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Photo-Rearrangement of Polychlorobenzenes
meta-Migration of Chlorine Atom

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Several polychlorobenzenes were irradiated by ultraviolet light (254 nm) in acetonitrile and the products were determined by gas chromatography. In addition to the abstraction of hydrogen atom from the solvent, photo-isomerization was shown to proceed giving isomeric polychlorobenzenes one of which chlorine atoms migrated to meta to the original position. The meta-rearrangement was rationalized by an MNDO calculation on o-chlorophenyl free radical.

Photochemical reactions of mono- and polychlorobenzenes have been reported by many authors.1-8) Among the photo-reactions of chlorobenzenes, photo-dechlorination in hydrogen-donating solvents and the arylation by photolytically generated aryl free radical in aromatic solvents were most extensively studied. Since the early mechanistic studies by Pinhey1) and by Mori,2) many photo-reactions of halobenzenes have been interpreted to proceed via aryl free radical intermediarily generated by the fission of carbon-halogen bond. However, the details about the mechanism is not known, and several apparently contradictive interpretations have been developed. Thus pi-chlorobenzene intermediate was suggested by Lemal3) and contradicted by Arnold.4) Tokumaru and coworkers5) also investigated the photolysis of chlorobenzene and proposed a mechanism in which the reactions through exciplex and through homolytic cleavage are supposed to proceed competitively. More recent study by Mori6) observed the photolytic cleavage of C-Cl bond after n-pi* excitation by TOF spectroscopy. Photo-reactions of polychlorobenzenes were studied by Hida et al.7) We have also studied their reactions in hexane and in benzene, and chlorine atom under sterically crowded circumstances were shown to be eliminated more easily.8)

In connection with these studies, photochemical reactions of polychlorobenzenes were examined in poor hydrogen-donating solvents. In general, substituted alkanes becomes less susceptible to hydrogen abstraction when the substituent becomes more electron-withdrawing, and this tendency is interpreted as a consequence of larger bond dissociation energy. In this investigation, the photolyses of several polychlorobenzenes were studied in acetonitrile which is expected to be less reactive towards the abstraction of hydrogen atom by free radical than hexane and other hydrocarbon solvents.9) The photo-reactions were carried out using a 30 W low pressure mercury lamp located at the center of concentrically surrounded quarz vessel containing the acetonitrile solution of a polychlorobenzene. The products were analyzed by gas chromatography.10) All rearranged products were identified by comparison of their GC peaks with those of the authentic samples. Product from several runs were given in Table 1.

Dehalogenation again occurs predominantly even in acetonitrile, but isomerization proceeds competitively giving minor products. Abstraction of hydrogen by the generated aryl free radical should partly be suppressed because of poor hydrogen donating ability of the solvent and the isomerization in competition with the abstraction becomes observable. All products from the photo-

Table 1. Products by the Photo-Reactions of Polychlorobenzenes in Acetonitrile

Starting polyhalobenzene (Concentration)	Reaction period	Products (n. d. = not detected)
o-Dichlorobenzene (**1**) (0.1 M)	8 h	C_6H_5Cl 26%, p-$C_6H_4Cl_2$ 3%, $ClCH_2CN$ 4%, m-$C_6H_4Cl_2$ n. d.
(0.2 M)	8 h	C_6H_5Cl 12%, p-$C_6H_4Cl_2$ 1.3%
1,2,3-Trichlorobenzene (**2**) (0.1 M)	8 h	m-$C_6H_4Cl_2$ 7%, o-$C_6H_4Cl_2$ 3%, 1,2,4-$C_6H_3Cl_3$ 4%, 1,3,5-$C_6H_3Cl_3$ n. d. $ClCH_2CN$ 2%
1,2,3,4-Tetrachlorobenzene (**3**) (0.1 M)	8 h	1,2,4-$C_6H_3Cl_3$18%,1,2,3-$C_6H_3Cl_3$ 2%, 1,2,4,5-$C_6H_2Cl_4$ 3%, $ClCH_2CN$ 1%, 1,2,3,5-$C_6H_2Cl_4$ n. d.
1,2,4,5-Tetrachlorobenzene (**4**) (0.04 M)	25 h	1,2,4-$C_6H_3Cl_3$19%,1,2,3,4-$C_6H_2Cl_4$ 2%, 1,2,3,5-$C_6H_2Cl_4$ n. d.
o-Chlorofluorobenzene (**5**) (0.1 M)	8 h	p-ClC_6H_4F 7%, C_6H_5F 69%
(0.2 M)	8 h	p-ClC_6H_4F 3%, C_6H_5F 38%
2,3-Dichloro-1-fluorobenzene (**6**) (0.1 M)	10 h	m-ClC_6H_4F 5%, 2,5-$Cl_2C_6H_3F$ 13%, 3,4-$Cl_2C_6H_3F$ 5%

