Formation of Polychlorinated Dibenzofurans in Ullman Reaction

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Polychlorinated dibenzofurans (PCDFs) were reported to be ones of toxic components in PCB preparations.(Vos et al. 1970) Subsequent researches revealed that PCDFs were present in various PCB preparations (Bowes et al.1973,1975; Roach and Pomerantz 1974; Miyata et al, 1975; Nagayama et al. 1976; Morita et al.1977) and in technical grade pentachlorophenol and tetrachlorophenol (Plimmer et al 1973; Buser 1975). PCDFs are also reported in Kanemi Yusho oil which was a contaminated food oil by PCBs employed as a heat transfer agent(Nagayama et al. 1976). PCDFs has been shown to increase in heated PCBs under the presence of oxygen (Morita et al.1977).

2,3,7,8-tetrachlorodibenzofuran, one of the most toxic PCDF isomers (Goldstein et al. 1974), is reported to be produced as a by-product in the synthesis of 2,4,5,2',4',5'-hexachlorobiphenyl (Moron et al. 1973). In order to elucidate any possible source of these highly toxic substances, we examined this type reaction (Ullman reaction) in detail employing six chloroiodbenzenes.

Materials and Method

Chloroiodbenzenes were synthesized by diazonation of commercially available chloroanilines followed by iodination with potassium iodide. Crude product was recrystalized with benzene before use. Three grams of chloroiodbenzenes and one gram of active copper powder were heated in 50 ml glass flasj equipped with condenser at 220°C for two hours. Copper powder was procedured through the reduction of copper sulphate with zinc powder (Org. Syn. col.vol. 42, 343). After cooling the flask to the room temperature, 20 ml of benzene was added and refluxed for ten minutes to extract the products. Benzene extract was filtered and concentrated to the volume of 3ml. The solution was chromatographed on Florisil column (100/200 mesh, 10mm×300mm). After the elution of PCBs with hexane, PCDFs were recovered

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by eluting with ether-hexane mixture (20:80). PCDFs fraction was concentrated to a small volume (3ml) and injected to gaschromatography mass spectrometer for qualitative and quantitative analysis. Gaschromatographic condition was reported earlier (Morita *et al*. 1977)

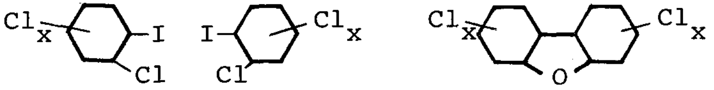
Results and Discussion

GC-MS analysis revealed that several chlorodibenzofurans were produced through Ullman synthesis of symmetrical chlorobiphenyls from chloroiodbenzenes except 3,4-dichloroiodbenzene. PCDFs were obtained at the yield of about 0.1%. Gaschromatograms of PCDFs fractions are illustrated in Fig. 1.

The chlorine number of major PCDFs was less by one or two than the twice of that of the starting chloroiodbenzene. No other PCDFs isomers were demonstrable. The formation of PCDFs with two different chlorine number suggested the contribution of two different reaction pathes.

