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# The Photolyses of 2,6- and 2,4-Difluorohalobenzenes

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Photolyses of 2,6- and 2,4-difluorobromobenzenes in acetonitrile gave isomerized and brominated products in addition to 1,3-difluorobenzene produced by the dehalogenation. The reactions were compared with similar reactions of the corresponding chloro- and iodoarenes. In general, photolytic cleavage of the C–X bond of 2,6-difluorohalo(X)benzene was shown to proceed more easily than the corresponding 2,4-difluorohalo compound.

Photolytic dehalogenation of polyhaloaromatic compounds has been investigated rather extensively in connection with the detoxication of polyhaloarenes.[1—6] Several years ago, we reported a novel photo-rearrangement of chlorine atom which occurs in the course of photo-dehalogenation of polychlorinated aromatic molecules.[7,8] The rearrangement was first found in acetonitrile solutions and shown to produce exclusively isomers which can be derived by the *meta*-migration of a chlorine atom. The photo-isomerization was eventually revealed to occur quite generally during the photolyses of chlorinated aromatic compounds in solvents of low reactivity towards hydrogen abstraction.[8—10] The isomerization is competing with hydrogen abstraction even in less active solvents such as acetonitrile. Abstraction of hydrogen atom from the solvent molecule proceeds almost exclusively in alkane and alcohol solutions which have easily abstractable hydrogen atoms.[9]

Besides chlorinated benzenes, chlorinated pyridines also gave rearranged products in acetonitrile solutions. 2,5-Dichloropyridine was produced from 2,3-dichloropyridine, for example.[11] The isomerization also took place in benzene solution.[10] Thus the photolysis of *o*-dichlorobenzene gave *p*-dichlorobenzene and isomeric 2- and 4-chlorobiphenyls. 4-Chlorobiphenyl can be expected to be produced via subsequent *meta*-rearrangement of the photo-phenylation product, 2-chlorobiphenyl.

Several experiments were carried out with the aim of characterizing the photo-isomerization. The reaction was proved to be first-order with the reactant by a kinetic measurement, and is proved to proceed primarily from the starting polychlorobenzene via a unimolecular process.[8] Our recent study on isotopically labeled 2-chloro[2-$^{13}$C]biphenyl excluded the possibility of a mechanism via the valence isomer.[12] As the fluoro-substituent has been shown to be intact under the photolysis conditions employed in the experiments, it can be a label to observe the site of migration of other halogen atoms. For this reason, the products of the photolyses of several fluorinated halobenzenes were examined.

In this research, photolyses of a series of 2,6- and 2,4-difluorohalobenzenes $C_6H_3F_2X$ (X=Cl, Br, and I) were studied in order to compare the effect of the nature of halogen on their photochemical behaviors and to examine the scope and the limitation of the novel photo-isomerization.

## Results and Discussion

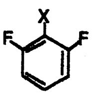
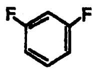
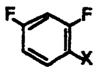
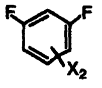
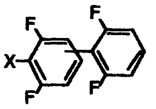
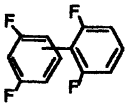
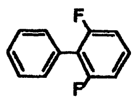
The photo-reaction of bromoarene was reinvestigated to examine the possibility of isomerization via bromine migration. In our previous investigations, isomerized compounds were not obtained, at least as major products. In this investigation, the reaction products at higher conversions were carefully analyzed and characterized by GC/MS measurements. Products after irradiation by a low pressure mercury arc lamp (254 nm) for 6 h (for 24 h in parentheses) are given in Table 1 for 2,6-difluorohalobenzenes **1**—**3** and in Table 2 for 2,4-difluorohalobenzenes **4**—**6** (Chart 1).

2,6-Difluorohalobenzene photolyzes more rapidly than the corresponding 2,4-difluorohalobenzene. This trend is general, irrespective of the nature of halogen atom. However, the acceleration effect is considerably exaggerated with bromo-compound (**2**) in comparison to chloro-compound (**1**). The effect can be attributed to the repulsive steric and electrostatic forces operating between the leaving halogen atom and neighboring fluorine atoms.[8]

The reaction of bromoarene is rather complicated, producing isomerized, debrominated ($C_6H_4F_2$), brominated ($C_6H_2F_2Br_2$), and dimerized products as shown in the Tables 1 and 2. As an example, the time-conversion curve for 2,6-difluorobromobenzene is given in Fig. 1.

