2926 © 1992 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 65, 2926—2933 (1992) [Vol. 65, No. 11

Photolyses of Polychloro- and Polybromobenzenes. Novel Isomerization in Solvents Resisting against Hydrogen Abstraction

Minoru Hirota* and Masahiro Nakada[†]
Department of Synthetic Chemistry, Division of Materials Science and Chemical Engineering,
Faculty of Engineering, Yokohama National University, Hodogaya-ku, Yokohama 240
[†] Chemical Laboratory, Chiba Institute of Technology,
Shibazono, Narashino 275

(Received May 14, 1992)

Polychloro- and polybromobenzenes were photolyzed in acetonitrile and perfluorohexane. Photolyses of polychlorobenzenes in acetonitrile gave isomerized products in addition to dechlorinated products, which appeared exclusively in the photolyses in hexane and other solvents carrying hydrogen atoms active to hydrogen abstraction. The photolyses in perfluorohexane gave isomerized products to a lesser extent. The reaction in this solvent gave predominantly polyhalobiphenyls which are assumed to be produced through coupling.

Without exception the isomerized products have the structure which can be expected to be formed via 1,3-migration of chlorine atom, though it is not sure at present whether it takes place actually. The isomerization was shown to proceed intramolecularly. Some evidence and theoretical rationalization in favor of the 1,3-chlorine migration mechanism are given.

In connection with the photochemical degradation of toxic polyhalobenzenes, several photo-dehalogenation procedures of polyhaloaromatic compounds were reported.[1-4] Pinhey and Rigby,[5] and Ichimura and Mori[6,7] have studied independently the mechanism of dehalogenation of simple halobenzenes, showing that the fission of the carbon–halogen bond which proceeds via π-π* triplet state is the initial photochemical process involved. In cases where the triplet energy is not sufficient for the C–Cl bond dissociation, other, probably less efficient, processes are thought to proceed alternatively. These may be reactions from the π–π* singlet state, the C–Cl bond fission via the excimer, or electron transfer from a solvent molecule to the π–π* singlet state. As the processes involve some yet unresolved problems, several alternative interpretations[8-14] were proposed in order to rationalize them more completely.

In contrast to the initial photophysical and photochemical processes, the subsequent reactions of generated aryl free radicals have been studied rather extensively.[8] The aryl free radical generated by this initial process is assumed to induce several subsequent reactions, such as abstraction of a hydrogen atom from a solvent molecule, and substitution of a hydrogen atom in a solvent molecule, etc. However, the behavior of photolytically induced halophenyl free radicals in less reactive solvents is not clarified yet.

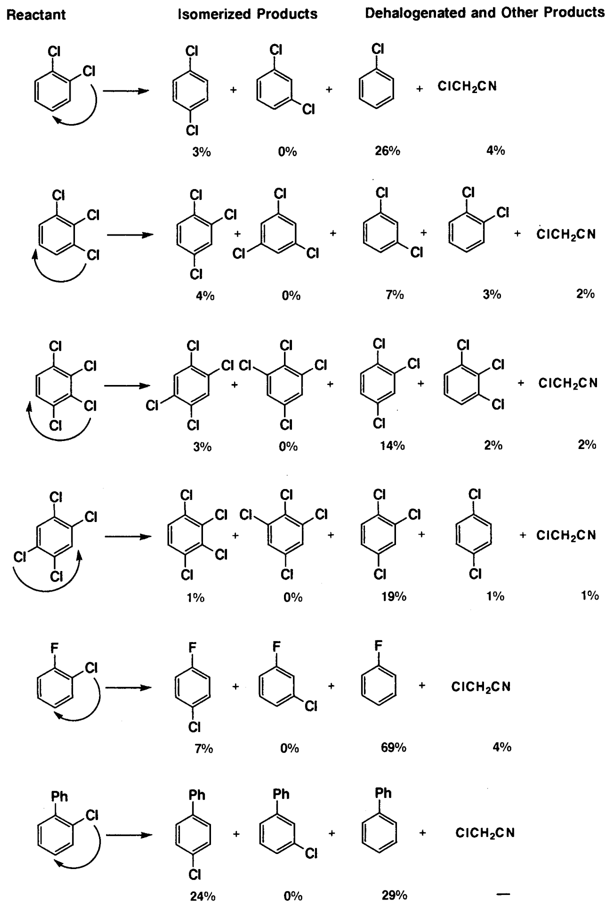
Previously we have examined the photoreactions of polyhalobenzenes in hexane[15] and in benzene,[16] showing that the reactivities of halogen atoms in the substrate depend both on its chemical environment and on the nature and the number of substituent halogen atoms.

