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THE MECHANISM OF THE PHOTO-INDUCED HOMOLYSIS OF ARYL HALIDES

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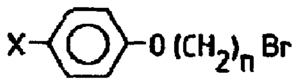
Summary. Irradiation of the ω-(4-halophenoxy)alkyl bromides (Ia,b n=10) in methanol usually leads to preferential cleavage of the aryl-halogen bond and data is presented supporting the conclusion that this occurs from the first excited single state.

Many examples are known of the photo-induced homolysis of carbon halogen bonds[1] and the subject is of current interest because of its relevance to the photo-induced degradation of chlorinated hydrocarbons (such as the pesticide aldrin[2]), chlorinated biphenyls[3,4] and polyvinyl chloride[5]. Recently, the photolysis of appropriately substituted halogen compounds has been shown to be a source of tertiary[6,7] and vinyl carbocations[8]. Allylic halides can undergo rearrangement reactions[9]. We now report the mechanism of the photo-induced homolysis of aryl halides and its relevance to synthetic applications of this reaction.

Irradiation of the ω-(4-halophenoxy)alkyl bromides (la,b) in methanol solutions gives the phenoxyalkyl bromides (lc). (TABLE 1).



I a, X = Br
b, X = Cl
c, X = H

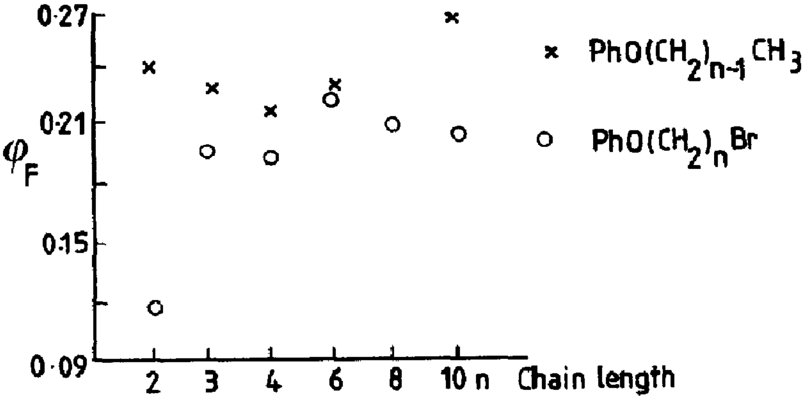
TABLE 1

X	n	Time (hrs)	Starting Material %	Product %		Product %
Cl	2	3	56.5	$PhOCH_2CH_2Br$	15.5	Phenol 25
Cl	3	3	46	$PhO(CH_2)_3Br$	26.5	Phenol 20
Cl	8	4	53	$PhO(CH_2)_8Br$	40	
Cl	10	6	60	$PhO(CH_2)_{10}Br$	38	
Br	2	2	52	$PhO(CH_2)_2Br$	35	Phenol 25
Br	3	4	5	$PhO(CH_2)_3Br$	81	Phenol 10
Br	6	4	20	$PhO(CH_2)_6Br$	74	
Br	8	4	39	$PhO(CH_2)_8Br$	59	
Br	10	4	47	$PhO(CH_2)_{10}Br$	50	

Despite the fact that aryl-chlorine and aryl-bromine bonds are stronger than alkyl-bromine bonds (e.g. PhCl = 94.5 kcal/mole, PhBr = 79.2 kcal/mole, CH_3CH_2Br = 60 kcal/mole[10]) the aryl-halogen bond is broken preferentially in all cases except for Ib, having n=2. Since the incident energy is gathered by the aryloxy group, the lack of reaction of the alkyl-bromine bond could be due to inefficient energy transfer from the aryloxy group to the CH_2-Br bond. It is known that the homolysis of CH_2-Br bonds can be sensitised by benzene[6] and we find that irradiation of Ic, n=6 in the presence of benzene gives n-hexyl phenyl ether.

Although sensitisation can be carried out it should be noted that the multiplicity of the excited species effecting sensitisation is not characterised. Examination of the fluorescence spectra of Ic shows that for n=2 and to a much less extent for n=3, and 4, the terminal bromine atom quenches the fluorescence of the aryloxy group (Figure 1). This effect of chain length is not surprising in the light of recent work on intramolecular exciplexes and excimers.[11] Thus it appears that for Ia and Ib having n > 3 that the bromine atom in the alkane chain cannot interact efficiently with the excited aryloxy-group and therefore sensitised homolysis does not occur.

