

FORMATION OF POLYCHLORODIBENZOFURANS (PCDFs) BY THE PHOTOLYSES OF POLY-
CHLOROBENZENES (PCBzs) IN AQUEOUS ACETONITRILE CONTAINING PHENOLS *

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ABSTRACT

Laboratory irradiation (at $\lambda \geq 285$ nm) of solutions of some polychlorobenzenes (PCBzs) in various mixtures of $H_2O: CH_3CN$ in the presence of phenol yielded polychlorinated dibenzofurans (PCDFs) containing 2 Cl atoms less than the starting PCBz. The chemical yields of PCDFs were $\leq 1\%$. It was confirmed that the photoconversion of PCBzs and phenol into PCDFs proceeded through the intermediacy of polychlorinated diphenyl ethers possessing o-Cl substituents.

INTRODUCTION

Polychlorobenzenes (PCBzs) are ubiquitous environmental contaminants that have been found in waste water, river water, lake water, and in fish in many locations around the world¹. The occurrence of PCBzs in the environment originates from its use as pesticides, solvents, and its use in electro- and chemical - industries². The secondary path of PCBzs is as a side reaction product during chlorination and minor sources are from lindane and HCB metabolism in plants, in soil and in cold - and warm blooded organisms³⁻⁸. Recently, a large number of organic compounds including PCBzs have been identified in the flue gas and fly ash from some municipal and industrial incinerators^{9,10}. Likewise, phenol occurs almost in every water body. Furthermore, the production of phenolic compounds, for instance in the US is estimated to be more than two millions tons/year¹¹. The release of these compounds into the aquatic environment has been shown to cause undesirable effects^{11,12}.

Three years ago, we reported that the photolysis of 1,3,5-Cl₃-Bz yields 2,3',4,5',6- pentachlorobiphenyl as minor product¹³. More recently, we observed that the formation of polychlorobiphenyls (PCBs) as minor process is also taking place during the solution phase acetone sensitized and non-sensitized photolyses of tetra- and pentachlorobenzenes in aqueous acetonitrile¹⁴.

It is very likely, that in our environment, water bodies contaminated with PCBzs also contain phenols. We therefore decided to study photoreactions of 1,3,5-Cl₃-Bz and Cl_n-Bzs (n=4-6) in the presence of phenolic compounds.

*This article is Part IV of the series "Photochemistry of Halogenated Benzene Derivatives".
For Part III, see Ref. 14.

EXPERIMENTAL

Sources of PCBzs (1 - 5)¹⁴, 2,4,5-trichlorodiphenyl ether¹⁵ and solvents¹⁴ have been described elsewhere. Phenol and 3,4-dichlorophenol were obtained from Aldrich Chemical Co. Experimental methods have been cited in details in a previous article¹⁴.

RESULTS AND DISCUSSION

The ultraviolet (UV) spectral data for the investigated chlorinated benzenes, *viz.* 1,2,3,4-tetrachlorobenzene (1,2,3,4-Cl₄-Bz) (1), 1,2,3,5-Cl₄-Bz (2), 1,2,4,5-Cl₄-Bz (3), pentachlorobenzene (Cl₅-Bz) (4) and Cl₆-Bz (5) together with phenol (6) and 3,4-dichlorophenol (7) in acetonitrile are recorded in Table 1. For example, the absorption maxima, *i.e.* λ_{\max} of the Cl₄-Bz 1 are at wavelengths (λ) of 277 and 286 nm; the values of logarithm of molar extinction coefficient *i.e.* $\log \epsilon_{\max}$ being 2.47 and 2.39, respectively. In case

TABLE 1. Ultraviolet (UV) spectra^a of some polychlorobenzenes (Cl_n-Bzs; n=4-6) and phenols in acetonitrile.

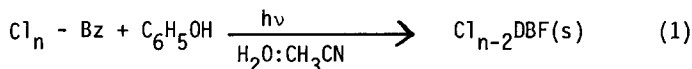
| No. | Compound | λ_{\max}^b (log ϵ_{\max}) | ϵ_{290} | ϵ_{300} | ϵ_{310} |
|----------|---------------------------------|---|------------------|------------------|------------------|
| <u>1</u> | 1,2,3,4-Tetra- chlorobenzene | 277 (2.47); 286 (2.39) | 220 | 7.2 | <0.1 |
| <u>2</u> | 1,2,3,5-Tetra- chlorobenzene | 279 (2.47); 288 (2.40) | 208 | 84.2 | <0.1 |
| <u>3</u> | 1,2,4,5-Tetra- chlorobenzene | 282 (2.90); 291 (2.89) | 759 | 35.5 | <0.5 |
| <u>4</u> | Pentachloro- benzene | 284 (2.53); 293 (2.51) | 279 | 123 | 11.1 |
| <u>5</u> | Hexachloro- benzene | 288 (2.53); 298 (2.43) | 302 | 270 | 71.4 |
| <u>6</u> | Phenol | 270 (3.29); 276 (3.21) | 5.28 | 0.41 | <0.4 |
| <u>7</u> | 3,4-Dichloro- phenol | 283 (3.41) 289 (3.36) | 2291 | 157 | 3.43 |

^aThese were recorded on a Cary-14 double-beam spectrophotometer.