The general trends of reactivity of halogen atoms can be summarized as follows: As easily expected from their bond dissociation energies, carbon–halogen bond becomes more susceptible to the photolysis in the order of increasing atomic number of halogen. Thus, the C–F bond is inert to the photolysis, and the C–Br bond is always more reactive than the C–Cl bond in similar circumstances. Without exception, the C–Br bond is cleaved prior to the C–Cl bond in poly-substituted bromochlorobenzenes.[15,16] When the reactivities of similar halogen atoms were compared intramolecularly, the carbon–halogen bond cleavage is always facilitated by the presence of neighboring halogen atoms. In this case, the photolysis might be accelerated by the relief from the steric congestion and by the repulsive electrostatic force operating between the contiguous halogen atoms. These trends are common with all series of reactions irrespective of the substrate subject to the attack of photolytically generated free radicals and the types of reaction, i.e. hydrogen abstraction, phenylation, etc. However, the overall rates of photoreactions are considerably different depending on the nature of the solvent. Thus, the reactions have been shown to proceed more promptly in a solvent more susceptible to hydrogen abstraction.

In this investigation, the photoreactions of polychlorobenzenes in acetonitrile and perfluorohexane were examined in the aim of clarifying their photochemical behavior in solvents less susceptible to hydrogen abstraction. Various reactions of photolytically generated haloaryl radicals were compared in connection with the properties of the solvents.

Results and Discussion

Photolysis in Acetonitrile and Perfluorohexane. When hexane and methanol were employed as solvents, dehalogenation proceeds exclusively producing (poly)-halobenzenes bearing one less halogen atom.[15] The halogen atoms were shown to be removed successively forming polydehalogenated products. The dehalogenation has been supposed to proceed via the successive thermal



Scheme 1. Photolysis of Polychlorobenzenes and related compounds in acetonitrile (0.1 M solution, yields after 8 h irradiation are given).

hydrogen abstraction by the aryl radical generated by the initial photolytic cleavage of the carbon–halogen bond. Thus the reaction was examined in some solvents resisting against hydrogen abstraction. From this point of view, several solvents such as benzene, acetonitrile, and perfluorohexane were chosen. The photolysis in benzene has already been reported previously.[16] Phenylation is generally far more favorable than hydrogen abstraction in this solvent, though both reactions proceed competitively.

Since the phenylation cannot occur in acetonitrile, the photolyses of several polyhalobenzenes in this solvent were examined. In some runs, the photo-isomerization via *meta*-migration of chlorine was shown to proceed. The products and their yields of the photoreactions accompanying the isomerization are shown in Scheme 1. The results of the reactions of other polyhalobenzenes are given in Table 1.

The hydrogen atoms of acetonitrile are less reactive towards abstraction by photolytically generated aryl free radicals than those of hexane and methanol. Decrease in reactivity is demonstrated by the fact that the overall rate in acetonitrile is lower than those in methanol and hexane (Table 6). However, dehalogenation is still the major path even in acetonitrile. Especially, the photolyses of polybromobenzenes gave the dehalogenated products exclusively. Again the most crowded halogen atom is eliminated most easily in the reactions of both polychloro- and polybromobenzene series. For example, 1,2,3-trihalo- and 1,2,3,4-tetrahalobenzenes gave *m*-dihalo- and 1,2,4-trihalobenzenes, respectively, as the major mono-dehalogenated products irrespective of the nature of halogen atom.

Besides the dehalogenated products, several polychlorobenzenes gave isomerized products as minor products. Without exception, the obtained isomer could be expected to be formed via 1,3(*meta*)-migration of either chlorine atom. Possible paths of migration are illustrated by arrowed bows in Scheme 1. Thus, *meta*-migration of chlorine atom might be the characteristic feature of this novel photo-induced rearrangement. The rearrangement was also shown to proceed with *o*-chlorobiphenyl in acetonitrile solution (0.1 M, 1 M= 1 mol dm^{-3}). It produced 22.4% of *p*-chlorobiphenyl (rearranged product) and 28.8% of biphenyl (dehalogenated product) after 48 h irradiation. Similar reactions had been shown to proceed in benzene.[16] This novel rearrangement reaction will be discussed further in the following section.

In order to examine the photochemical behavior of polychlorobenzenes under the conditions where the possibility of hydrogen abstraction from the solvent is excluded, perfluorohexane was used as the solvent. The results are given in Table 2. The experiments were planned in the expectation that the newly found isomerization would become predominant in this solvent. Most of photoreactions in this solvent were carried out on (poly)chlorofluorobenzenes because of their higher solubility than the corresponding polychloro compounds. Quite unexpectedly, the major product was an isomeric mixture of halogenated biphenyls. The abundance of the produced biphenyls could not be determined exactly because they crystallized out on the wall of the reaction vessel from the solution. In this case, photolytically generated halophenyl radical seemed to react with another molecule of the reactant polychlorofluorobenzene forming halogenated biphenyl bearing one less chlorine atom. (Hereafter, this sort of reaction is termed "coupling" for simplicity.) For example, the run on *o*-chlorofluorobenzene gave at least three isomeric chlorodifluorobiphenyls which are identified by GC/MS measurement by monitoring the molecular ion peak at m/z 224. The molecular ion peak is the most intense peak (base peak) accompanied by an isotope peak at m/z 226. The $(M-35)^+$ and $(M-36)^+$ peaks were the second and the third intense peaks in their mass spectra revealing the fact that the molecular ion fragments by eliminating Cl or HCl.

