

## Photolytic Decomposition of Polyhalogenocyclohexanes – A Pathway to the Formation of Substituted Halogenobenzenes.

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**Summary:** Liquid phase photohalogenation of benzene/halogenobenzenes give polyhalogenocyclohexane adducts; these adducts are accompanied by substituted products eg. mono- and dihalogenobenzenes. Photochemical decomposition of adducts like  $C_6H_6Br_6$  and  $C_6H_5ClBr_6$  later gave the same products, i.e. bromobenzene, and dibromobenzenes or bromochlorobenzenes. The distribution of the dihalogenobenzene isomers was found markedly different from the reported ratio for such isomers in the heterolytic reactions; meta-isomers are found to a significant extent. Evidence adduced suggests an addition-elimination mechanism as a possible pathway to the bromo-substituted arenes in these photochemical reactions.

The most usual method for obtaining polyhalogenocyclohexanes (hereinafter called adduct/s, e.g. hexabromocyclohexane  $C_6H_6Br_6$  and hexabromochlorocyclohexane  $C_6H_5ClBr_6$ ) is by photochemical halogenation of benzene or a substituted benzene. Ultraviolet light is used as a free radical initiator. Various isomers of these adducts have been isolated<sup>1</sup>. The formation of these adducts involves a free radical addition of halogen atoms to the aromatic nucleus<sup>2,3</sup>. Analogous heterolytic reactions between benzene (or substituted benzene) and bromine, using metal catalysts, gives substituted products only<sup>4,5</sup>.

A study of the products from the photochemical reaction of benzene and bromine has revealed (g.l.c.) that besides hexabromocyclohexane, small quantities of bromo- and dibromo-benzenes were also formed. The yield of these substituted products increased when the reaction was repeated at *ca.* 60°.

In view of these observations the above reaction was studied using chlorobenzene and fluorobenzene in place of benzene. A mixture of chlorobenzene and bromine was exposed to ultraviolet light for twelve to sixteen hours. Both the addition and the substituted products were formed. The adduct of  $C_6H_5ClBr_6$ , and isomeric monobromochlorobenzenes were isolated. It was reported earlier that these arenes may have been formed through the subsequent decomposition of the adduct (like  $C_6H_5ClBr_6$ ) during the photochemical reactions<sup>2</sup>. This is also now supported by the photochemical decomposition of samples of adducts which gave bromo-substituted arenes, accompanying hydrogen bromide

and molecular bromine – the normally expected products of such reactions.

### Discussion

The basic purpose of this work was (a) to obtain bromo-substituted arenes by photochemical bromination of benzene or halogenobenzenes at *ca.* 60° and (b) to study the mode of their formation.

The evidence mentioned above suggests a homolytic mechanism for these reactions. The hypothetical radical intermediate (1) may lead to the formation of bromoarenes by two possible routes; (a) a direct substitution reaction analogous to the heterolytic mode (reaction I) and (b) an addition-elimination reaction (reaction II). The possibility of the former route is less since hydrogen abstraction by bromine is not a favourable step on thermochemical grounds ( $D(C_6H_5-H) \sim 100 \text{ kcal mole}^{-1}$ ). Besides, the olefinic system so produced (1) is sufficiently reactive to undergo further addition rather than substitution, and is therefore not expected to lead exclusively to the formation of the substitution products. The addition-elimination mechanism appears to be more significant in this reaction than in other homolytic aromatic substitutions. Scheme 2 further outlines the formation of mono- and di-bromobenzenes. The loss of hydrogen bromide from 2 or 3 to give these substitution products is not unexpected. Mayo and Hardy<sup>6</sup> reported the loss of hydrogen bromide from 1,2,3,4-tetrahydro-tetrabromonaphthalene on heating, thus producing mono- and di-bromonaphthalenes. We have also found

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that samples of pure adducts  $C_6H_5XBr_6$  (4) decompose photolytically in organic solvents (toluene) through the elimination of hydrogen bromide and molecular bromine giving bromo-substituted arenes (Scheme 3). The amount of these arenes formed is, however, low and some unidentified products were formed. Orloff and Kolka<sup>8</sup>, following the earlier work of Matthews<sup>7</sup>, however, reported the decomposition of (4) using alcoholic potassium hydroxide. This results in quantitative conversion of (4) into 1,2,4-tribromobenzene through dehydrobromination. The photochemical decomposition of (4) (this work) must, however, proceed by a different mechanism since an entirely different product distribution was found (more dibromobenzene and very much less tribromobenzene).