^bIn nm.

of PCBzs as well as phenols, a bathochromic shift of both absorption maxima appears as more and more substituents are added to the benzene nucleus (see Table 1). For the studied compounds 1 - 7, the values of ϵ_{290} , ϵ_{300} and ϵ_{310} , which represent molar extinction coefficients (ϵ) at 290, 300 and 310 nm, are also documented in Table 1.

Table 2 summarizes the results of photochemical studies performed on the solutions of five PCBzs (ca 1 mM/L) 1 - 5 in various mixtures of H₂O: CH₃CN containing phenol (6) (ca 5 mM/L). This Table clearly indicates that the exposure of each Cl_n-Bz in the presence of phenol gives rise to the formation of polychlorinated dibenzofuran(s), viz. Cl_{n-2}-DBF(s) (cf Reaction 1):



where n = 4,5,6 as minor products with chemical yields amounting ca. 1% (see also footnote (c) of Table 2). In cases of chlorobenzenes 4 and 5, polychlorinated dibenzofurans with chlorine contents of n-3 are also formed. Furthermore, the photoreaction of 1,2,4,5-tetrachlorobenzene (3) in water-acetonitrile (4:6, v/v) with added 3,4-dichlorophenol for 16 hours provides two isomers of dichlorodibenzofurans (Cl₂-DBFs) in chemical yields of 1.56 and < 0.60%.

The tentative identifications¹⁴ of PCBs, polychlorophenylacetonitriles, chloroacetophenones (in the presence of acetone only), and 1- (polychlorophenyl) -2- propanones (in the presence of acetone only) during the direct and acetone sensitized photolyses of some PCBzs 1-4 in H₂O: CH₃CN evidently reveals that the photoreactions of polychlorinated benzenes proceed via the intermediate chlorophenyl radicals. It is apparent from Table 1 that all substrates i.e. compounds 1-5 strongly absorb UV light in the region 290-310 nm as compared to phenol (6); thereby indicating that the main photoreaction in the present systems will initiate from chlorobenzenes. The formation of polychlorodibenzofurans (PCDFs), when PCBzs 1-5 (1mM/L) irradiated in the presence of phenol (5mM/L), can best be explained by the following Scheme formulated for the case of 1,2,4,5-Cl₄-Bz (3).

According to this postulated Scheme, homolytic cleavage of a carbon-chlorine bond of the photoexcited molecules of the Cl₄-Bz 3 takes place to yield 2,4,5-trichlorophenyl radicals (8) (step a). UV exposure of phenol (6) probably results in the formation of intermediate species 9 produced via the partial scission of the hydrogen-oxygen bond of 6 (step b). Likewise the compound 6 is attacked by free radical species $\dot{\text{R}}$ (which may have been generated previously); whereby species 10 bearing partial radical character on the oxygen atom being produced (step c). Then the interactions between the trichlorophenyl radicals 8 and species 9, and 10 occur giving rise to the production of intermediate 2,4,5-trichlorodiphenyl ether (2,4,5-Cl₃-DPE) (11) (see steps d and e). The intermediate ether 11 undergoes further photochemical reaction to give 2,3-dichlorodibenzofuran (2,3-Cl₂-DBF) (12) as secondary photoproduct. Free phenoxy radicals (C₆H₅O) are seemingly not involved in the production of ether 11 and finally DBF 12, because in the present and other photolyzates of Cl_n-Bzs 1 - 4, the presence of Cl_n-DPEs and Cl_{n-1}-DBFs are not noticed. Such products could be formed through the action of C₆H₅O species on the starting polychlorobenzenes in the ground state and through further photoreaction. In addition, chloroarylation of phenol (6) by chlorophenyl radicals 8 to provide 2,4,5-trichloro-2'-hydroxybiphenyl (13), which may yield DBF 12, is not ruled out. When the irradiation of the substrate 3 in the presence of 6 is terminated after 7 hr (for further conditions see Table 2), the presence of 2,4,5-Cl₃-DPE (12) in the

Table 2. Generation of polychlorinated dibenzofurans (C_{1n-2} -DBFs) by the photolysis of aqueous acetonitrile solutions of polychlorinated benzenes (C_{1n} -Bzs; n=4-6) containing phenols.