In this solvent, isomerization did not proceed as the major path, giving only 0.7% of the *p*-isomer from *o*-

Table 1. Products by the Photolyses of Polyhalobenzenes in Acetonitrile

Reactant	C/%[a]	Products (Yield/%)[b]
(a) Polychlorobenzenes		
m-$\mathrm{Cl_2C_6H_4}$	6	$\mathrm{C_6H_5Cl}$ (6)
p-$\mathrm{Cl_2C_6H_4}$	2.5	$\mathrm{C_6H_5Cl}$ (2.5)
1,2,4-$\mathrm{Cl_3C_6H_3}$	11	o-$\mathrm{Cl_2C_6H_4}$ (0.5), m-$\mathrm{Cl_2C_6H_4}$ (0.5), p-$\mathrm{Cl_2C_6H_4}$ (10), $\mathrm{ClCH_2CN}$ (1.2)
1,3,5-$\mathrm{Cl_3C_6H_3}$	2	m-$\mathrm{Cl_2C_6H_4}$ (2)
1,2,3,5-$\mathrm{Cl_4C_6H_2}$	15	m-$\mathrm{Cl_2C_6H_4}$ (0.5), p-$\mathrm{Cl_2C_6H_4}$ (0.5), 1,2,4-$\mathrm{Cl_3C_6H_3}$ (8), 1,3,5-$\mathrm{Cl_3C_6H_3}$ (6), $\mathrm{ClCH_2CN}$ (2)
$\mathrm{Cl_5C_6H}$	27	1,2,4-$\mathrm{Cl_3C_6H_3}$ (1.0), 1,2,3,4-$\mathrm{Cl_4C_6H_2}$ (3), (1,2,3,5+1,2,4,5)-$\mathrm{Cl_4C_6H_2}$ (23)
(b) Polybromobenzenes		
o-$\mathrm{Br_2C_6H_4}$	17	$\mathrm{C_6H_5Br}$ (17)
m-$\mathrm{Br_2C_6H_4}$	4	$\mathrm{C_6H_5Br}$ (4)
p-$\mathrm{Br_2C_6H_4}$	7	$\mathrm{C_6H_5Br}$ (7)
1,2,3-$\mathrm{Br_3C_6H_3}$	20	o-$\mathrm{Br_2C_6H_4}$ (5), m-$\mathrm{Br_2C_6H_4}$ (14)
1,2,4-$\mathrm{Br_3C_6H_3}$	11	o-$\mathrm{Br_2C_6H_4}$ (1.1), m-$\mathrm{Br_2C_6H_4}$ (3), p-$\mathrm{Br_2C_6H_4}$ (7)
1,3,5-$\mathrm{Br_3C_6H_3}$	4	m-$\mathrm{Br_2C_6H_4}$ (4)
1,2,3,5-$\mathrm{Br_4C_6H_2}$	20	1,2,4-$\mathrm{Br_3C_6H_3}$ (6), 1,3,5-$\mathrm{Br_3C_6H_3}$ (14)
(c) Polychlorofluorobenzenes		
o-$\mathrm{ClC_6H_4F}$	76.2	$\mathrm{C_6H_5F}$ (69.1), p-$\mathrm{ClC_6H_4F}$ (7.1)
m-$\mathrm{ClC_6H_4F}$	46.4	$\mathrm{C_6H_5F}$ (46.4)
p-$\mathrm{ClC_6H_4F}$	1.0	$\mathrm{C_6H_5F}$ (1.0)
2,3-$\mathrm{Cl_2C_6H_3F}$	24.6	o-$\mathrm{ClC_6H_4F}$ (2.3), m-$\mathrm{ClC_6H_4F}$ (4.6), 2,5-$\mathrm{Cl_2C_6H_3F}$ (10.6), 3,4-$\mathrm{Cl_2C_6H_3F}$ (4.4)
2,4-$\mathrm{Cl_2C_6H_3F}$	18.5	p-$\mathrm{ClC_6H_4F}$ (14.4), Unidentified (2.1)[c]
2,5-$\mathrm{Cl_2C_6H_3F}$	12.7	o-$\mathrm{ClC_6H_4F}$ (1.4), m-$\mathrm{ClC_6H_4F}$ (10.1)
2,6-$\mathrm{Cl_2C_6H_3F}$	20.6	o-$\mathrm{ClC_6H_4F}$ (8.3), p-$\mathrm{ClC_6H_4F}$ (5.8), 2,4-$\mathrm{Cl_2C_6H_3F}$ (6.5)
3,4-$\mathrm{Cl_2C_6H_3F}$	51.3	m-$\mathrm{ClC_6H_4F}$ (0.7), p-$\mathrm{ClC_6H_4F}$ (46.0), 2,5-$\mathrm{Cl_2C_6H_3F}$ (4.6)
3,5-$\mathrm{Cl_2C_6H_3F}$	18.1	m-$\mathrm{ClC_6H_4F}$ (15.7), Unidentified (1.9)[c]

a) C=conversion of the reactant. b) Yields after irradiation for 8 h were given in parentheses. Time-conversion curves of the reactions showed that the reactant decreased exponentially and that the monodehalogenated and isomerized products produced primarily from the reactant. (See Fig. 1 as an example). c)The amount of the unidentified products were estimated by assuming that their G.C. peaks have intensities similar to chlorofluorobenzene.