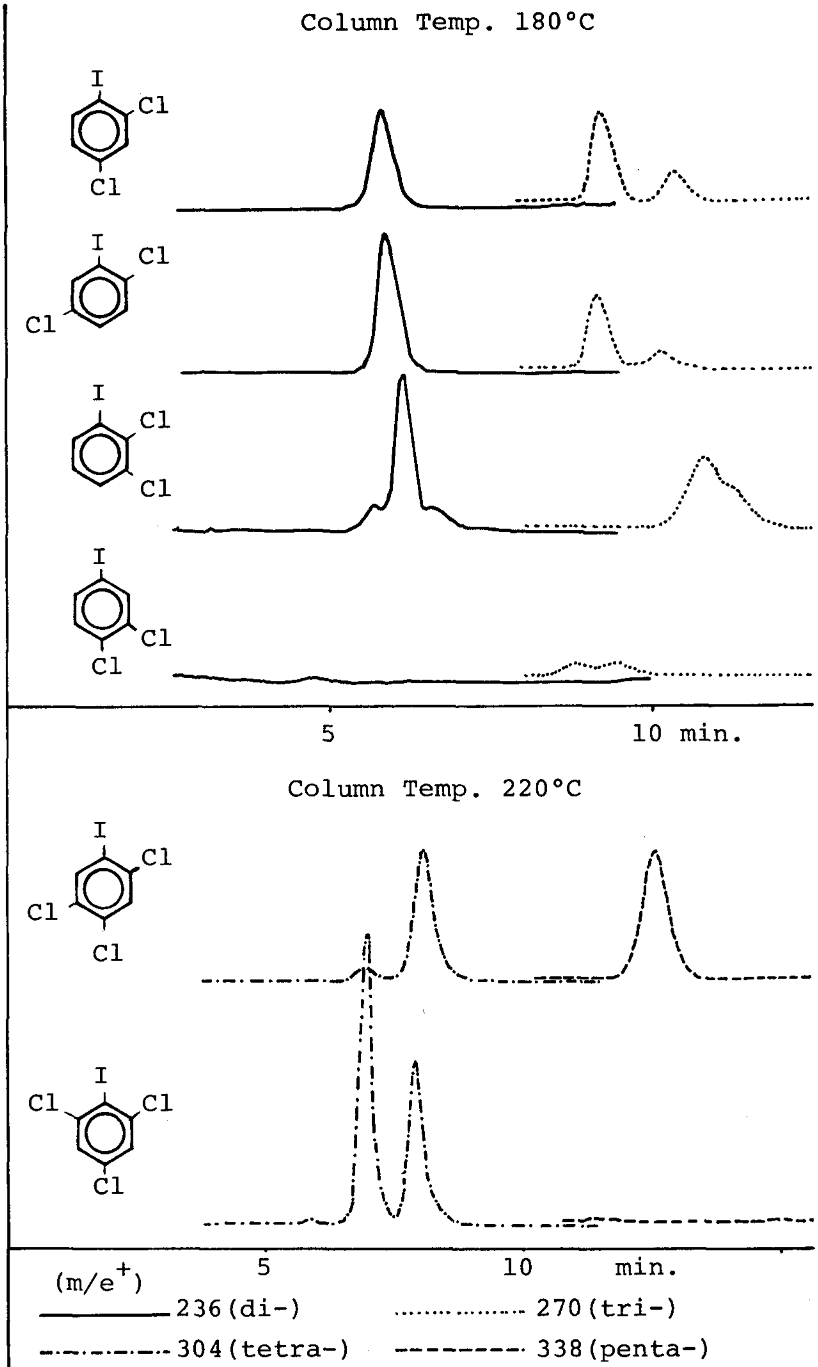
Moron *et al*. assigned the PCDF isomer obtained from 2,4,5-trichloroiodbenzene to be 2,3,7,8-tetrachlorodibenzofuran. The reaction may be represented as scheme 1. Substraction of iodine followed by dechlorination of adjacent chlorine atom leads to the formation of PCDF.

(1)



This reaction mechanism was compatible with our present result. 3,4-dichloroiodbenzene which has no adjacent chlorine did not gave detectable amount of any PCDF isomers. While, all chloroiodbenzene with ortho chlorine atom gave one dominant chlorodibenzofuran respectively. In some case, minor chlorodibenzofuran components were found in the chromatograms. The minor components may be produced by other reaction mechanism such as rearrangement of chlorine during the reaction or by the proceeding of dechlorination before deiodination. Assuming the formula (1), major PCDF components whose chlorine number was less by two than the twice of that of the starting chloroiodbenzene were assigned tentatively as listed in Table 1.

Morita et al. suggested another possible formation mechanism as shown in formula (2). (Morita *et al*. 1977) This mechanism could well explain the present result: PCDFs were not formed not only from 3,4-

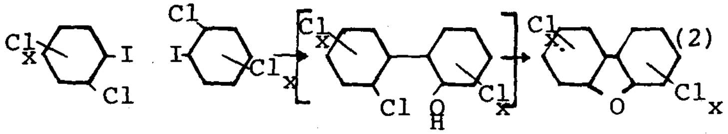


Column Temp. 180°C

Column Temp. 220°C

Fig.1. Mass chromatogram of PCDFs.

dichloroiodbenzene which had no adjacent chlorine but also from 2,4,6-trichloroiodbenzene which had no vacancy at the ortho position.



Assuming the formula (2), PCDF isomers whose chlorine number was less by one than that of the twice of the starting chloroiodbenzene were tentatively assigned as listed in Table 1.

Table 1. Chlorodibenzofuran isomers formed by Ullman reaction.

Starting benzenes	Dibenzofurans	
	(1)	(2)
2,3,dichloroiod-	4,6-dichloro-	1,2,6-trichloro-
2,4-dichloroiod-	3,7-dichloro-	1,3,7-trichloro-
2,5-dichloroiod-	2,8-dichloro-	1,4,8-trichloro-
3,4-dichloroiod-	-------------	----------------
2,4,5-trichloroiod-	2,3,7,8-tetrachloro-	1,3,4,7,8-tetrachloro-
2,4,6-trichloroiod-	1,3,7,9-tetrachloro-	----------------

Sandstrom obtained only one PCDF component from 2,4,5-trichloroiodbenzene but we obtained two almost equivalent amount of PCDFs with different chlorine number in the similar reaction. Sandstrom obtained 2,3,7,8-tetrachlorodibenzofuran at the yield of c.a. 3% while we got fairly lower yield of c.a. 0.1%. The difference of isomer component and yield may be attributable to the difference of copper, temperature, and heating hours employed in the reaction. Thus, this reaction may be fairly complex. Full identification of individual isomers seem to be necessary to confirm the above mentioned reaction mechanism.

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