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Photoreactions of Polyhalobenzenes in Benzene. Formation of Terphenyls

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Polychlorobenzenes, polybromobenzenes, and polychloropolybromobenzenes ($C_6H_{6-n}X_n$) were photolyzed in benzene solutions; the products were analyzed by the GC/MS method. Both dehalogenation and phenylation were shown to take place competitively, producing (poly)halobenzenes bearing one less halogen atom ($C_6H_{7-n}X_{n-1}$) and (poly)halobiphenyls ($C_6H_{6-n}X_{n-1}$-C_6H_5) as the major products. Besides these products, terphenyl was produced by a consecutive phenylation of the halobiphenyl formed. Polychlorobenzenes were shown to form the corresponding terphenyls only when a pathway via 2-chlorobiphenyl is possible; however, polybromobenzenes can produce terphenyls through any of the isomeric bromobiphenyls intermediarily formed. Isomerization through *m*-migration of a chlorine atom was also shown to occur to a considerably lesser extent.

In connection with the photochemical degradation of toxic polyhalobenzenes, several photo-dehalogenation procedures of polyhaloaromatic compounds have been reported.[1-4] Pinhey and Rigby,[5] as well as Ichimura and Mori,[6,7] have independently studied the mechanism of dehalogenation of simple halobenzenes, showing that the initial photochemical process is the fission of the carbon-halogen bond proceeding via a pi-pi* triplet state, of this reaction involved. In contrast to the initial photophysical and photochemical processes involved, the subsequent reactions of the aryl free radicals generated from monohalobenzenes have been extensively studied.[8] The aryl free radical generated by this initial process is assumed to induce several subsequent reactions, such as the abstraction of a hydrogen atom from the solvent, substitution of a hydrogen atom in the solvent molecule, etc. However, relatively few investigations have been reported on the photolytic behavior of polyhalobenzens.[3,4]

We previously examined the photoreactions of polyhalobenzenes in both hexane[9] and acetonitrile,[10] showing that the reactivities of halogen atom in the substrate depend both on its chemical environment and on the nature and number of substituent halogen atoms. It was also shown that a more crowded halogen atom leaves more easily. The photolyses were also dependent on the nature of the solvent, giving isomerized products in solvents which resist hydrogen abstraction.

In this paper, we discuss the photochemical behavior of polyhalobenzenes in benzene solutions, where both dehalogenation and phenylation take place competitively. Special attention is paid to the formation of terphenyls by the consecutive phenylation of the halobiphenyls primarily formed.

Experimental

Materials. The polyhalobenzenes and chlorobiphenyls employed in this research are all known compounds. They were either purchased commercially or prepared by the known methods[11,12] 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 a nitrogen atmosphere, unless otherwise noted.

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-PTF apparatus equipped with a Silicone SE 30 or an Apiezon L column (3 mm×2 m).

Results and Discussion

General Trends of the Photoreactions. As described in our previous papers,[9,10] the photoreactions were pursued by quantitative GC analyses of the products and the unreacted starting halobenzene. Since our interests were focused on the products in various solvents, only the relative reactivity is presented and discussed. The reaction mixture was sampled at regular intervals and the products were analyzed. The products at halfway conversions of various polyhalobenzenes are given in Table 1.[13]

The reactions in benzene solutions proceeded far more slowly than those in hexane. They are even slower than those in acetonitrile, which is assumed to be a less reactive solvent towards hydrogen abstraction. For example, *o*-dichlorobenzene was photolyzed 26.5-times faster in hexane and 17.6-times faster in acetonitrile when compared with a similar reaction in benzene. The retardation by benzene is quite general in the photolyses in Table 1; it might be ascribable to light absorption by the solvent.

