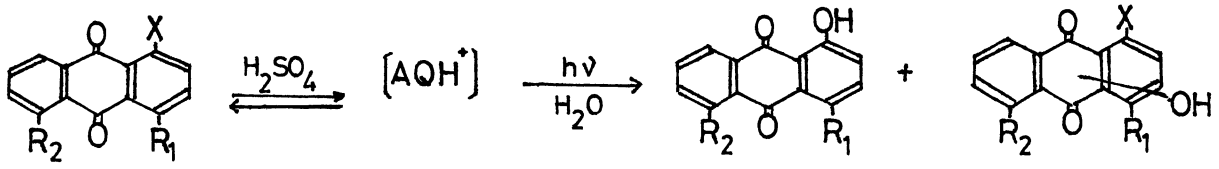
The photo-reaction of halogen-substituted anthraquinones in sulfuric acid was studied with near UV or visible light. α-Chloro-substituted anthraquinones were photo-hydroxylated mainly to form α-hydroxyanthraquinones in fairly good yields. However, β-halogeno-anthraquinones gave no dehalogenated products under the same conditions.

It is well-known that halogenoanthraquinones, methoxyanthraquinones, and anthraquinonesulfonic acid derivatives undergo photochemical substitution reactions with ammonia or amines under the basic conditions.$^{1)}$ Mihai and co-workers recentl reported that anthraquinone in sulfuric acid was photo-hydroxylated to form 2-hydroxyanthraquinone.$^{2)}$ We now report a new result that the chlorine atom of α-chloroanthraquinone derivatives is predominantly replaced by the hydroxyl group in concentrated sulfuric acid by irradiation.

Typically 1-chloroanthraquinone (1a) (1.3×10^{-3}M) dissolved in 97% sulfuric acid was irradiated in a Pyrex tube with a 400W high-pressure mercury lamp for 100h The resulting deep red solution was poured onto crushed ice. The photo-products were extracted with a mixture of benzene and ethyl acetate and analyzed by HPLC.$^{3)}$



AQ (1) (2) (3α + 3β)

a) X = Cl, $R_1 = R_2$ = H b) X = R_1 = Cl, R_2 = H c) X = R_2 = Cl, R_1 = H

The photo-reactions of chloroanthraquinones (1a∼1c) afforded mainly hydroxy-dechlorinated products (2), accompanying minor hydroxydeprotonated products, the α-hydroxy (3α) and the β-hydroxy isomers (3β).$^{4)}$ However, 2-chloroanthraquinone (4) and 2-bromoanthraquinone (5) gave no dehalogenated product as shown in the Table. No dark reaction was observed under the same conditions. Photo-products and their derivatives methylated with dimethyl sulfate were identified either by comparison with authentic samples or by NMR and IR spectra.$^{5)}$

As shown in the Figure, the decrease in acidity function (Ho) led to the increase in the yield of dechlorinated hydroxyanthraquinone as well as the increase in mole fraction of AQH^+, two lines becoming parallel in the case of 1c. Therefore, the photo-substitution reactions in the concentrated sulfuric acid must have proceeded through a protonated anthraquinone.

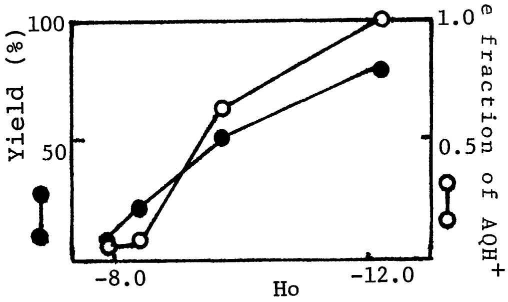
Table Photo-reactions of halogenoanthraquinones