Table 2. Products by the Photolyses of Chloro- and Dichlorofluorobenzenes in Perfluorohexane

Reactant	C/%	Products (Yields (%) after the irradiation for 12 h)[a]
o-$\mathrm{ClC_6H_4F}$	47.8	$\mathrm{C_6H_5F}$ (3.1), p-$\mathrm{ClC_6H_4F}$ (0.7), $\mathrm{F_2ClBP}$ (44.0)
m-$\mathrm{ClC_6H_4F}$	24.9	$\mathrm{F_2ClBP}$ (24.9)
p-$\mathrm{ClC_6H_4F}$	52.5	$\mathrm{C_6H_5F}$ (0.7), $\mathrm{F_2ClBP}$ (51.8)
2,3-$\mathrm{Cl_2C_6H_3F}$	31.5	o-$\mathrm{ClC_6H_4F}$ (0.2), $\mathrm{F_2Cl_3BP}$+$\mathrm{F_2Cl_2BP}$ (31.3)[b]
2,4-$\mathrm{Cl_2C_6H_3F}$	38.6	$\mathrm{C_6H_5F}$ (0.2), p-$\mathrm{ClC_6H_4F}$ (0.3), $\mathrm{F_2Cl_3BP}$+$\mathrm{F_2Cl_2BP}$ (38.1)[b]
2,5-$\mathrm{Cl_2C_6H_3F}$	32.8	$\mathrm{F_2Cl_3BP}$+$\mathrm{F_2Cl_2BP}$ (32.8)
2,6-$\mathrm{Cl_2C_6H_3F}$	29.8	o-$\mathrm{ClC_6H_4F}$ (0.1), $\mathrm{F_2Cl_3BP}$+$\mathrm{F_2Cl_2BP}$ (29.7)[b]
3,4-$\mathrm{Cl_2C_6H_3F}$	25.0	p-$\mathrm{ClC_6H_4F}$ (0.2), $\mathrm{F_2Cl_3BP}$+$\mathrm{F_2Cl_2BP}$ (24.8)
3,5-$\mathrm{Cl_2C_6H_3F}$	20.9	$\mathrm{F_2Cl_3BP}$ (20.9)[c]

a) BP=biphenyl. All polyhalogenated biphenyls ($\mathrm{F_2Cl_3BP}$ and $\mathrm{F_2Cl_2BP}$) are identified only by GC/MS. They were shown to be a mixture of several isomers, but the positions of halogen atoms were not determined. The total amount of the biphenyls were estimated as the difference between the conversion and all other products identified because they tend to crystallize on the wall of the reaction vessel, which made their quantitative determination difficult. b) Small amounts (less than 10% from the intensity of their GC peak) of unidentified products are included. They are assumed to be further dechlorinated products from their GC/MS. c) Only a very small amount of $\mathrm{F_2Cl_2BP}$ was detected.

chlorofluorobenzene, and seemed even less favorable than in acetonitrile. Dehalogenation product was detected in a small amount. It was thought to be produced through hydrogen abstraction from another polyhalobenzene molecule. The rate of the consumption of starting polyhalobenzene is almost comparable to the reaction of the same compound in acetonitrile. However, the percentage of the isomerized product is far less than the relevant photolysis in acetonitrile. In constrast, coupling was not observed in acetonitrile. As perfluorohexane is a nonpolar solvent with poor solubilizing power, the solute may exist as a multimolecular aggregate, which is favorable to produce the coupling species.

Characterization of the Novel Isomerization Involving 1,3-Migration of Chlorine Atom. The isomerization involving 1,3-migration was observed with polychlorobenzenes[17] carrying a sterically crowded chlorine atom. Therefore, the relief from the crowdedness might be the driving force of the migration. Since the isomerization occurs in competition with the hydrogen abstraction and other reaction paths, it became observable when the photolysis was carried out in solvents less reactive towards hydrogen abstraction. Acetonitrile is the most favorable solvent for the isomerization. It was also observed in benzene and in perfluorohexane to lesser extents. Since acetonitrile can form a solvent cage rather favorably, 1,3-migration of chlorine atom can be expected to proceed via an aryl–chlorine radical pair whose lifetime is prolonged in the solvent cage. Along with the isomerized product, a small amount of chloroacetonitrile was detected in almost all runs in acetonitrile (Scheme 1). Formation of chloroacetonitrile can be rationalized by the coupling reaction (1) of cyanomethyl radical with chlorine atom forming a radical pair. Thus a considerably long lifetime of chlorine atom as the radical pair was indirectly proven.

$$\cdot CH_2CN + [Ar\cdot/Cl\cdot]_{cage} \longrightarrow ClCH_2CN + Ar\cdot \qquad (1)$$

In order to characterize the reaction of isomerization more definitely, several additional experiments were carried out. In the first place, the migrating tendency of halogen atoms was examined. *o*-Difluorobenzene was intact under the conditions for the isomerization of the chlorinated benzenes and gave neither isomerized product nor defluorinated product. On the other hand, *o*-dibromo- and other polybromobenzenes gave only debrominated products. Thus, the isomerization is characteristic of haloarenes carrying a congested chlorine atom.