As foreseen from the previous results,[8,14] both dehalogenation and phenylation reactions proceed com-

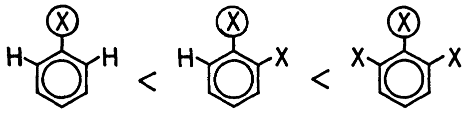
Table 1. Products by the Photolyses of Polyhalobenzenes[a]

Reactant	t/h	C/%	Products (Yield/%)
(a) Polychlorobenzenes			
o-$\mathrm{C_6H_4Cl_2}$[13]	40	58.5	2-Cl-BP(42.7), BP(14.0), *o*-TP(1.2)
m-$\mathrm{C_6H_4Cl_2}$	40	42.2	3-Cl-BP(40.9), BP(0.8)
p-$\mathrm{C_6H_4Cl_2}$	40	26.7	4-Cl-BP(25.8), BP(0.5)
1,2,3-$\mathrm{C_6H_3Cl_3}$	40	36.8	2,6-$\mathrm{Cl_2}$-BP(20.6), 6′-Cl-*o*-TP(2.6), 2-Cl-BP(2.2), *o*-TP(1.5), BP(1.4), *m*-$\mathrm{Cl_2}$-B(1.0)
1,2,4-$\mathrm{C_6H_3Cl_3}$	40	36.0	2,5-$\mathrm{Cl_2}$-BP(22.3), 3-Cl-BP(2.9), 4-Cl-BP(1.1), *p*-$\mathrm{Cl_2}$-B(0.5)
1,3,5-$\mathrm{C_6H_3Cl_3}$	40	33.0	3,5-$\mathrm{Cl_2}$-BP(31.4), *m*-$\mathrm{Cl_2}$-B(0.8)
1,2,3,4-$\mathrm{C_6H_2Cl_4}$	40	39.5	2,3,6-$\mathrm{Cl_3}$-BP(21.2), 1,2,4-$\mathrm{Cl_3}$-B(2.7), 4′-Cl-*o*-TP(1.8), 3′,6′-$\mathrm{Cl_2}$-*o*-TP(1.2), 2,5-$\mathrm{Cl_2}$-BP(0.9), BP(0.6)
1,2,3,5-$\mathrm{C_6H_2Cl_4}$	40	13.3	2,4,6-$\mathrm{Cl_3}$-BP(6.7), 2,3,5-$\mathrm{Cl_3}$-BP(4.5), 1,3,5-$\mathrm{Cl_3}$-B(2.1)
1,2,4,5-$\mathrm{C_6H_2Cl_4}$	40	12.5	2,4,5-$\mathrm{Cl_3}$-BP(8.9), 3,4-$\mathrm{Cl_2}$-BP(1.8), 1,2,4-$\mathrm{Cl_3}$-B(1.8)
(b) Polybromobenzenes			
o-$\mathrm{C_6H_4Br_2}$	20	80.7	BP(24.2), 2-Br-BP(16.0), Br-B(12.7), *o*-TP(1.4)
m-$\mathrm{C_6H_4Br_2}$	20	62.0	3-Br-BP(36.3), *m*-TP(17.9), Br-B(9.9), BP(7.5)
p-$\mathrm{C_6H_4Br_2}$	20	78.0	4-Br-BP(20.0), Br-B(19.6), BP(10.5), *p*-TP(8.8)
p-$\mathrm{C_6D_4Br_2}$	15	57.5	4-$\mathrm{BrC_6D_4C_6H_5}$(20.3), BP(9.3),[c] $\mathrm{C_6HD_4Br}$(8.6), *p*-TP-d_4(4.0)
1,2,3-$\mathrm{C_6H_3Br_3}$[c]	24	47.0	2,6-$\mathrm{Br_2}$-BP(14.0), 2,3-$\mathrm{Br_2}$-BP(12.0), *m*-$\mathrm{Br_2}$-B(9.5), 2′-Br-*m*-TP(3.3)
1,2,4-$\mathrm{C_6H_3Br_3}$[c]	24	20.0	3-Br-BP(9.3), *p*-$\mathrm{Br_2}$-B(1.3), 2,5-$\mathrm{Br_2}$-BP(1.0), 4′-Br-*m*-TP(trace)
