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PHOTOBROMINATION AND IONIC BROMINATION OF HALOGENO- AND DIHALOGENOBENZENES,

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When a mixture of chlorobenzene and bromine is irradiated in a pyrex vessel with visible light, a reaction, although very slow, is found to proceed. The distribution of the products arising from replacement of hydrogen by bromine is unexpected: meta bromochlorobenzene predominates(up to 80%) in sharp contrast with the usual ortho-para directing effect of a chlorine substituent in ionic brominations. There might exist a parallelism between this photochemical reaction and the results obtained at high temperature(usually 300-600°C) by WIBAUT (2-6) and by KOOYMAN(7-10). To our knowledge,this is the first report of a meta-directing effect observed in the room temperature bromination of a halogenobenzene Among the products,some bromobenzene is isolated Although the radical replacement of a bromine substituent by a chlorine is well documented(11,12),nothing is reported about the reverse process here observed.

These unexpected observations prompted us to investigate the photobromination of halogeno- and dihalogenobenzenes.Surprisingly there is very little information on the ionic bromination of the dihalogenobenzenes although trihalogenobenzenes are interesting intermediates. Therefore, iron promoted brominations of all the compounds have also been investigated and compared with the photobrominations.In all experiments closed pyrex tubes containing the reactants have been irradiated and reactions have been restricted to less than 25% conversion(usually 5-15%) in order to avoid extensive consecutive halogenation.Analysis of the reaction mixture could be achieved only by GLC with open capillary columns. The products have been identified by 3 methods: (1) Isolation from the reaction medium and analysis(IR ,Fus°, n_D, ..) (2) GLC comparisons(retention times) with authentic samples (3) GLC comparisons between different reaction mixtures affording identical products.

Orientation in the substitution of hydrogen by bromine

As can be seen from table 1, fluorine is the most powerful para-

Table 1: Isomers distribution(%) in the brominations of halogenobenzenes([13]).

Bromination reactants	Br_2 + Fe			Br_2 + hν			NBrS + hν		
SUBSTRATES	ISOMERS[a,b]								
	1,2-	1,3-	1,4-	1,2-	1,3-	1,4-	1,2-	1,3-	1,4-
Fluorobenzene	2	0	98	20-25	15-20	55-65	10	63	27
Chloro-	12	0	88	10-20	60-80	10-20	2	94	4
Bromo-	12	0	88	15-25	30-50	35-55	7	72	21
	1,2,3-	1,2,4-	1,3,5-	1,2,3-	1,2,4-	1,3,5-	1,2,3-	1,2,4-	1,3,5-
1,3-Dichloro-	2	98	0	25	75	0	6	81	13
1,3-Dibromo-	2	98	0	12	88	0	12	88	0
1,3-Fluorochloro-	1	99	Tr.	16	84	Tr.	5	66	29*
1,3-Fluorobromo-	1	99	0	16	84	Tr.	3	83	14
1,3-Chlorobromo-	2	98	0	15	85	Tr	7	91	2
	1,2,3-	1,2,4-		1,2,3-	1,2,4-		1,2,3-	1,2,4-	
1,2-Difluoro-	Tr*	100*		9*	91*		15*	85*	
1,2-Dichloro-	8	92		89	11		95	5	
1,2-Dibromo-	9	91		44	56		39	61	
1,2-Fluorochloro-	1	99		39	61		68	32	
1,2-Fluorobromo-	1	99		30	70		68	32	
1,2-Chlorobromo-	9	91		38	62		57	43	

(a) For chlorine containing compounds, other products are also observed (See text). With dihalogenobenzenes bearing different halogens, two "1,2,4" and two "1,2,3" isomers are obtained. Although their individual proportions are usually different and vary with experimental conditions, only the total percentage for each pair of isomers is given in this preliminary communication

(b) Isomers which have not yet been identified with all certainty are marked with an asterisk.

orienting halogen in the ionic bromination while chlorine is the most effective meta-directing in the photobromination of monohalogenobenzenes.N-Bromosuccinimide brominations are better to get meta derivatives probably because radical substitution predominates in this case