The kinetic measurements served to elucidate the mechanism of the rearrangement. In the aim of eliminating any ambiguity in the interpretation of the reaction paths, precise rate measurements was carried out on *o*-chlorofluorobenzene. Its C–F bond is inert to the photolysis and only its C–Cl bond is subjected to the photolytic cleavage. The ratios of isomerized product vs. dehalogenated product were measured as a function of the concentrations of the starting *o*-chlorofluorobenzene in order to determine the molecularity of the reaction. Results are given in Table 3.

If the isomerization involves an intermolecular halogen transfer process, its rate should be dependent on the concentration and should be favorable when the concentration of the substrate is high. In such a case, the ratio ([*p*-FC_6H_4Cl]/[C_6H_5F]) should increase as the concentration of the starting *o*-chlorofluorobenzene increases. However, the ratio does not vary considerably at three concentrations. This can be evidence to assume that the migration should take place intramolecularly. Tokumaru and co-workers[14] observed the fact that the photolysis of neat chlorobenzene gave an isomeric mixture of chlorobiphenyls in an anomalous ratio, and explained this ratio by a mechanism through excimer. Isomerization through excimer can also occur in our experiments since the coupling did take place actually in the perfluorohexane solution of a similar concentration. However, the bimolecular mechanism is not pertinent to the experiment on the concentration dependency in acetonitrile.

In order to exclude a possibility that the isomerized product is formed secondarily by the chlorination of the dechlorinated product, the amount of isomerized product was pursued as a function of the reaction period (Table 4). The yields of the isomerized products behave as primary products from the reactant, and are not dependent on the concentrations of the dechlorinated product. A typical example of the time-conversion curve is illustrated in Fig. 1. The rate of formation of the isomerized product is proportional to the decrease in the reactant. Thus the isomerization is shown to

Table 3. Effect of Concentration on the Isomerized Product vs. Dechlorinated Product Ratio During the Photolysis of *o*-Chlorofluorobenzene in Acetonitrile

Concentration	0.05 M	0.1 M	0.2 M
Product[a] *p*-FC_6H_4Cl(%)	4.9 (7.5)	2.7 (4.7)	0.7 (1.3)
Product[a] C_6H_5F(%)	39.1 (65.7)	19.8 (35.8)	6.0 (11.2)
Ratio (*r*)	0.125 (0.114)	0.136 (0.131)[b]	0.117 (0.116)

a) Yields (%) in reference to the starting *o*-FC_6H_4Cl after the irradiation for 4 h (8 h in parenthese) are given.
b) In another run, the yields (after 4 h) of *p*-FC_6H_4Cl and C_6H_5F are 4.7% and 42.0%, respectively, giving 0.112 as the ratio.

Table 4. Products of the Photolysis of *o*-Chlorofluorobenzene (0.1 M) in Acetonitrile

Reaction period	4 h	8 h	16 h	24 h
Product *p*-ClC_6H_4F(%)	2.4	4.7	6.2	7.1
Product C_6H_5F(%)	22.8	42.0	59.3	69.1
Ratio ([*p*-ClC_6H_4F]/[C_6H_5F])	0.105	0.112	0.105	0.103

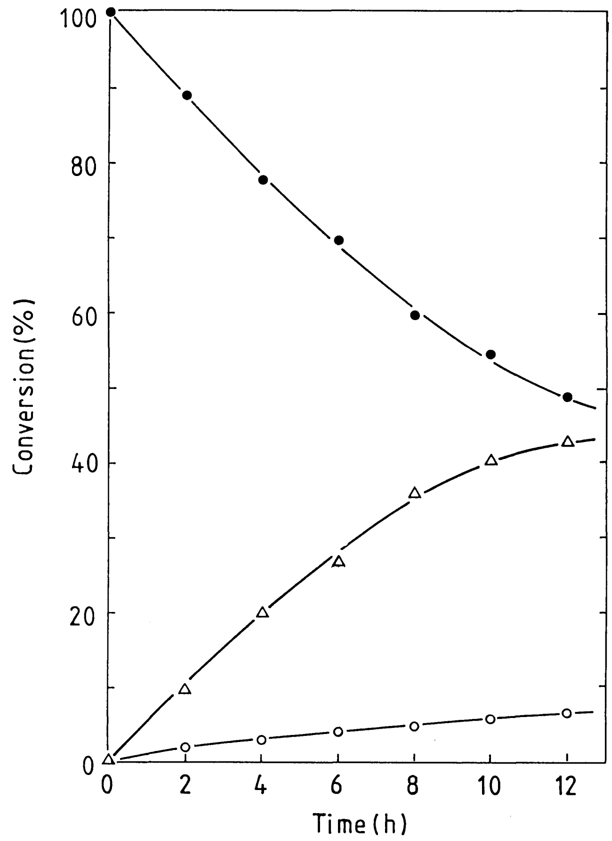


Fig. 1. Time-conversion curve for the photolysis of *o*-chlorofluorobenzene (shown by filled circles) in the 0.1 M acetonitrile solution. Open circles and triangles refer to *p*-chlorofluorobenzene (isomerized product) and fluorobenzene (dechlorinated product), respectively.

proceed primarily from the starting (poly)chlorobenzene.

