Photolysis of Halogeno-phenols in Aqueous Alkali and Cyanide[1]

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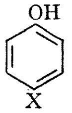
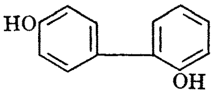
Summary Irradiation of *p*-halogeno-phenols in aqueous alkali gave 2,4′-dihydroxybiphenyl as the major product in addition to the formation of phenol and hydroquinone, whereas irradiation in aqueous cyanide gave *p*-cyanophenol.

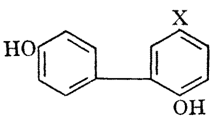
GRABOWSKI[2] has found polarographically that some monohalogeno-phenols in aqueous alkali are hydrolysed photochemically (>3000 Å) to give the corresponding dihydroxybenzenes. Joschek and Miller[3] have shown qualitatively that photolysis (2537 Å) of dilute aqueous solutions of monobromo-phenols yields symmetrical dihydroxybiphenyls as well as dihydroxybenzenes. Both groups of workers interpret the primary photo-process of these reactions as the homolytic fission of a carbon–halogen bond. We have examined the photolysis of monohalogeno-phenols in aqueous alkali (0·087 M) and found that *p*-substituted halogeno-phenols (I) give, in addition to already known products, phenol and the unsymmetrical dihydroxybiphenyls, neither of which has previously been found in this series of reactions. We have also found that the chlorine in *m*-chlorophenol is particularly easily replaced by a hydroxy-group.



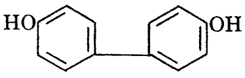
(I) a, X=Cl
b, X=Br
c, X=I



(II)



(III)a, X=Cl
b, X=Br
c, X=I



(IV)

A solution of *p*-chlorophenol (2·25 g.) and KOH (*ca.* 10 g.) in water (200 ml.) was irradiated for 5 hr. with a *ca.* 40 w low-pressure mercury lamp with Vycor housing (2537 Å) under bubbling nitrogen at *ca.* 40°. The products identified are shown in Table 1.[4] Similar irradiations were carried out with *p*-bromo- and *p*-iodo-phenols (Table 1). In addition to the expected products, *p*-bromo- and *p*-iodophenols gave 4,4′-dihydroxybiphenyl (IV), albeit in poor yield, which was found by Joschek *et al.*[3] in the aqueous irradiation of the bromo-derivative. The compound (II) was the major product in every case. The yield of phenol decreases in the order of I > Br > Cl, while that of hydroquinone decreases in the order of Cl > Br > I.

On irradiation of *o*-chlorophenol, large quantity of intractable resinous product was obtained, though *m*-chlorophenol gave resorcinol in good yield. This is consistent with the recent finding by Pinhey *et al.*[6] that the chlorine in *m*-chlorophenol can be replaced with the OR group of alcohols on irradiation.[7]

The halogens in these phenols, especially *p*-halogenophenols, can be replaced by a CN group by irradiation in aqueous cyanide.[8] For example, solution of *p*-chlorophenol (2·23 g.), KOH (0·99 g.), and KCN (11·4 g.) in distilled water (200 ml.) was irradiated with a low-pressure mercury lamp (Vycor) for 5 hr. at 10—20°. The products identified are shown in Table 2.

Similar irradiations were carried out on *p*-bromo-, *p*-iodo-, and *o*- and *m*-chloro-phenols (Table 2). In all cases the *p*-substituted phenols, gave cyanophenol in good yield, accompanied by small amounts of hydroquinone and 2,4′-dihydroxybiphenyl (II). Irradiation of *m*-chlorophenol yielded resorcinol in high yield, accompanied by a small

TABLE 1. *Photolysis of halogeno-phenols in aqueous alkali*

$HO{\cdot}C_6H_4{\cdot}X$	Recov. (%)	Phenol (%)[a]	$HO{\cdot}C_6H_4{\cdot}OH$ (%)[a]	Dihydroxybiphenyls (%)[a]
X = *p*-Cl	45	4·8	27	(II) 28, (IIIa) 6·9, (IV) 0
p-Br	15	11·5	9·0	(II) 23, (IIIb) *ca.* 0, (IV) 1·5
p-I	38	13·1	0	(II 34, (IIIc) *ca.* 0, (IV) 3·2
o-Cl	18	negligible	0	Negligible
m-Cl	30	negligible	74	Mixture of dihydroxybiphenyls, *ca.* 4

[a] Yields were calculated on the basis of the reacted phenol.

TABLE 2. *Photolysis of halogeno-phenols in aqueous cyanide*

$HO{\cdot}C_6H_4{\cdot}X$	KCN (eq.)	Time (hr.)	Recov. (%)	$HO{\cdot}C_6H_4{\cdot}CN$ (%)[a]	$HO{\cdot}C_6H_4{\cdot}OH$ (%)[a]	Dihydroxy-biphenyls (%)[a]
X = *p*-Cl	10	5	64	71	2·3	(II) 7·4
p-Br	10	5	74	68	4·9	(II) 7·2
p-I	20	106	1·9	45	0	(II) 1·0
o-Cl	20	28	trace	0	0	negligible
m-Cl	20	72	1·6	7·5	72	not examined

[a] Yields were calculated on the basis of the reacted phenol.

amount of *m*-cyanophenol. This difference in reactivity between the *p*- and *m*-isomers could be explained by assuming that the excited molecule of *m*-chlorophenol is so reactive towards nucleophilic attack that it can react not only with a hydroxide ion but also possibly with a water molecule. As in the irradiation in aqueous alkali, *o*-chlorophenol gave only a large quantity of resinous product.

p-Chloro-, *p*-bromo-, and *p*-iodo-phenol gave no detectable amount of the corresponding *o*-halogeno- or polyhalogeno-(2,4-di- or 2,4,6-tri-substituted) phenols. It is considered therefore that the halogen is removed from the parent molecule as halide ion rather than atomic halogen. The apparent nucleophilic substitution of a halogen by a cyanide in *p*-halogeno-phenols may shed light on the primary photodissociative processes which have been discussed in terms of the homolytic fission of an aromatic carbon-halogen bond.[2,3]

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[1] Previous paper, K. Ogura and T. Matsuura, to be published.

[2] Z. R. Grabowski, *Z. phys. Chem. (Frankfurt)*, 1961, **27**, 239.

[3] H. I. Joschek and S. I. Miller, *J. Amer. Chem. Soc.*, 1966, **88**, 3269.

[4] The structure of (IIIa) was given by elemental analysis, u.v., n.m.r., and by reduction on Pd–charcoal to give (II).[5]

[5] E. Licke, *J. prakt. Chem.*, 1873, **8**, 43.

[6] J. T. Pinhey and R. D. G. Rigby, *Tetrahedron Letters*, 1969, 1267.

[7] Grabowski (ref. 2) has reported that *o*-chlorophenol can give catechol, while the *m*-isomer does not give resorcinol.

[8] For the photocyanation of an aromatic molecule by a cyanide ion see (*a*) K. W. Rosenmund, K. Luxat, and W. Tiedemann, *Ber.*, 1923, **56**, 1950; (*b*) R. L. Letsinger and J. H. McCain, *J. Amer. Chem. Soc.*, 1966, **88**, 2884.