1,3,5-$\mathrm{C_6H_3Br_3}$[c]	24	30.5	3,5-$\mathrm{Br_2}$-BP(22.0), 5′-Br-*m*-TP(7.2), *m*-$\mathrm{Br_2}$-B(1.0), 1,3,5-$\mathrm{Ph_3}$-B(trace)
1,2,3,4-$\mathrm{C_6H_2Br_4}$	20	60.1	4′-Br-*m*-TP(21.1), 1,2,4-$\mathrm{Br_3}$-B(11.7), BP(2.9), 3-Br-BP(1.4), $\mathrm{Br_3}$-BP(23.0)[b]
1,2,3,5-$\mathrm{C_6H_2Br_4}$	20	41.5	3,4,5-$\mathrm{Br_3}$-BP(16.9), 2,4,6-$\mathrm{Br_3}$-BP(16.1), 1,3,5-$\mathrm{Br_3}$-B(4.9), 3,5-$\mathrm{Br_2}$-BP(2.7), BP(0.6), 5′-Br-*m*-TP(trace)
1,2,4,5-$\mathrm{C_6H_2Br_4}$	20	44.9	*m*-TP(36.2),[b] 2,4,5-$\mathrm{Br_3}$-BP(5.6), 3-Br-BP(1.5), 1,2,4-$\mathrm{Br_3}$-B(1.5), 4′-Br-TP(trace), BP(trace)
$\mathrm{C_6HBr_5}$[d]	20	59.9	4′,6′-$\mathrm{Br_2}$-*m*-TP(35.1), BP(5.1), 1,2,4,5-$\mathrm{Br_4}$-B(19.7), 3-Br-BP(trace)
(c) Polybromochlorobenzenes			
o-$\mathrm{C_6H_4BrCl}$	30	45.4	2-Cl-BP(27.2), BP(16.8), *o*-TP(1.4)
m-$\mathrm{C_6H_4BrCl}$	30	44.7	3-Cl-BP(42.9), BP(1.8)
p-$\mathrm{C_6H_4BrCl}$	30	30.0	4-Cl-BP(28.2), BP(1.2)
2,6-$\mathrm{Cl_2C_6H_3Br}$	30	59.2	2,6-$\mathrm{Cl_2}$-BP(42.2), 3′-Cl-*o*-TP(6.7), 2-Cl-BP(3.5), *m*-$\mathrm{Cl_2}$-B(3.4)
2,3-$\mathrm{Cl_2C_6H_3Br}$	20	43.1	2,3-$\mathrm{Cl_2}$-BP(28.3), 3-Cl-BP(13.9), 3′-Cl-*o*-TP(1.9)
2,6-$\mathrm{Br_2C_6H_3Cl}$	20	82.5	2-Cl-3-Br-BP(28.3), BP(19.2), 3-Br-BP(16.6), 2′-Cl-*m*-TP(16.4), *o*-$\mathrm{C_6H_4ClBr}$(2.0)
2,4-$\mathrm{Cl_2C_6H_3Br}$[c]	22	30.8	2,4-$\mathrm{Cl_2}$-BP(14.0), 4-Cl-BP(10.0), 3-Cl-4-BrBP(4.2), 4′-Cl-*o*-TP(1.6)
2,5-$\mathrm{Cl_2C_6H_3Br}$	20	63.0	2,5-$\mathrm{Cl_2}$-BP(44.4), 3-Cl-BP(13.1), 4′-Cl-*o*-TP(4.0)
3,4-$\mathrm{Cl_2C_6H_3Br}$	20	33.4	3,4-$\mathrm{Cl_2}$-BP(16.4), *o*-$\mathrm{Cl_2}$-B(8.6), 2-Cl-5-Br-BP(4.1), 4-Cl-BP(1.2)
2,5-$\mathrm{Br_2C_6H_3Cl}$	20	37.2	2-Cl-4-Br-BP(17.1), 4-Br-BP(8.2), 3-Cl-4-Br-BP(4.3), *m*-$\mathrm{C_6H_4ClBr}$(2.7), 3-Cl-BP(1.6)
3,5-$\mathrm{Cl_2C_6H_3Br}$	20	46.8	3,5-$\mathrm{Cl_2}$-BP(44.5), 3-Cl-BP(1.1), *m*-$\mathrm{C_6H_4ClBr}$(1.1)
3,5-$\mathrm{Br_2C_6H_3Cl}$	20	92.4	5′-Cl-*m*-TP(36.1), 3-Cl-BP(30.3), 3-Cl-5-Br-BP(25.2), *m*-$\mathrm{C_6H_4ClBr}$(1.0)