Reactions in deuteriated solvents are often very effective in making clear the origin of hydrogen in the isomerized product. For this purpose, *o*-chlorofluorobenzene was photolyzed in trideuterioacetonitrile. The reactant and the products were analyzed by GC/MS. It is a remarkable fact that about 90% of *p*-chlorofluorobenzene retains hydrogen after isomerization by 12 h irradiation. Deuterium is incorporated only partly. However, the content of deuterium in the isomerized product seemed to increase as the reaction period was prolonged.

As easily understood from the time-conversion curve in Fig. 1, the isomerization proceeds competitively with the hydrogen abstraction. The hydrogen abstraction is too predominant over the isomerization to form a detectable amount of the isomerized product when the photolysis was carried out in solvents very susceptible to hydrogen abstraction. For this reason, the isomerization products could not be identified with the photolyses in hexane and in methanol. Phenylation predominates over hydrogen abstraction and isomerization in benzene. Consecutive phenylation producing terphenyl proceeds so slowly as to allow the competitive isomerization to proceed to an observable extent.

Based on these experiments, the mechanism of the chlorine migration is discussed. Photo-isomerizations of aromatic compounds have been studied extensively in relation to the valence isomerization of benzene. The valence isomerization of benzene can proceed through several of its valence isomers. Most important paths are the isomerization through benzvalene and prismane. The interconversions among valence isomers proceed unimolecularly and can be expected to give an isomer without hydrogen exchange. From this respect, the mechanism through the valence isomers is compatible with our experiment. However, the path through a benzvalene is expected to induce 1,2(*ortho*)-migration, and the path through a prismane should induce 1,2- and 1,4(*para*)-migration. 1,3-Migration can be expected to take place via valence isomers, only when we assume the fission and reorganization of C–C bonds in the valence isomers. Even if we admit that the reorganization proceeds extensively, there is no explanation for the very clear preference for 1,3-migration, however. In contrast, the isomerization proceeds exclusively through 1,3-migration and, until now, we have not detected the isomerized product which could not be produced through 1,3-migration. Moreover, inertness of *o*-difluorobenzene cannot be explained properly by this mechanism. For this reason, the isomerization does not seem to proceed via valence isomers.

Regarding the photolysis of chlolobenzene, the π-chlorobenzene intermediate had been proposed by Lemal and co-workers[9] in order to explain the formation of chlorocyclohexane during the photolysis of chlorobenzene in cyclohexane. He thought that the lifetimes of very reactive chlorine atoms were prolonged by the complex formation with phenyl free radical. However, this hypothesis was contradicted by Arnold.[11] He explained the formation of chlorocyclohexane by the photo-sensitized addition of hydrogen chloride to cyclohexene. His contradiction was based on the fact that (3-chloropropyl)benzene was not found as a product of the photolysis of *o*-chloropropylbenzene.

Our cage-protected radical pair is rather similar to π-chlorobenzene if the chlorine atom is complexing with the π-electrons of aryl free radical. From this point of view, the π-chlorobenzene mechanism by Lemal is compatible in several points with our experiments on photo-isomerization. Tentative INDO-UHF molecular orbital calculation on *o*-halophenyl free radical showed that a considerable positive spin density should be induced at the *meta*-position in addition to the free radical center (*ipso*-position).[18] The spin at the *meta*-position occupies the π-orbital and favorable to interact with the chlorine atom in the initial stage of 1,3-migration (Fig. 2).

Formation of chloroacetonitrile is evidence favorable to this mechanism because it suggests the coupling of long-lived chlorine atom (supposedly in the solvent

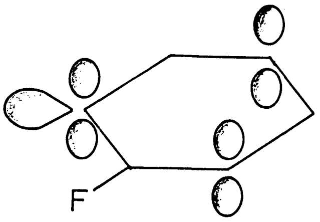


Fig. 2. Schematic illustration of the spin distribution in *o*-fluorophenyl radical. Tentative MNDO calculation without spin annihilation gave positive spins on the *p*-orbitals of *meta*-carbon atoms in addition to the *ipso*-carbon atom.

cage) with cyanomethyl radical which is generated by the hydrogen abstraction by the aryl radical. The slower overall rates in acetonitrile can be accounted for by the reversion to the starting *o*-chlorofluorobenzene from the radical pair. The partial incorporation of deuterium from the solvent acetonitrile can be expected if we assume that the intramolecular shift of hydrogen atom is competing with the hydrogen abstraction from the solvent. The reversion explains also the fact that the amount of deuterium incorporated in the isomerized product increases gradually as the reaction period is prolonged.