isomerization in Table 1 are explained by the 1,3- or meta-migration of the most and the next crowded chlorine atom in the molecule. The meta-migration mechanism seems to be the most favorable path to give the isomerized products. Neither ortho- nor para-migration can produce the isomers obtained in detectable amounts by the experiments except the case of 2,3-dichlorofluorobenzene (**6**). Photolysis of **6** gave a small amount(1% or less) of 2,4-dichlorofluorobenzene (**7**) in addition to the products in Table 1. However it is not clear at present whether **7** is the primary product or not. p-Dichlorobenzene and 1,2,4-trichlorobenzene, as well as several polybromobenzenes, were also irradiated under similar conditions. However, only dehydrogenation products were identified in the reaction mixture. As revealed by the reactions of **1** and **5** in two concentrations, the ratio of isomerized vs. reduced products is apparently independent of the concentration. This fact might excludes the involvement of excimeric or dimeric species in the process of isomerization.

In order to interpret the meta-migration of chlorine atom, transitory formation of aryl-chlorine free radical pair was assumed. The radical pair can be identical or similar with the pi-chlorobenzene previously suggested by Lemal.3) However, we have no evidence about the structure of the radical pair. INDO-UHF calculation on o-chlorophenyl free radical gave positive spin populations on carbon atoms meta to the free radical center in addition to the very large positive spin population on the ipso carbon atom. This implies the fact that the meta migration is next favorable if we assume the mechanism through radical pair. The most favorable, but not observable, path should be the recombination in cage of the both free radicals producing the starting polychlorobenzene. The aryl radical in the radical pair may attack the C-H bond of surrounding solvent molecule, forming dechlorinated products. On the other hand, chloroacetonitrile is produced either by the coupling of chlorine atom and cyanomethyl free radical generated by the above abstraction reaction or by the attack of chlorine atom towards the solvent molecule. However, the latter path seems less probable, since the chlorination of acetonitrile via free radical mechanism has been shown to proceed very slowly.9)

Table 2. Spin Populations of 2-Chlorophenyl Free Radical a)

	C_1	C_2	C_3	C_4	C_5	C_6
2s	0.198	-0.031	0.037	-0.032	0.036	-0.035
$2p_x$	0.750	-0.044	0.063	-0.034	0.059	-0.046
$2p_y$	0.074	-0.041	0.036	-0.043	0.036	-0.028
$2p_z$	0.521	-0.471	0.440	-0.447	0.442	-0.463

a) Minus signs in the Table stand for negative spin densities.

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10) Gas chromatographic analyses of the reaction products were carried out on a Shimadzu GC-4B-PTF or a GC-6A apparatus using a wide bore glass capillary column (0.56 mm x 30 m) containing Silicone oil DV 17 as stationary phase. Temperature of the column was programmed so as to rise at a rate of 4 ^{o}C per min starting from 50 ^{o}C and to reach finally 150 ^{o}C. Retention times under these conditions are 1.31 min for C_6H_5F, 1.85 min for $ClCH_2CN$, 2.70 min for m-ClC_6H_4F, 3.10 min for p-ClC_6H_4F, 3.63 min for o-ClC_6H_4F, 5.20 min for 3,5-$Cl_2C_6H_3F$, 7.45 min for 3,4-$Cl_2C_6H_3F$, 7.60 min for 2,5-$Cl_2C_6H_3F$, 7.83 min for 2,4-$Cl_2C_6H_3F$, 9.04 min for 2,3-$Cl_2C_6H_3F$, and 9.08 min for 2,6-$Cl_2C_6H_3F$. A PEG 20 M column (glass, 3 mm x 2 m) was employed in the measurements on polychlorobenzenes. As to the chromatogram, see Cui Xiang Hao, M. Nakada, T. Yamaguchi, S. Fukushi, and M. Hirota, Bull. Chem. Soc. Jpn., 58, 1707 (1985).

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