In free radical reactions polar factors are not usually as dominant as they are in ionic reactions. Therefore groups which are ortho-para directing in electrophilic substitution do not necessarily direct incoming radicals to these positions<sup>9</sup>. Moreover, as explained above, in the formation of bromo-substituted arenes the site of attack and the site of ultimate substitution may not necessarily be the same. The origin of these species may depend upon the various possible modes of the decomposition of dihydro-dibromo adduct (1). Such observations also support an addition-elimination mechanism. Examination of the distribution of the dihalogenobenzene isomers (Table 1) also leads to the same conclusion. The isomer ratios are close when the dihalogenobenzenes  $C_6H_4XBr$ , are obtained by (a) photobromination of benzene or halogenobenzenes using u.v. light and (b) by photolytic decomposition of hexabromocyclohexanes or the corresponding derivatives thereof. This suggests a common mechanism for the formation of bromoarenes in these reactions i.e. as proposed in scheme 1. It is also evident from Table 1 that there is a significant difference between the ionic and the photobromination reactions in which the *meta* isomers (*m*- $C_6H_4BrX$ ) are formed to a significant extent. This is in contrast to the ionic reactions where this position is usually unreactive. Such an observation has also been recorded in the gas phase halogenation of benzene derivatives<sup>11</sup>.

## Experimental

### Hexabromochlorocyclohexane

This was prepared by exposing a mixture of bromine (32 g, 0.2 mole) and chlorobenzene (500 ml) to sunlight for two weeks. When most of the colour of bromine had

disappeared, the chlorobenzene was evaporated under reduced pressure. Crystallisation from ethanol gave pure compound (23 g, 60%) m.p. 125° (lit. 126°)<sup>12</sup>. Found: C, 12.1; H, 0.84; Br, 80.0; Cl, 6%. Calculated for  $C_6H_5ClBr_6$ : C, 12.1; H, 0.84; Br, 80.8; Cl, 5.9.

### Dihalogenobenzenes

Authentic samples of bromo-, isomeric dibromo-, bromochloro- and bromofluorobenzenes used as standards for gas chromatography were obtained from BDH and Aldrich Chemicals.

### Photobromination of benzene

Bromine (16 g, 0.1 mole) was dissolved in redistilled dry benzene (500 ml). The mixture was placed in a u.v. photochemical reactor for 16 hours at ca. 60°. At the end, bromine consumption and the amount of hydrogen bromide was estimated by titration<sup>13</sup>. After washing with aqueous sodium metabisulphate solution, excess of benzene was evaporated by fractional distillation. Gas chromatography of the product showed the presence of bromobenzene ( $15 \times 10^{-3}$  mole) and isomeric dibromobenzene ( $10 \times 10^{-3}$  mole). The crude product on recrystallisation from toluene gave hexabromocyclohexane ( $13 \times 10^{-3}$  mole). Found: C, 12.9; H, 1.0; Br, 86.0%. Calculated for  $C_6H_6Br_6$ : C, 12.9; H, 1.0; Br, 86.0.