Solvent Effect on the Photolyses. Throughout a series of our investigations on the photolyses of polyhalobenzenes,[15,16,19] the important role of solvents has become clear. In most cases, the solvent usually serves as a reactant with the photolytically generated aryl radical and can be expected to play an important role in the secondary reactions. For this reason, solvents of various reactivity towards hydrogen abstraction were chosen, and the solvent effect was examined. In practice, these five solvents, namely methanol, hexane, acetonitrile, benzene, and perfluorohexane were employed in this series of research.

As a conclusion from the photolyses in these solvents, the photolysis was shown to proceed through one or several of the following paths depending on the nature of the solvent:

i) Dehalogenation to produce polyhalobenzene bearing one less halogen atom(s) proceeds in all solvents investigated. Dehalogenation can proceed consecutively forming multiply dehalogenated products.

ii) Phenylation to produce halogenated biphenyl proceeds in benzene solutions. Consecutive phenylation gave terphenyls in several runs.[16] The steric requirement in the terphenyl formation is considerably different between the photolyses of polychloro- and polybromobenzenes. The former produced *o*-terphenyl exclusively, while the latter prefers to form *m*- and *p*-terphenyls.[19]

iii) Isomerization was shown to take place in solvents resisting towards hydrogen abstraction, giving a 1,3-migrated product selectively. This path occurs only with polychlorobenzenes.

iv) The last path is coupling. Strictly speaking, this term refers to the reaction in which photo-excited polyhalobenzene, or its descent, reacts with another polyhalobenzene molecule in the ground state producing halogenated biphenyl. Coupling was observed only in perfluorohexane solutions. The reaction has often been observed with neat (poly)halobenzenes and accounted to proceed via excimer.

The relative importance of the paths in various solvents are shown in Table 5 by the examples of the photolysis of *o*-dichlorobenzene. The C–H bond dissociation energies of acetonitrile, methanol, hexane,[20] and benzene are 86, 92, 94.5, and 112 kcal mol^{-1}, respectively.[21] The reactivity towards hydrogen abstraction decreases in the increasing order of the C–H bond dissociation energies except for acetonitrile. Acetonitrile had been shown to be far less reactive than alkenes in the free radical chlorination, the rate determining step of which is supposed to be hydrogen abstraction process. Russell[22] reported that the rates of chlorination relative to CH_4 are 3.6 and 0.004 for the secondary CH_2 of pentane and for CH_3 of acetonitrile, respectively. This can be attributed to the electrophilic nature of chlorine atom. Thus, the reactivity sequence of the solvents was rationalized. Perfluorohexane has no hydrogen atoms.

In order to estimate more clearly the reactivities of a series of polyhalobenzenes in these five solvents, the relative rate for the consumption of the starting polyhalobenzenes were determined from the time-conversion curves (Table 6). The rate data revealed some interesting trends of the photolytic reactions.

Table 5. Solvent Effect on the Reaction Paths in the Photolysis of *o*-Dichlorobenzene

Solvent	Dehalogenation	Isomerization	Coupling	Phenylation
C_6H_{14}	100%	0%	0%	—
C_6H_6	0%	0%	0%	100%
CH_3OH	100%	0%	0%	—
CH_3CN	89% (82%)[a]	11% (18%)[a]	0%	—
C_6F_{14}[a]	3%	2%	>20%[b]	—

a) Data for *o*-chlorofluorobenzene. b) In addition to coupling products, several unidentifed products were obtained as pasty solid.

Table 6. Relative Overall Rates of the Photolyses of Polyhalobenzenes in 0.1 M Solutions Measured by the Decrease of the Reactant[a)]

(a) Polychloro- and Polybromobenzenes

Solvent	C_6H_6	CH_3CN	n-C_6H_{14}	CH_3OH	CH_3CN	n-C_6H_{14}
X	Cl	Cl	Cl	Cl	Br	Br
o-$X_2C_6H_4$	0.51 (1.00)	1.00[b)]	1.50 (1.00)	2.92 (1.00)	1.00[c)]	16 (1.00)
m-$X_2C_6H_4$	0.32 (0.62)	0.21	0.34 (0.23)	0.46 (0.16)	0.16	14 (0.9)
p-$X_2C_6H_4$	0.18 (0.35)	0.043	0.092 (0.061)	0.066 (0.023)	0.40	19 (1.2)
1,2,3-$X_3C_6H_3$	0.27 (0.52)	0.41	3.7 (2.4)	2.6 (0.89)	1.13	47 (2.9)
1,2,4-$X_3C_6H_3$	0.26 (0.51)	0.32	1.6 (1.1)	1.8 (0.60)	0.63	50 (3.1)
1,3,5-$X_3C_6H_3$	0.23 (0.46)	0.066	0.27 (0.18)	0.19 (0.066)	0.22	29 (1.8)
1,2,3,4-$X_4C_6H_2$	0.29 (0.57)	0.73	5.0 (3.3)	6.8 (2.3)	—	3.9×10^2 (24)
1,2,3,5-$X_4C_6H_2$	0.083 (0.16)	0.43	2.6 (1.7)	3.8 (1.3)	1.36	2.8×10^2 (17)
1,2,4,5-$X_4C_6H_2$	0.077 (0.15)	0.72	2.3 (0.80)	3.7 (1.3)	—	3.2×10^2 (20)
C_6HX_5	—	0.92	3.7 (2.45)	—	—	