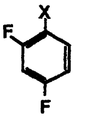
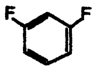
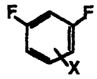
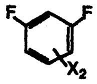
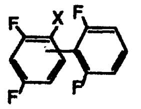
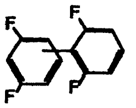
In cases of the photolyses of bromodifluorobenzenes $C_6H_3F_2Br$ (**2** and **5**), small amounts of isomerized products were obtained together with debrominated ($C_6H_4F_2$) and brominated ($C_6H_2F_2Br_2$) products. However, the yields of

Table 1. Reactions of 2,6-Difluorohalobenzenes[a)]

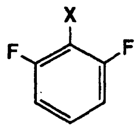
| | | | |  |  |  |  |  |  |  | $XCH_2CN$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| X | Solvent | $C$/mol dm$^{-3}$ | $t$/h | (A) | (B) | (C) | (D) | (E) | (F) | (H) | (G) |
| Br | $C_6H_6$[b)] | 0.05 | 6 | 64.2 | 0.0(0) | 0.5(1) | 0.0(0) | 0.0(0) | 0.0(0) | 35.1(98) | — |
| | | | 24 | 27.6 | 0.9(1) | 1.2(2) | 0.0(0) | 0.0(0) | 0.0(0) | 69.4(96) | — |
| Br | $C_6F_{14}$ | 0.05 | 6 | 98.1 | 0.0(0) | 0.4(20) | 0.0(0) | 1.5(80) | 0.0(0) | — | — |
| | | | 24 | 95.6 | 0.0(0) | 1.5(30) | 0.0(0) | 3.4(70) | 0.0(0) | — | — |
| Br | $CH_3CN$ | 0.05 | 6 | 39.9 | 39.6(66) | 3.8(6) | 8.6(14) | 1.9(3) | 4.4(7) | — | 2.2(4) |
| | | | 24 | 15.0 | 55.1(65) | 6.9(8) | 12.2(14) | 0.4(<1) | 7.0(8) | — | 3.7(4) |
| Br | $CH_3CN$ | 0.1 | 6 | 82.4 | 11.2(64) | 0.5(3) | 3.7(21) | 0.9(5) | 1.1(6) | — | 0.3(2) |
| | | | 24 | 60.1 | 24.3(61) | 2.4(6) | 7.7(19) | 1.4(4) | 3.4(9) | — | 1.2(3) |
| Br | $CH_3CN$ | 0.2 | 6 | 88.9 | 6.1(55) | 0.4(4) | 2.0(18) | 1.0(9) | 0.6(5) | — | 0.3(3) |
| | | | 24 | 74.9 | 13.6(54) | 1.4(6) | 4.9(20) | 1.6(6) | 2.3(9) | — | 0.9(4) |
| Cl | $CH_3CN$ | 0.05 | 6 | 86.5 | 9.3(69) | 1.7(13) | 0.0(0) | 0.8(6) | 0.5(4) | — | 0.8(6) |
| | | | 24 | 52.0 | 33.1(69) | 6.2(13) | 0.0(0) | 3.5(7) | 2.4(5) | — | 2.6(5) |
| I | $CH_3CN$ | 0.05 | 6 | 52.7 | 36.7(78) | 0.0(0) | 0.0(0) | 0.6(1) | 3.3(7) | — | 2.6(5) |
| | | | 24 | 28.2 | 57.9(81) | 0.0(0) | 0.0(0) | 2.0(3) | 7.5(10) | — | 6.7(9) |

a) Products after irradiation by a low pressure mercury arc lamp (254 nm) for $t$ h are given. The percentages of the products in reference to the consumed reactant (A) are given in parentheses. b) Bromobenzene was produced in a yield of 1.6% (3.5%) in addition to the products in the Table.

