Tetrahedron Letters No.16, pp. 1267-1270, 1969. Pergamon Press. Printed in Great Britain.

PHOTO-REDUCTION OF CHLORO- AND BROMO-AROMATIC COMPOUNDS

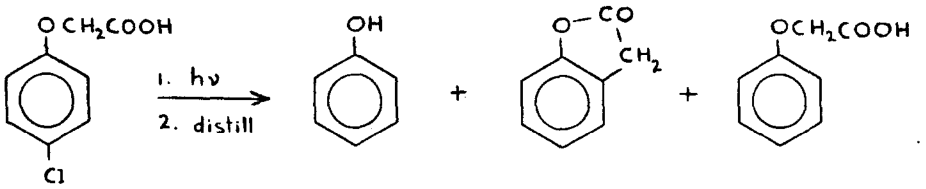
J. T. Pinhey and R. D. G. Rigby

Department of Organic Chemistry, University of Sydney, Sydney, 2006
Australia

(Received in UK 18 February 1969; accepted for publication 4 March 1969)

It is generally accepted[1,2] that the photochemical reactivity of the carbon-halogen bond is directly related to the strength of the bond, and whereas there have been numerous studies of light-induced reactions of iodoaromatic compounds[1] there have been relatively few investigations involving bromoaromatics[1-10], and still less devoted to chloro-aromatics[1,2,4,5,10,16]. The present view, that there is little photochemical cleavage of the C-Cl bond in chlorobenzenes, has been clearly stated in two photochemical reviews[1,11], although a recent communication by Henderson and Zweig[4] would indicate that at least in certain cases this is not so. We wish to report a photo-reduction of chlorobenzene and bromobenzene, and some simple derivatives, which proceeds quite rapidly and in good yield.

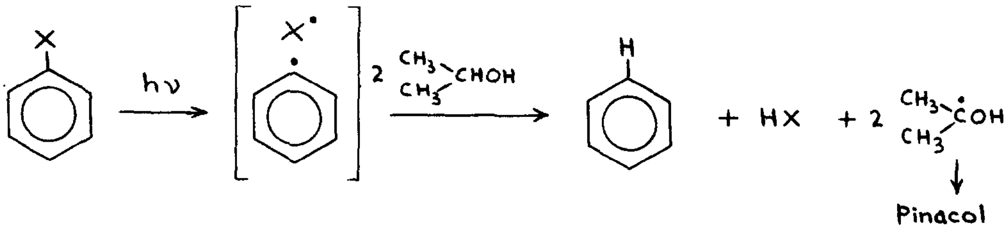
During our investigation of the photo-rearrangement of phenoxyacetic acids[12,13], we found that 2,4-dichlorophenoxyacetic acid afforded a complex mixture in which phenol was the major volatile phenolic constituent. To investigate this loss of chlorine from the aromatic ring we turned first to a less complex example, p-chlorophenoxyacetic acid. On irradiation in 95% ethanol it yielded, after distillation of the reaction mixture, the same volatile products as obtained from phenoxyacetic acid[12,13] (see Table). No p-chlorophenol or 5-chloro-2-coumaranone could be detected by gas liquid chromatography (g.l.c.). Since phenoxyacetic acid was also produced in low yield, the loss of chlorine does occur, at least



in part, prior to homolysis of the O-CH_2COOH bond. The comparatively rapid reduction of p-chlorophenol and 2-hydroxy-5-chlorophenylacetic acid (see Table) indicates that the absence of these products from the irradiation mixture does not preclude the alternative, O-CH_2COOH bond homolysis and rearrangement followed by reduction, as a competing pathway.

We have found that this reduction of chloroaromatic compounds proceeds faster and in higher yield in isopropanol and even for chlorobenzene replacement of chlorine is quite rapid. Standard conditions were employed for the photolyses in isopropanol, thus the times, which were reproducible, indicate the relative rates of reduction. Although the photoreduction of iodoaromatic compounds has been studied under other conditions[1] we have included three for comparison purposes. From the Table it may be seen that, for the groups of compounds studied, the chloro-, bromo- and iodo-compounds are reduced at comparable rates, while yields, although slightly better for the iodo-compounds, are good in all cases. Of the compounds examined, the o- and p-halophenols[14] are the most reactive. The photochemical method would therefore appear to be a useful alternative to Raney-nickel/alkali reduction[15] of chloro- and bromo-aromatic compounds as well as iodoaromatics.