(b) Mono- and Dichlorofluorobenzenes

Solvent	CH_3CN	n-C_6F_{14}
X[d)]	Cl	Cl
o-ClC_6H_4F	1.00[e)]	0.449 (1.00)
m-ClC_6H_4F	0.574	0.302 (0.67)
p-ClC_6H_4F	0.302	0.565 (1.26)
2,3-$Cl_2C_6H_3F$	0.225	0.396 (0.88)
2,4-$Cl_2C_6H_3F$	0.227	0.233 (0.52)
2,5-$Cl_2C_6H_3F$	0.184	0.252 (0.56)
2,6-$Cl_2C_6H_3F$	0.268	0.207 (0.46)
3,4-$Cl_2C_6H_3F$	0.661	0.166 (0.37)
3,5-$Cl_2C_6H_3F$	0.236	0.126 (0.28)

a) Polychlorobenzenes and polychlorofluorobenzenes were photolyzed using 32 W low pressure lamp and a quartz reaction vessel closely surrounding the light source. Polybromobenzenes were photolyzed using 100 W high pressure lamp in the same reaction vessel. The relative rates were guaranteed by the correction (usually small) using chemical actinometer. b) The absolute rate is $1.20\times10^{-5}\ s^{-1}$. However, only the relative rates are meaningful. c) The absolute rate is $6.7\times10^{-6}\ s^{-1}$ under the conditions given in footnote a. d) X is the reactive atom in this case. e) The absolute rate is $4.37\times10^{-5}\ s^{-1}$ under the conditions given in footnote a.

When the reaction of a polychlorobenzene was compared with that of the polybromobenzene of the same pattern of substitution, the steric effect by the neighbor halogen atom seemed to act more stringently in polychlorobenzenes, accelerating the cleavage of sterically crowded C–Cl bond more selectively than the C–Br bond under similar circumstances. When the reactivities were compared among isomers, again the more crowded polyhalobenzene tends to be photolyzed more easily. As a whole, the overall rate is rather insensitive to the degree of halogen substitution (number of halogen atom) on the benzene ring. However, the reactions of highly substituted polychlorobenzenes tend to be deactivated more significantly as the reactivity of the solvent decreases. Similar trend was observed with the photolyses of polybromobenzenes. An only exception is the fact that the photolysis of polybromobenzenes in hexane is accelerated as the number of halogen atoms on the aromatic nucleus increases.[15)]

Experimental

Materials. All of halobenzenes employed in this research are known compounds. They were either purchased commercially or prepared by the known methods[23,24)] and used after purification by distillation or by column chromatography.

Photoreactions. The photoreactions 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 solution of the reactant polyhalobenzene. They were carried out under nitrogen atmosphere unless otherwise remarked. In some runs, a merry-go-round type apparatus was employed.

Spectral and Gas Chromatographic Measurements. Gas chromatography/mass spectrometry measurements were carried out on a Hitachi RMU-6L, a Shimadzu LKB-9000-B, or a Shimadzu QP1000 mass spectrometer. Routine gas chromatographic analyses of the products were carried out on a Shimadzu GC-6A or a GC-4B-PFT apparatus equipped with a Silicone SE 30 or Apiezon L column (3 mm×2 m).

The authors thank Professor Sachio Fukushi, Chiba Institute of Technology, for his advice and encouragement throughout this work. They are grateful to Dr. Kazuhisa Sakakibara, Dr. Hiroko Suezawa, Mr. Yasuki Miura, Mr. Kenji Morisaki, and Mr. Futoshi Higashi, Yokohama National University, and to Mr. Chihiro Miura, Mr. Kazuo Ogawa, and Miss Reiko Hayashida, Chiba Institute of Technology, for their cooperation to this work. This research was supported partly by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, to which they are also grateful.

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19) We have no evidence at present, but the following mechanism may explain the photolysis of chlorobiphenyls and also the difference in photochemical behaviors between chloro- and bromobiphenyls. The photoreaction sensitized by benzene can proceed in competition with the reaction induced by the direct absorption of light by the halobenzene molecule. Thus an exciplex is formed between the benzene molecule in the excited state and the halobenzene molecule in the ground state. Phenylcyclohexadienyl free radical is consecutively formed from the exciplex. The photolysis may proceed from π–π^* singlet state.

20) As we could not find out the value for CH_2 groups in hexane, the bond dissociation energy of the CH_2 group of propane was cited instead. Both are of the secondary carbon atoms and can be expected to be similar.

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