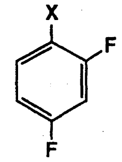
Table 2. Reactions of 2,4-Difluorohalobenzenes[a)]

| | | | |  |  |  |  |  |  | $XCH_2CN$ |
|---|---|---|---|---|---|---|---|---|---|---|
| X | Solvent | $C$/mol dm$^{-3}$ | $t$/h | (A) | (B) | (C) | (D) | (E) | (F) | (G) |
| Cl | $CH_3CN$ | 0.05 | 6 | 89.4 | 8.5(80) | < 0.5(< 5) | 0.0(0) | 0.6(6) | 0.5(5) | 0.5(5) |
| | | | 24 | 58.1 | 36.5(87) | 1.4(1) | 0.0(0) | 1.2(3) | 1.2(3) | 1.6(4) |
| Br | $CH_3CN$ | 0.05 | 6 | 84.1 | 12.9(81) | 0.4(3) | 0.6(4) | 0.7(4) | 0.3(2) | 0.5(3) |
| | | | 24 | 66.4 | 27.5(82) | 0.9(3) | 1.3(4) | 1.2(4) | 0.8(2) | 1.1(3) |
| I | $CH_3CN$ | 0.05 | 6 | 84.2 | 11.9(75) | 0.0(0) | 0.0(0) | 0.6(4) | 1.1(7) | 0.9(6) |
| | | | 24 | 68.5 | 22.1(70) | 0.0(0) | 0.0(0) | 1.1(3) | 3.1(10) | 1.9(6) |

a) Products after irradiation by a low pressure mercury arc lamp (254 nm) for $t$ h are given. The percentages of the products in reference to the consumed reactant (A) are given in parentheses.



**1: X=Cl**
**2: X=Br**
**3: X=I**



**4: X=Cl**
**5: X=Br**
**6: X=I**

Chart 1.

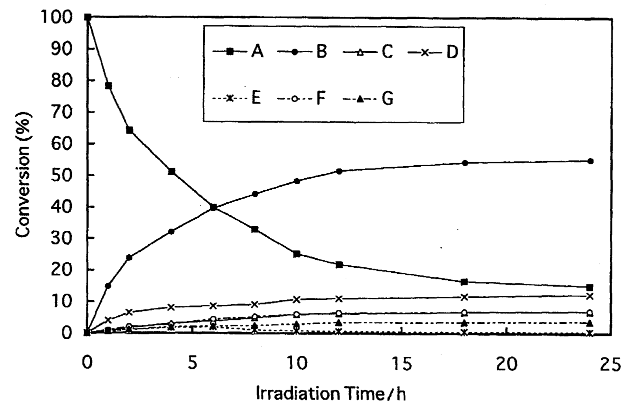


Fig. 1. Time-conversion curve for the photolysis of 2, 6-difluorobromobenzene in acetonitrile solution (0.05 mol dm$^{-3}$). (A), 2, 6- $F_2C_6H_3Br$ (reactant); (B), $m$- $F_2C_6H_4$; (C), 2, 4- $F_2C_6H_3Br$; (D), $C_6H_2Br_2F_2$; (E), $F_2C_6H_3C_6H_2F_2Br$; (F), $F_2C_6H_3C_6H_3F_2$; and (G), $ClCH_2CN$.