a) Reactions were carried out by using a 32-W low pressure mercury arc lamp under nitrogen atmosphere at ambient temperature (ca. 25 °C). The concentrations of the reactants were 0.10 mol $\mathrm{l^{-1}}$ except the runs otherwise remarked. Following abbreviations were used: C=conversion of the reactant, B=benzene, BP=biphenyl, and TP=terphenyl. Yields were calculated with respect to the reactant. b) The overlap of other weaker GC peak(s) is suspected. c) 20-W Lamp was employed for the irradiation. d) 0.04 mol $\mathrm{l^{-1}}$.

petitively. In all runs in Table 1, the phenylation proceeds more predominantly than the dehalogenation when compared with the products of the primary photolysis of the starting polyhalobenzenes. This trend is shown illustratively in the time-conversion curves of Fig. 1. The preference of phenylation becomes more significant in the cases of chlorinated benzenes than in the cases of brominated benzenes. Dihydrobiphenyl derivatives can also be expected to be generated by the disproportionation of the arylcyclohexadienyl radical intermediate (**1**).[15,16] Actually, they were detected in neither case.

The orientation of the photochemical dechlorination and phenylation in benzene is similar to those observed previously with the reactions in hexane;[9] i.e., the C-Cl bond scissored by two adjacent(ortho) halogen atoms is cleaved most easily and the one scissored by two hydrogen atoms most difficultly. Thus, the reactivity of the encircled halogen atom increases in the following order:



Scheme 1.