The formation of pinacol (g.l.c. and isolated) in>50% yield in the reactions in isopropanol indicates that, after absorption of light, the excited haloaromatic compound undergoes carbon-halogen bond homolysis, producing radicals which then abstract hydrogen from the solvent as shown below. The detection of hydrogen halides in the photolysis mixtures is in keeping with such a mechanism. A radical mechanism has also been suggested[16] to account for the formation of benzene, among other products, on irradiation of chlorobenzene in ethanol.



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) dissolved in the solvent (670 ml). The g.l.c. yields are corrected for detector response.

Compound	Solvent	Time(hr)	Product(s) (Yield)
p-chlorophenoxyacetic acid (5.0 g)	ethanol	9.0	2 coumaranone (29% isolated) phenol (8% isolated)
p-chlorophenol	ethanol	5.25	phenol (63% isolated)
2-hydroxy-5-chlorophenylacetic acid	ethanol	4.0	The acid was heated to give 2-coumaranone (70% isolated)
chlorobenzene	isopropanol	12.0	benzene (72%)
bromobenzene	isopropanol	6.0	benzene (72%)
iodobenzene	isopropanol	12.0	benzene (82%)
p-chlorophenol	isopropanol	3.5	phenol (93%)
p-bromophenol	isopropanol	6.0	phenol (89%)
p-iodophenol	isopropanol	5.5	phenol (98%)
o-chlorophenol	isopropanol	6.5	phenol (86%)
o-bromophenol	isopropanol	8.0	phenol (91%)
o-iodophenol	isopropanol	3.5	phenol (98%)
o-chloroanisole	isopropanol	8.0	anisole (95%)
p-chloroanisole	isopropanol	11.0	anisole (83%) pinacol (54%)

REFERENCES

1 R.K. Sharma, and N. Kharasch, N., Angew. Chem. Intern. Ed. Engl., 1968, 1, 36.

2 N. Kharasch, R.K. Sharma, and H.B. Lewis, Chem. Commun., 1966, 418.

3 H.-I. Joschek and S.I. Miller, J. Am. Chem. Soc., 1966, 88, 3269.

4 W.A. Henderson and A. Zweig, J. Am. Chem. Soc., 1967, 89, 6778.

5 B. Milligan, R.L. Bradow, J.E. Rose, H.E. Hubbert, and A. Roe, J. Am. Chem. Soc., 1962, 84, 158 and refs. therein.

6 J.T. Echols, V.T.-C. Chuang, C.S. Parrish, J.E. Rose, and B. Milligan, J. Am. Chem. Soc., 1967, 89, 4081.

7 B. Milligan, and R.L. Bradow, J. Phys. Chem., 1962, 66, 2118.

8 Szychlinski, J., Zeszyty Nauk. Mat., Fiz., Chem., Wyzsza Szkola, 1963, 3, 127. (Chem. Abstr. 1966, 64, 7992a).

9 T. Latowski and A. Basinski, Roczniki Chem., 1963, 37, 341 and refs. therein.

10 D.F. Nijhoff, and E. Havinga, Tetrahedron Lett., 1965, 4199.

11 V.I. Stenberg, "Organic Photochemistry", (Ed. O.L. Chapman) p. 127 et seq. (Marcel Dekker : New York 1967).

12 D.P. Kelly and J.T. Pinhey, Tetrahedron Lett., 1964, 3427.

13 D.P. Kelly, J.T. Pinhey and R.D.G. Rigby, Aust. J. Chem., in press.

14 For reactions of the m-halophenols see the following communication.

15 N.P. Buu-Hoi, N.D. Xuong and N. van Bac, Bull. Soc. Chim. France, 1963, 2442.

16 J. A. Barltrop, N. J. Bunce, and A. Thomson, J. Chem. Soc. (C), 1967, 1142.