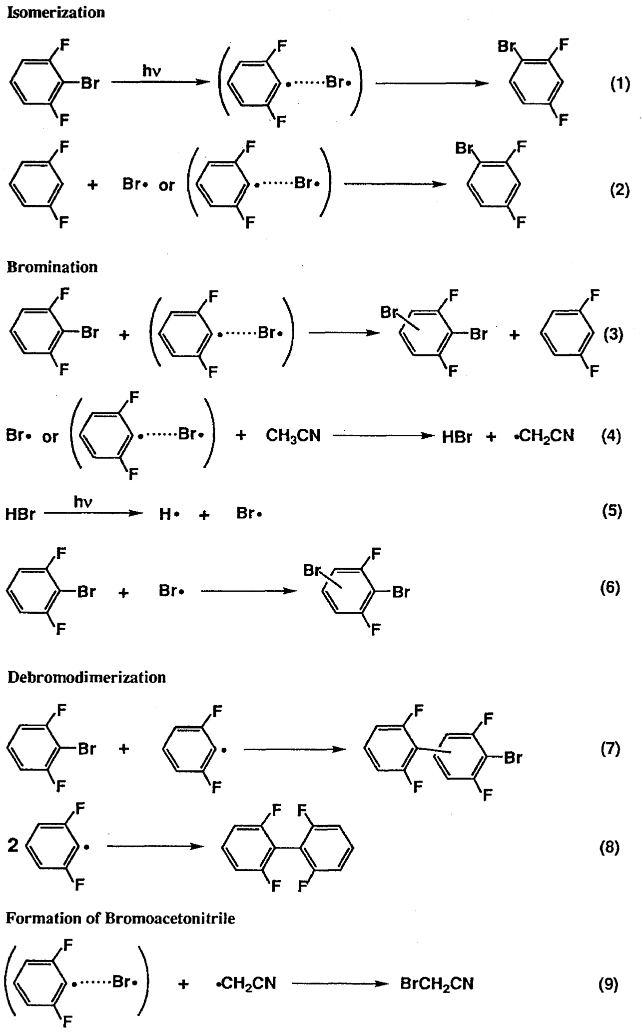
isomerized products were considerably lower than the yield from the photolysis of the corresponding chloro-analogs, if we compare the percentage of the products in reference to the consumed starting material (given in parentheses). As expected, difluoroiodobenzenes (**3** and **6**) did not give detectable amounts of the isomerized products.

In the free radical pair (Ar•/Cl•) photolytically generated from chloroarenes, chlorine atom was assumed to be stabilized, in other word, its life-time is prolonged, by forming a sort of π-complex. Its prolonged life-time is evidenced by the formation of chloroacetonitrile, the coupling product of Cl• and •$CH_2CN$. A bare chlorine atom must be too short-lived to form a detectable amount of the coupling product. Meta-migration of chlorine atom can be ascribed to the high π-spin densities at the *meta*-carbons in comparison to other carbon atoms, which was predicted by an MO calculation.[13] Analogously, formation of the isomerized product from bromoarene may suggest the intermediary presence of a relatively long-lived difluorophenyl/bromine radical pair, if we extend our aryl/chlorine radical pair hypothesis.[7,8] This sort of long-lived radical pair can be similar to the π-chlorobenzene proposed by Lemal.[14]

In sharp contrast to the runs of chloro-(**1**,**4**) and iodoarenes (**3**,**6**), the bromination of the reactant producing dibromo-derivatives was shown to occur during the photolyses of **2** and **5**. The products were characterized unambiguously by GC/MS spectrometry by observing their parent peaks at $m/z = 270$ and the well separated isotope peaks of 1 : 2 : 1 intensity rations. Neither from chlorodifluorobenzenes (**1** and **4**) nor from difluoroiodobenzenes (**3** and **6**) could similar halogenated products be obtained in detectable amounts. 1,2,3-Trifluorobenzene, which corresponds to X = F of formula 1, is inert to the irradiation of the ultraviolet light (254 nm) and remained intact even after the irradiation for 3 d. No indications of the generation of its isomer were observed.

Formation of the brominated products $C_6H_2F_2Br_2$ can be rationalized only through a bimolecular mechanism. One of the following two paths must take place in this case. In the first place, the results can be interpreted as shown by paths (4) to (6) (in Scheme 1), which involves the homolytic dissociation of the generated hydrogen bromide by the irradiation of light and the successive bromination of the reactant bromodifluorobenzene by the secondarily generated bromide atom. Here we must remark the fact that only hydrogen bromine among four hydrogen halides is known to induce the free radical reactions by the irradiation of ultraviolet light at 254 nm.[16] Secondly, the long-lived radical pair (Ar•/Br•) can attack another reactant molecule, resulting in disproportionation products ($C_6H_2F_2Br_2$ and $C_6H_4F_2$), as shown by path (3).