Figure 1



That intramolecular sensitised homolysis of alkyl-bromine bonds can occur for compounds having n=2 & 3 is shown by the fact that Ic n=2 and 3 are far more reactive than Ic having n > 3. Irradiation of Ic n=2 gives phenol in high yield.[12] (Table II)

TABLE II

X	n	Time (hrs)	Starting Material %	Product %
H	2	6	12	Phenol 80
H	3	6	15	Phenol 65
H	4	6	70	Phenol 16
H	6	6	88	Phenol 8
H	10	24	100	No reaction

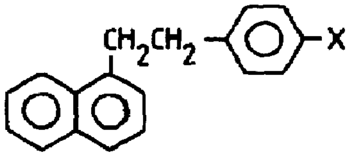
$$\begin{aligned}
&PhOCH_2CH_2Br \xrightarrow{h\nu} PhOCH_2\dot{C}H_2 + B\dot{r}\\
&Br^{\cdot} + CH_3OH \rightarrow HBr + \dot{C}H_2OH\\
&PhOCH_2\dot{C}H_2 \rightarrow PhO^{\cdot} + CH_2{:}CH_2\\
&PhO^{\cdot} + HBr \rightarrow PhOH + Br^{\cdot}
\end{aligned}$$

In the case of Ia n=2 no such fragmentation is observed and the aryl-bromine bond is cleaved to the total exclusion of the alkyl bromine bond. This demonstrates that cleavage of the aryl bromine bond is very rapid and this is probably responsible for the short lifetime of the excited states of the 4-bromophenoxy group. By way of contrast Ib n=2 (this is slower than Ic n=2) to give 4-chlorophenol which in turn gives phenol.[13] Since the aryl-chlorine bond is far stronger than the aryl bromine bond, the homolysis of the aryl-halogen bond will be slower in Ib n=2 than for Ia n=2 and consequently the excited state of Ib n=2 is sufficiently long lived to allow energy transfer to the alkyl-bromine bond.

The presence of a halogen atom in the aryl ring of Ia and Ib, and the bromine atom in the side chain of Ia-c having n=2 should favour intersystem crossing and lead to a high yield of triplets and therefore makes the triplet state the likely species responsible for reaction. Examination of the phosphorescence spectra of 4-bromo-anisole, 1,4-dibromobenzene and 1-bromo-4-cyanobenzene shows the quantum yield of phosphorescence of the former (which is barely detectable) to be far less than that of the latter two compounds. However, on irradiation in methanol these three compounds rapidly debrominate (relative rates 1.04 : 1 : 1.23). This data, together with that reported on chlorinated biphenyls[3] shows that there is no correlation between the quantum yields of phosphorescence and reaction. The intermediacy of triplet states in the reactions of Ia and Ib is also unlikely since the triplet energy of the halophenoxy group is likely to be lower than 80 kcal/mole.[14]

From the results on Ia n=2 and 3 we conclude that homolysis of the aryl-bromine bond takes precedence over energy transfer and is therefore likely to be a very fast process and one that successfully competes with intersystem crossing. This fact, together with the lack of correlation between phosphorescence yields, efficiency of photochemical reaction and the energetics of the system suggest that reaction is occurring from the singlet manifold.

It is probable that reaction occurs from the excited singlet state or possibly a vibrationally excited ground state[15]. In order to substantiate that reaction does not occur from a triplet state we photolysed (IIa) in methanol. A major, primary product is IIb. Thus homolysis of the aryl-bromine bond has successfully competed with energy transfer to the naphthalene nucleus even though it is strategically placed to deactivate the excited states of the bromo-phenyl group.



II a, X = Br
b, X = H

Since cleavage of the aryl-bromine bond is very fast and competes effectively with intramolecular energy transfer and probably intersystem crossing, photolysis of multifunctional compounds containing bromo-phenyl groups should lead to phenyl radicals, which if the substitution is appropriate undergo intramolecular reactions.[15,16] With chlorophenyl groups this may not be the case of the less efficient cleavage of the aryl-chlorine bond. In cases where an electrocyclic reaction may compete with the homolysis process (as in (III)) the electrocyclic process should decrease in efficiency as the substituent is changed Cl → Br → I.[17]

(III)

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