### Photobromination of chlorobenzene

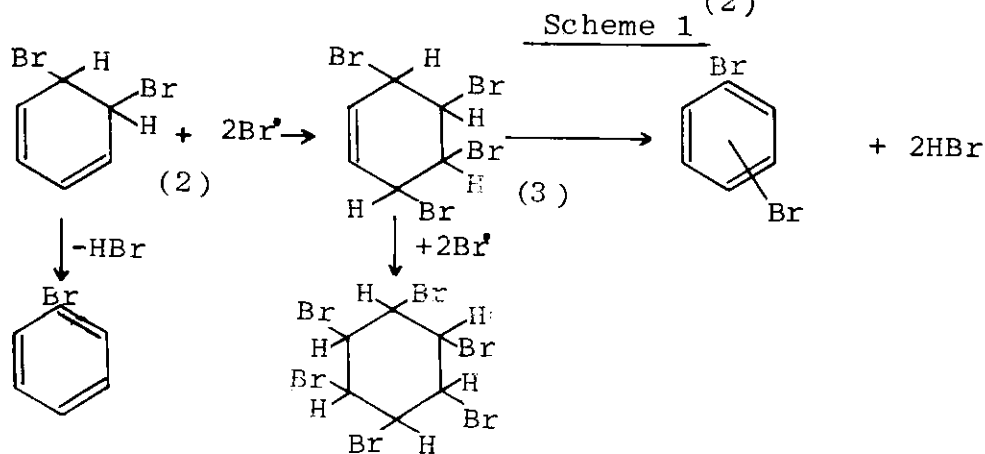
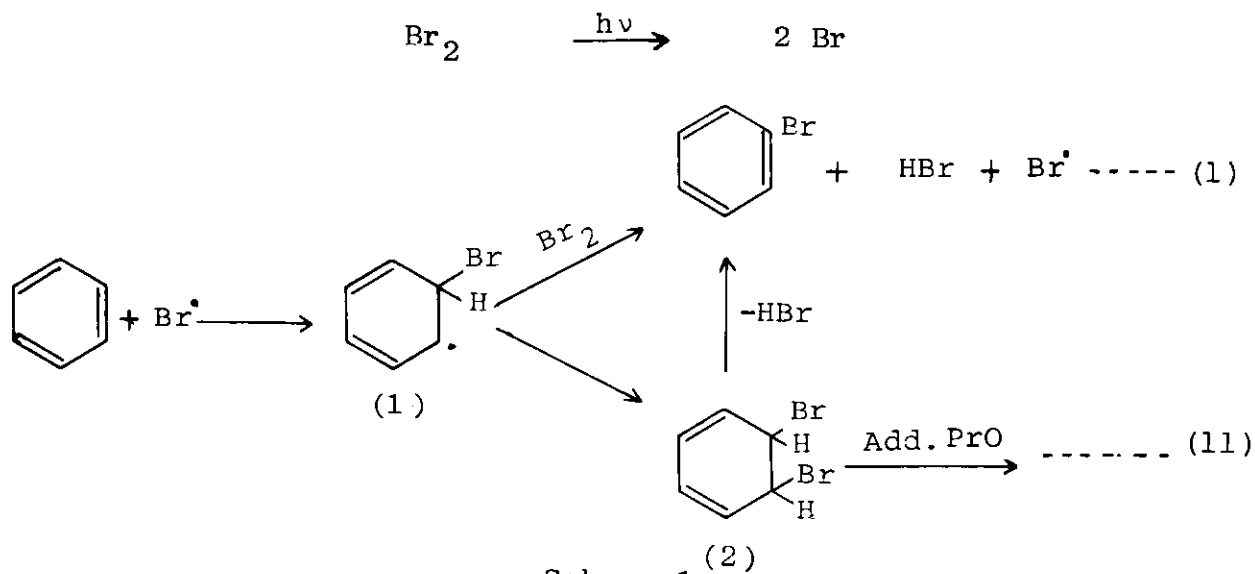
The same method was used as for benzene. Gas chromatography showed the presence of isomeric bromochlorobenzenes ( $40 \times 10^{-3}$  mole). Recrystallisation from ethanol gave adduct m.p. 126°. Found: C, 12.1; H, 0.84%. Calculated for  $C_6H_5ClBr_6$ : C, 12.1; H, 0.84.

### Photobromination of Fluorobenzene

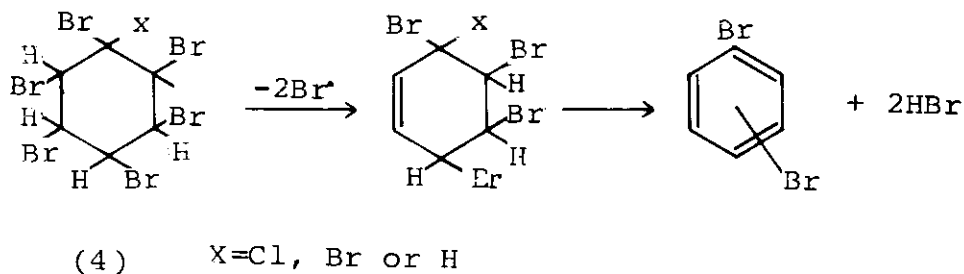
Gas chromatography of the products revealed the presence of isomeric bromofluorobenzenes ( $39 \times 10^{-3}$  mole) only.

### Photochemical decomposition of hexabromocyclohexane at 60°

Hexabromocyclohexane (5 g; 9 m. mole) was dissolved in dried and redistilled toluene (500 ml). The mixture was irradiated for 8 hours. After washing with sodium metabisulphite solution, the amount of hydrogen bromide formed was estimated. Gas chromatography showed the presence of bromobenzenes ( $1.3 \times 10^{-3}$  mole) and dibromobenzene ( $1 \times 10^{-3}$  mole). In addition to these benzyl bromide ( $8 \times 10^{-3}$  mole) and bibenzyl ( $1.5 \times 10^{-3}$  mole) were formed.



Scheme 2



Scheme 3

Table 1

Reactants	Catalyst	X	C <sub>6</sub> H <sub>4</sub> XBr%		p-
			o-	m-	
Benzene + bromine	u. v. light	Br	19	34	47
Chlorobenzene + bromine <sup>10</sup>	„	Cl	16	65	19
Chlorobenzene + bromine <sup>10</sup>	Fe <sup>++</sup>	Cl	12	0	88
Fluorobenzene + bromine <sup>10</sup>	u. v. light	F	30	6	64
Hexabromocyclohexane in toluene	„	Br	20	30	50
Hexabromochlorocyclohexane in toluene	„	Cl	13	72	15

*Photochemical decomposition of hexabromochlorocyclohexane at 60°*

The same method was used as for the above reaction. Isomeric bromochlorobenzenes ( $5 \times 10^{-3}$  mole) were found.

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