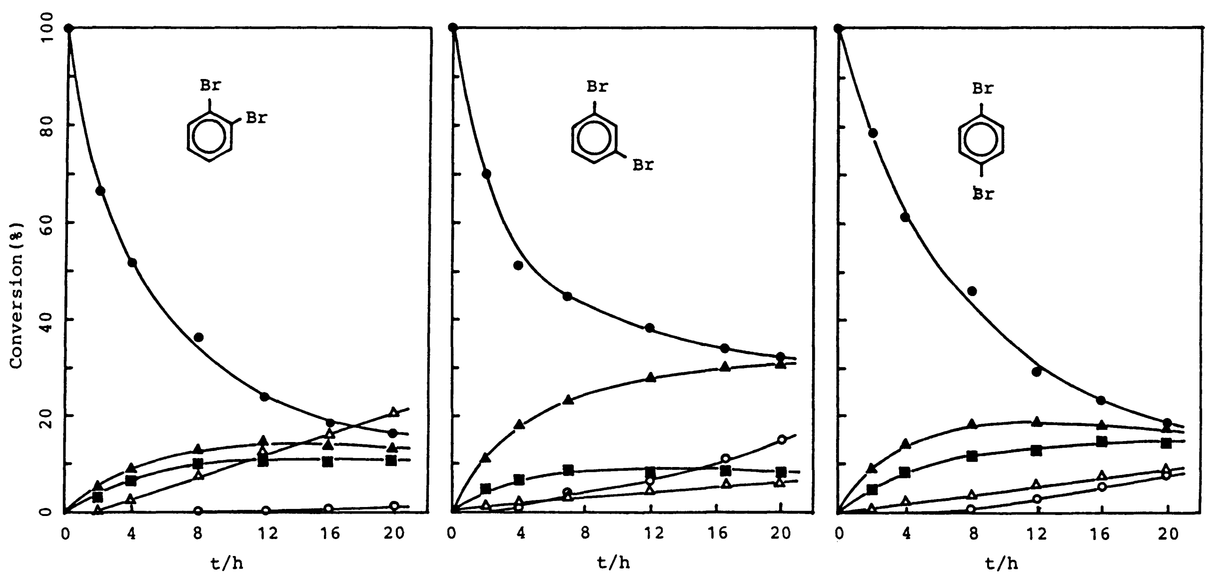
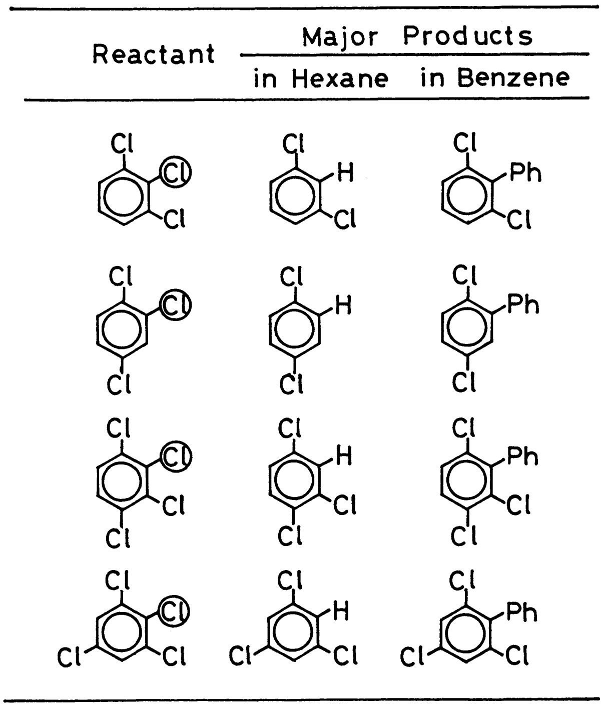


Fig. 1. Time conversion curves for the photolyses of dibromobenzenes (—●—, dibromobenzene (reactant); —▲—, bromobiphenyl; —■—, bromobenzene; —○—, terphenyl; —△—, biphenyl),

This trend is more significant with the photolyses of polychlorobenzenes in benzene solution; the reaction occurs far more preferably on the most crowded C-Cl bond in benzene. Thus, 2,6-dichloro-, 2,5-dichloro-, 2,3,6-trichloro-, and 2,4,6-trichlorobiphenyls were obtained almost exclusively as the phenylated products of the photolyses in benzene of 1,2,3-trichloro-, 1,2,4-trichloro-, 1,2,3,4-tetrachloro-, and 1,2,3,5-tetrachlorobenzenes, respectively.

Corresponding dechlorination products (H in place of C_6H_5) were also found, except for the runs on dichlorobenzenes. These are known as the major products of photolyses in hexane.[9] This fact suggests that the reactions in both solvents proceed via a common haloaryl free-radical intermediate generated by a photolytic cleavage of the encircled chlorine atom in Scheme 2.



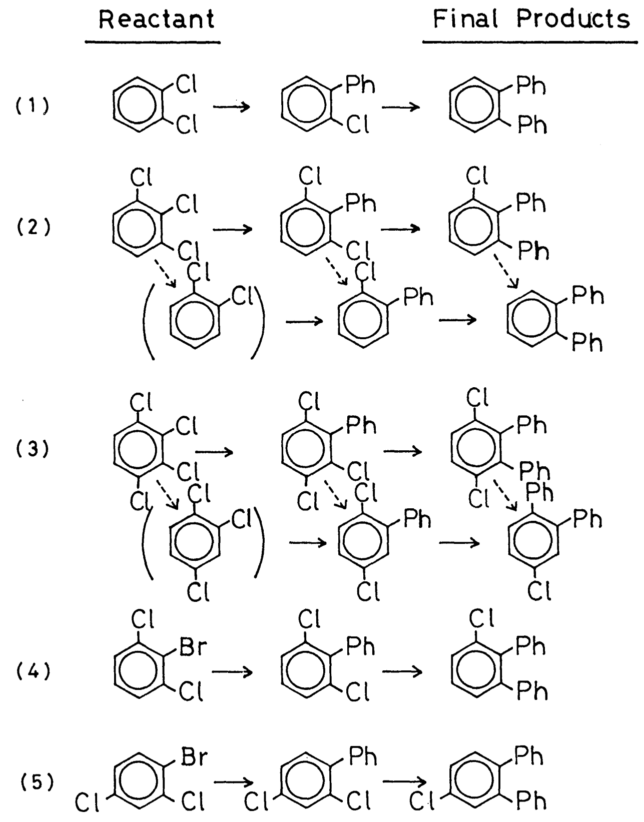
Scheme 2.

