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NUCLEOPHILIC PHOTO-SUBSTITUTION IN HALOPHENOLS AND HALOANISOLES

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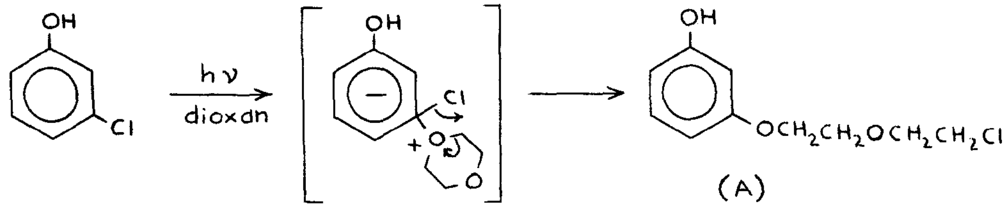
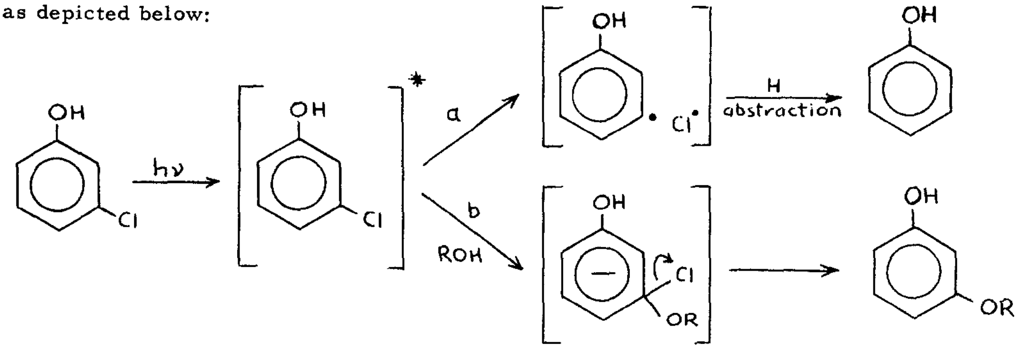
During our preliminary investigation[1] of the photo-reduction of chloro- and bromo-aromatic compounds we found that o- and p-chlorophenols were readily reduced on irradiation in isopropanol, affording phenol in high yield. On attempting to extend this reaction to m-substituted phenols we found that m-chlorophenol gave phenol as a minor product only (see Table for conditions and yields), while the major product was m-isopropoxyphenol. Also produced in very low yield was resorcinol. In view of our previous results[1], the formation of phenol indicated that, at least in part, homolysis of the C-Cl bond was occurring. However, production of m-isopropoxyphenol and resorcinol by an initial homolysis step seemed unlikely, and it appeared that this was another example of aromatic nucleophilic photo-substitution[2,3,4,5]. In support of a nucleophilic substitution mechanism, irradiation of m-chlorophenol in ethanol afforded a considerably higher ratio of substitution product (m-ethoxyphenol) to reduction product.

The high reactivity of m-chlorophenol to nucleophiles is displayed on irradiation in dioxan/water (95:5), which gave phenol as the major product but also yielded 2-(β-chloroethoxy)ethyl m-hydroxyphenyl ether (A; m.p. 40-42°[6]) in considerable amount. A second substitution product, resorcinol, was present as a very minor constituent. The formation of the ether (A) may be visualised as occurring *via* an intermediate of the type shown below, although there are alternative mechanisms which cannot be excluded.



(A)

These results show that, on absorption of light, *m*-chlorophenol is promoted to an excited state which may react by two competing pathways, a) homolysis of the C-Cl bond, or b) substitution of chlorine by a nucleophile. An indication of the nature of the pathway for the latter reaction may be obtained from the photolysis in aqueous dioxan. A comparison of the yields of resorcinol and compound (A) suggests that the excited species formed is a rather indiscriminate electrophile. This is consistent with a bimolecular reaction with the phenol in a short-lived excited state as depicted below:



Alternatively, fission to give $C_6H_4OH^+$ and Cl^- might also explain our results since the aryl cation, because of its high reactivity, would be non-selective in its reactions with nucleophiles.

The behaviour of *m*-bromophenol and *m*-iodophenol (see Table) is in accord with the existence of two reaction paths for the excited phenol. Compared with the reaction

TABLE

All irradiations were performed under nitrogen using a 125-W medium pressure mercury arc in a water cooled quartz well. Unless otherwise stated yields are from g.l.c. on reactions of the compound (4 g) in solvent (670 ml). The yields are corrected for detector response. The reactions were followed by g.l.c. so that the times are approximately those required for complete reaction of starting material.

Compound	Solvent	Time(hr)	Product(s) (Yield)
m-chlorophenol	isopropanol	10.0	*m*-isopropoxyphenol (62%), phenol (19%), resorcinol(2.4%)
m-chlorophenol	ethanol	6.5	*m*-ethoxyphenol (80%), phenol (13.5%)
m-chlorophenol	dioxan/water (95:5)	11.5	phenol (67%), Compound A (30%), resorcinol ($<$ 0.5%)
m-bromophenol	isopropanol	13.0	phenol (73%), *m*-isopropoxyphenol (8.6%), *m*-bromophenol (3%)
m-iodophenol	isopropanol	3.5	phenol (82%)
m-chloroanisole	isopropanol	9.5	anisole (75%), 1-isopropoxy-3-methoxyphenol (9%)
m-chloroanisole	methanol	6.0	anisole (63%), 1,3-dimethoxybenzene (28%)
o-chloroanisole	methanol	11.0	anisole (80%)
p-chloroanisole	methanol	11.0	anisole (60%), 1,4-dimethoxybenzene (14%)

of *m*-chlorophenol, irradiation of *m*-bromophenol in isopropanol showed a very marked increase in the formation of reduction product with a corresponding decrease in the yield of substitution product, while in the case of *m*-iodophenol, the only detectable product was phenol. The increase in the yield of phenol in this series is consistent with the decreasing strength of the carbon-halogen bond, which would be expected to facilitate pathway (a) in the above scheme.

To determine whether the substitution reaction is confined to the phenols we turned next to an ether, m-chloroanisole. Irradiation in isopropanol afforded anisole as the major product, although the yield was lower than for the o- and p-isomers[1]. Also produced in the reaction was 1-isopropoxy-3-methoxybenzene formed in $< 10\%$ yield; however, in methanol the same ether gave a significant amount of 1,3-dimethoxybenzene. A small yield of 1,4-dimethoxybenzene was produced on photolysis of p-chloroanisole in methanol, but no 1,2-dimethoxyanisole could be detected when o-chloroanisole was reacted under the same conditions.

The light-induced replacements of the nitro group of p-nitroanisole by pyridine and hydroxide ion[7,8] appear to be the only photo-substitution reactions reported to date which may be related to those outlined above.

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