AQ	Yield(%)[a)] 2	$3\alpha + 3\beta$[b)]	NMR ($CDCl_3$)[c)] δ	IR (KBr)[c)] ν(C=O) cm^{-1}
1-Cl	62.2	15.7	12.60(1H), 8.30(2H), 7.75(4H), 7.36(1H)[d)]	1680, 1640
1,4-DiCl	61.8	26.3	13.00(1H), 8.07(2H), 7.55(3H), 7.04(1H)[e)]	1669, 1636
1,5-DiCl	72.7	14.2	12.10(1H), 8.17(1H), 7.53(4H), 7.08(1H)[f)]	1679, 1640
2-Cl	0[g)]	71.5[h)]		
2-Br	0[g)]	67.1[h)]		

a) The yields based on halogenoanthraquinones reacted. b) 3a included the isomers hydroxylated at the 4-, 5-, 6-(or 7-), and 8-positions of 1-chloroanthraquinone; the product distributions were 27, 14, 56, and 3%, respectively. The product distributions from 1b$\sim$5 could not be completely determined because it was difficult to resolve their isomers by HPLC. c) Compound 2. d) *dd, J=8, 2 Hz*. e) *d, J=8.5 Hz*. f) *dd, J=7, 2 Hz*. g) 2-Hydroxyanthraquinone. h) Hydroxy-2-halogenoanthraquinone.

As for attacking species, neither the hydroxy radical nor the sulfate anion radical observed under the basic or neutral conditions[6)] was responsible for these substitution reactions, because only a trace quantity of dechlorinated products was obtained in the reactions of chloroanthraquinones (1a$\sim$1c) with Fenton's reagent and with potassium persulfate-Fe^{2+}.[7)] Therefore, it is considered that water and/or hydrogen sulfate may operate as nucleophiles for this photo-substitution. The results in the Table are also consistent with the fact that halogen atoms, particularly those in the α-position are fairly labile.[8)] The reaction mechanism and scope of the reaction are now under investigation.

Fig. Effects of Ho on yield of 2c and mole fraction of AQH^+



References and Notes

1) M. Hida, et al., *Bull. Chem. Soc. Jpn.*, 46, 1759 (1973); J. Griffiths and C. H. Hawkins, *J. Chem. Soc. Chem. Commun.*, 1973, 111; G. Wubbels, et al., *J. Am. Chem. Soc.*, 95, 3820 (1973).

2) G. G. Mihai, et al., *J. Chem. Soc., Perkin Trans. 1*, 1975, 1374.

3) Column; 15cm Zorbax ODS, eluent; MeOH :H_2O (pH 3) = 80 : 20.

4) 1,6-Dichloro and 1,8-dichloroanthraquinones also gave their hydroxydechlorinated products in 15% and 5% yields, respectively.

5) IR was useful to discriminate intra and intermolecular hydrogen bonding structures in 2, 3α, and 3β. More information about the hydroxylated positions in 2 and 3 was derived from NMR spectra. Ring protons adjacent to the hydroxy or the methoxy group resonated at higher fields than other ring protons did, and showed the characteristic splitting patterns depending on the positions of the substituents, X and R. For examples, isolated main photo-products from 1a showed the following characteristic NMR ($CDCl_3$) and IR (KBr) spectra (hydroxylated position in parentheses). 3a(8-OH); δ 12.27(1H), 8.20(1H), 7.71(4H), 7.28(1H, *dd, J=2, 8 Hz*); ν(C=O) 1639, 1667cm^{-1}. 3a(6-OH or 7-OH); insoluble in $CDCl_3$; ν (C=O) 1676cm^{-1}, ν(OH) 3370cm^{-1}, and the O-methylated derivative; δ 8.25(2H), 7.68(3H), 7.30(1H, *dd, J=2, 8 Hz*), 3.96(3H). 3a(4-OH) and 3a(5-OH) were the same as 2b and 2c, respectively. 2a; see the Table.

6) The product distributions from the reaction of 1a with Fenton's reagent were as follows: 0% (2a), 19% (4-OH), 12% (5-OH), 13% (8-OH), and 56% (3β).

7) A. D. Broadbent and R. P. Newton, *Can. J. Chem.*, 50, 381 (1972); V. A. Kuzmin and A. K. Chibisov, *J. Chem. Soc. Chem. Commun.*, 1971, 1559; C. Walling, et al., *J. Am. Chem. Soc.*, 97, 363 (1975); 100, 4814 (1978).

8) Rodd's Chemistry of Carbon Compounds IIIB, p1390.

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