In the cases of polybromobenzenes, the reactions proceed less selectively, giving most of the possible phenylated and debrominated products. The distribution of products is not so selective as in the reactions of polychlorobenzenes, on the whole becoming more similar to the reactions in hexane. For example, the photolysis of 1,2,3-tribromobenzene gave comparable amounts of 2,6-dibromobiphenyl (14.0%, a phenylation product), 2,3-dibromobiphenyl (12.0%, the other phenylation product), and *m*-bromobenzene (9.5%, a dehalogenation product). This illustrated that the phenylation does not proceed so regioselectively and is not so overwhelming, as in the photolysis of 1,2,3-trichlorobenzene, which gave 28.3% of 2,6-dichlorobiphenyl and its descents and only 1.0% of *m*-chlorobenzene (all could be derived by the replacement of 2-chlorine atom) without giving detectable amounts of products derived by the replacement of the 1-chlorine atom. Similarly, considerable amounts of *m*-dibromo-, *p*-dibromo-, 1,2,4-tribromo-, 1,3,5-tribromo-, and 1,2,4,5-tetrabromobenzenes were produced as debromination products during the photolyses of 1,2,3-tribromo-, 1,2,4-tribromo-, 1,2,3,4-tetrabromo-, 1,2,3,5-tetrabromo-, and pentabromobenzenes, respectively, in benzene.

In a series of (poly)bromochlorobenzenes, $C_6H_{6-n-m}Br_nCl_m$, bromine is always easier to leave, giving a product formed by the replacement of bromine.

When two different bromine atoms in the same molecule are compared, the reactivity is still governed by the same rule (that the replacement of the most crowded halogen atom takes place most favorably), as is the cases for other polyhalobenzenes. For example, 2-chloro-4-bromobiphenyl, which is produced by the replacement of more crowded bromine atom, is the major photo-product from 2,5-dibromochlorobenzene.

Consecutive Phenylation Forming Terphenyls. As could easily be deduced from the fact that terphenyls were found as the products of the photolyses of dihalobenzenes (Table 1), the primarily produced halobiphenyls were further subjected to subsequent photoreactions producing terphenyl (phenylation) and biphenyl (dehalogenation). Judging from the products of the photolyses of dihalobenzenes, which contain lesser amounts of terphenyls than biphenyl, phenylation should proceed less predominantly than dehalogenation during the photolyses of halobiphenyls. The arylation by the photochemically generated biphenylyl radicals seemed to be dependent both on the nature and the location of the leaving halogen atom. 2-Chlorobiphenyls tend to produce the corresponding *o*-terphenyls far more favorably than 3- and 4-chlorobiphenyls. This trend is considerably different from the photolyses of polyhalobenzenes, which produce phenylated product far more predominantly. As given in Scheme 3, all terphenyls from polychlorobenzenes could be explained by a series of ortho-phenylation (solid arrows) and dehalogenation (broken arrows) reactions. In contrast, the C–Br bonds were shown to behave quite differently from the C–Cl bond. Thus, 3- and 4-bromobiphenyls are inclined to form the corresponding terphenyls more favorably than 2-bromobiphenyls.