If we adopt the former mechanism, the involvement of intramolecular bromine migration via the radical pair (Ar•/Br•) is also suspected in the cases of the isomerization of bromoarenes. If we admit the intermolecular migration, the formation of the isomerized product can be interpreted alternatively by the debromination to form 1,3-difluorobenzene and successive bromination by use of the bromine atom generated during the debromination process (stepwise mechanism, path (2)). As a matter of course, a bromine atom generated from HBr can participate in this bromination. In fact, introduction of gaseous hydrogen bromide into the reaction system increased the isomerized and the brominated products, which supported the involvement of path (5). However, this experiment could not be accounted for quantitatively. Isomerized bromodifluorobenzene was detected as the product of an early (low conversion) stage of the photolysis. As this fact cannot be harmonized with the consecutive debromination–bromination mechanism, we think at present that the intramolecular bromine migration mechanism can participate in the isomerization at least partly.



Scheme 1. Reaction path in acetonitrile.

The reactions in other solvents were also examined. During the irradiation of 2,6-difluorobromobenzene (**2**) in benzene, photolytically generated bromine atoms tend to react more frequently with benzene than with the less abundant and assumedly less reactive halogenated benzenes ($C_6H_3F_2Br$ and $C_6H_4F_2$). Thus, the brominated product (D) was not obtained in benzene. Alternatively, bromobenzene and a small amount of biphenyl was detected in this solvent. The product ($C_6H_4F_2$) by hydrogen abstraction could be detected only in the reaction mixture after prolonged irradiation in benzene. The photolysis in benzene gave 2,6-difluorobiphenyl almost exclusively. As shown previously, the yields of dehalogenated products were relatively low in cases of the photolysis of polyhalobromobenzenes in benzene. For example, 44.2% of 2,6-dichlorobiphenyl and 3.4% of *m*-dichlorobenzene had been obtained from 2,6-dichlorobromobenzene in our previous experiment.[10].

The photolysis of 2,6-difluorobromobenzene (**2**) in perfluorohexane proceeds very slowly and gave mono-debrominated dimer $C_6H_3F_2C_6H_2F_2Br$ as the major product, which was identified by mass spectrometry. Even the difluorobenzene derivatives (**2** and **5**) which contain more than one fluorine atom are sparingly soluble in the perfluorinated solvent. As a result, the aggregation of the solute molecule might induce the preferential formation of the dimeric products. Similar phenomena were observed in our previous experiments in perfluorohexane.[2)]

## Experimental

**Materials.** All halobenzenes employed in this research are known compounds. 2,6-Difluorohalobenzenes were prepared by the known method[17)] starting from 2,6-difluoroaniline. Other halogenated benzenes and solvents were purchased commercially. All materials were used after purification by distillation or by column chromatography.

**Photo-reactions.** The photo-reactions were carried out using a 32 W (or 20 W) low pressure mercury arc lamp placed at the center of a concentrically surrounding quartz vessel containing the reactant polyhalobenzene. The reactions were carried out under nitrogen atmosphere. In obtaining the time conversion curve, a merry-go-round type apparatus for the irradiation was employed.

**Spectral and Gas Chromatographic Measurements.** Gas chromatography/mass spectrometry measurements were carried out on a Shimadzu LKB-9000B or a Shimadzu QP 1000 mass spectrometer. Routine gas chromatographic analyses of the products were carried out on a Shimadzu GC-14A apparatus equipped with an FID detector. The photo-products were identified by comparing the GC retention times with those of authentic samples. The chemical constitution of important GC eluents was checked by mass spectrometry. The quantitative determinations of the products were carried out by using the calibration diagrams drawn on the basis of the measurements on the reference samples of known compositions.

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16) Among three hydrogen halides active to addition reactions (namely HCl, HBr, and HI), only HBr is shown to react homolytically with olefins under the conditions near ambient. HCl and HI react heterolytically under similar conditions. This fact can be evidence for the homolytic fission of HBr. See, for example: M. S. Kharasch and C. Hannum, *J. Am. Chem. Soc.*, **56**, 1782 (1934).

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