Given the observed meta-directing effect,meta dihalogenobenzenes were expected to give 1,3,5-trihalogenobenzenes. However,even in the most favorable conditions(NBrS) no more than a few percents of these isomers are obtained

Large differences are observed between ionic and photochemical reactions during the bromination of ortho dihalogenobenzenes.The photochemical experiments,mainly when NBrS is used,yield interesting proportions of 1,2,3-trihalogenobenzenes.Considering the prominence of these isomers,it can be anticipated that the radical reaction is much less influenced by steric factors than the ionic process.This probably reflects a different mechanism and may support KOOYMAN's proposal:the selectivity would depend on the acidity of the different protons in a ionic species obtained by one electron transfert between the ring and the halogen(8-10). In the ionic brominations where catalysts like $FeBr_3$ and HBr are present,isomerisations of the trihalogenobenzenes are not impossible(14).Search for such reactions are now in progress.

Brominations of para dihalogenobenzenes have not been reported in table 1. Except for derivatives containing a fluorine substituent, the photobromination is extremely slow(15). A somewhat faster reaction is obtained when bromine itself is used as solvent and also when **hydrobromic** acid is added to the reaction medium.

Substitution of chlorine by bromine

Table 2:Substitution of a chlorine by bromine during the photobromination,with molecular bromine,of halogenobenzenes(13)

Halogenobenzenes	Chlorine substitution
Chloro-	5 - 10%
1,2-Fluorochloro-	1%
1,3-Fluorochloro-	0%
1,4-Fluorochloro-	12%
1,2-Dichloro-	15 - 20%
1,3-Dichloro-	0%
1,4-Dichloro- (+CCl_4)	50%(16)
1,2-Bromochloro-	Traces
1,3-Bromochloro-	0%
1,4-Bromochloro-(+CCl_4)	30%

The substitution of a chlorine by a bromine is never observed during ionic brominations With light, a meta chlorine is never substituted, an ortho chlorine is replaced only in the reaction of 1,2-dichlorobenzene while a para chlorine is always substituted to some extent (Table 2). With NBrS the percentage of chlorine substitution is larger and not only para but also ortho and meta chlorines are substituted (Table 3).

Consecutive reactions

Substitution of chlorine by bromine initiates consecutive chlorination reactions The chlorine released in the medium can itself substitute a hydrogen or a bromine in an other molecule of halogenobenzene(Table 3).It must be pointed out that these consecutive reactions occur when the concentration of HBr is very low as,for example,in brominations with NBrS (Table 3).

Table 3: Products obtained by the substitution of chlorine by bromine and by consecutive chlorinations in photobrominations with NBrs (13).

Reactants	Chlorine substitutions by bromine	Consecutive chlorinations
Chlorobenzene	Bromobenzene(14%)	Dichlorobenzenes(9%)
1,2-Dichloro-	1,2-Bromochloro-(39%)	Trichloro-(30%)
1,3-Dichloro-	1,3-Bromochloro-(34%)	Trichloro-(29%)
1,2-Bromochloro-	1,2-Dibromo-(11%)	1,2-Dichloro-(11%)
1,3-Bromochloro-	1,3-Dibromo-(9%)	1,3-Dichloro-(8%)
1,2-Chlorofluoro-	1,2-Bromofluoro-(21%)	1,2,4-Fluorodichloro-(9%)
1,3-Chlorofluoro-	1,3-Bromofluoro-(5%)	1,3,4-Fluorodichloro-(10%)
1,4-Chlorofluoro-	1,4-Bromofluoro-(43%)	1,2,4-Fluorodichloro-(13%)

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(13) The percentages given in the tables are chromatographic ratios of products.

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(15) The ionic bromination is also slower for the para than for the ortho and meta derivatives.

(16) In CCl_4 but with added hydrogen bromide, 80% of p.bromochlorobenzene are obtained;only 2% with bromine used as solvent.