Scheme 3.

In order to confirm the fact that the produced halobiphenyls are subjected to the consecutive photolyses producing terphenyls and biphenyl, the photolyses of chlorobiphenyls were examined in benzene solutions. The photolyses of chlorinated biphenyls had been shown to give dehalogenated products when carried out in solvents susceptible to hydrogen abstraction (alkanes and alcohols).[17,18] Photolysis in benzene has never been reported, however. The reactions of the three isomeric chlorobiphenyls were carrid out under exactly the same conditions as the reactions of dichlorobenzenes in benzene solutions, except for the duration of the reaction. The products and their yields are given in Table 2.

As expected from the results on dichlorobenzenes, 2-chlorobiphenyl photolyzes far faster than the other two isomers, giving biphenyl, *o*-terphenyl, and 4-chlorobiphenyl. *m*- and *p*- Terphenyls were not detected as the products of runs starting from 3- and 4-chlorobiphenyls. In the latter two runs, dechlorination also proceeded much more slowly than the *o*-isomer. The three runs on isomeric chlorobiphenyls (in Table 2) agreed with the assumption that *o*-terphenyl was formed by the successive photolysis of 2-chlorobiphenyl, which is a primary product of the photolysis of *o*-dichlorobenzene. Therefore, the above pathway of the reaction was supported by experiments. In line with the expectation from the results in Table 1, the dechlorination predominates over the phenylation in this series of compound.

The formation of terphenyls from dibromobenzenes can also be assumed to proceed via the concecutive phenylation of bromobiphenyl, which is a primary photoproduct, since the amount of formed terphenyls could be accounted for almost quantitatively from the amounts of bromobiphenyls present in the reaction mixture. To be more concrete, the time-conversion curve (Fig. 1) shows that the amount of the newly produced terphenyl is approximately proportional to the amount of the bromobiphenyl present in the reaction system at the time of measurement.

Isomerization of *o*-Dichlorobenzene and 2-Chlorobiphenyl. We have recently reported the novel

Table 2. Products by the Photolyses of Chlorobiphenyls[a)]

Chlorobiphenyl	t/h	C/%	Products (Yield/%)
2-$ClC_6H_4C_6H_5$	48	29.8	BP(26.7), *o*-TP(2.4), *p*-ClBP(0.7)
3-$ClC_6H_4C_6H_5$	48	2.3	BP(2.3)
4-$ClC_6H_4C_6H_5$	48	0.3	BP(0.3)

a) See footnotes of Table 1.

photo-rearrangement of a chlorine atom in polychlorobenzenes bearing two or more contiguous halogen atoms on the ring. The meta-migration of the chlorine atom has been shown to take place exclusively, giving, for example, *p*-dichlorobenzene from *o*-dichlorobenzene in acetonitrile.[10] This reaction is very specific; products from ortho- and para-migrations were detected in neither case. The rearrangement seems to compete with the hydrogen abstraction reaction and becomes observable with the photoreactions in solvents resistive to hydrogen-abstraction. The C–H bond of benzene can be expected to be a little less susceptible to hydrogen-abstraction than acetonitrile, since its bond dissociation energy (469 $\mathrm{kJ\,mol^{-1}}$) is slightly higher than that of acetonitrile (429 $\mathrm{kJ\,mol^{-1}}$).[20] Thus, the photoproducts from *o*-dichlorobenzene and 2-chlorobiphenyl in benzene were carefully examined in search of the rearranged products.

A small amount (0.7%) of 4-chlorobiphenyl was found in the photoproduct from 2-chlorobiphenyl. Although routine GC analyses gave no evidence of its presence, a trace amount of 4-chlorobiphenyl was also detected by a careful GC/MS examination of the products from the photolysis of *o*-dichlorobenzene. Its yield was estimated to be 0.2%. Rearranged products could not be detected with the runs starting from *m*- and *p*-dichlorobenzenes, even if the products were analyzed by exactly the same conditions using GC/MS.

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