| No. | Substrate, Polychlorinated Benzene (C_{1n} -Bz) | $H_2O:CH_3CN$ (v/v) | Concentration of C_{1n} -Bz, mM/L | Phenol (Concentration, mM/L) | Photolysis Time, hr | Percentage Disappearance of C_{1n} -Bz % | Polychlorinated Dibenzofurans (C_{1n-2} -DBFs) Identified Amongst the photoproducts ^c (Chemical yields) |
|-----|--|---------------------|-------------------------------------|------------------------------|---------------------|--|---|
| 1 | 1,2,3,4- C_{14} -Bz | 1 : 1 | 1.065 | Phenol (4.911) | 40 | 46.16 | C_{12} -DBF (\leq 0.40%) |
| 2 | 1,2,3,5- C_{14} -Bz | 1 : 1 | 1.019 | Phenol (4.911) | 40 | 66.01 | Two C_{12} -DBFs (0.77%; 1.20%) |
| 3 | 1,2,4,5- C_{14} -Bz | 4 : 6 | 1.250 | Phenol (4.911) | 16 | 60.69 | 2,3- C_{12} -DBF (0.95%) |
| 4 | 1,2,3,4,5- C_{15} -Bz | 4 : 6 | 0.958 | Phenol (4.911) | 24 | 46.54 | C_{12} -DBF (0.17%), Two C_{13} -DBFs (0.72%; 0.24%) |
| 5 | 1,2,3,4,5,6- C_{16} -Bz | 1 : 9 | 0.982 | Phenol (4.911) | 7 | 32.42 | C_{13} -DBF (\leq 0.05%), 1,2,3,4- C_{14} -DBF (0.40%) |
| 3 | 1,2,4,5- C_{14} -Bz | 4 : 6 | 0.972 | 3,4-Dichlorophenol (4.086) | 16 | 58.07 | Two C_{12} -DBFs (1.56%; \leq 0.60%) |

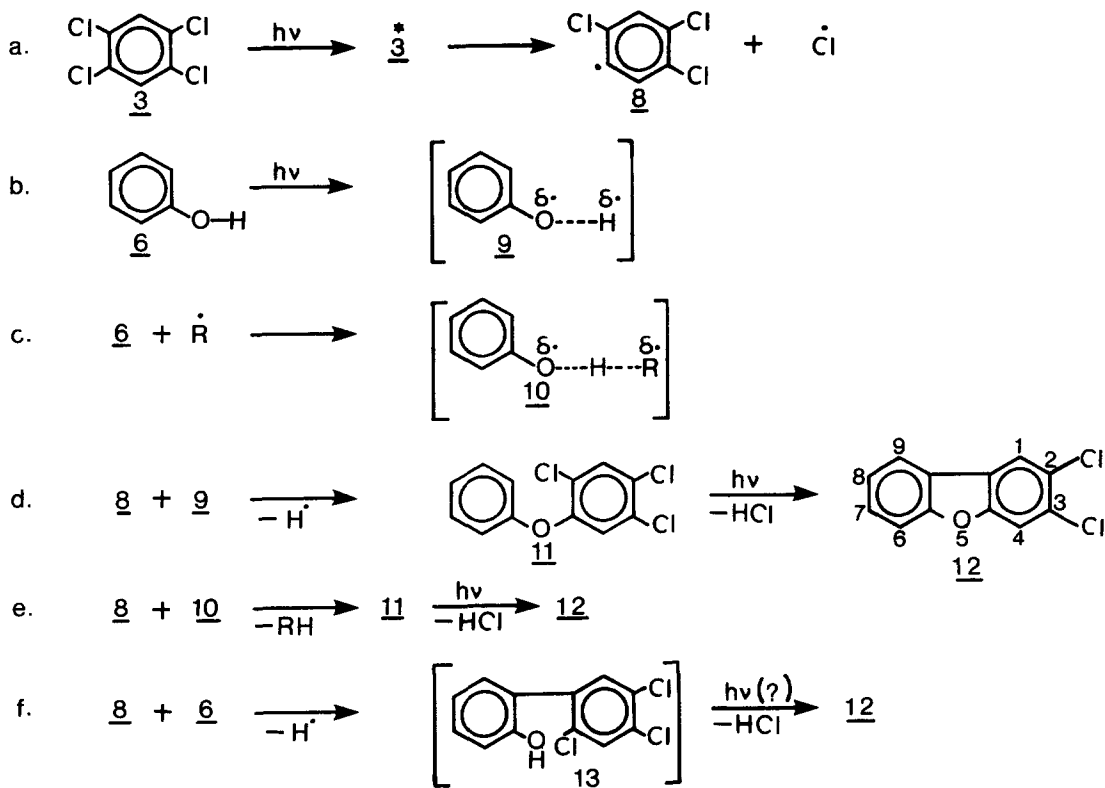
^a Theoretically (see cf. Scheme), from C_{1n} -Bzs, viz. 1, 2, 3, 4 and 5 in the presence of phenol three, two, one, four and one isomer(s) of C_{1n-2} -DBF were expected.

^b Theoretically (see cf. Scheme), from the chlorobenzene 3 in the presence of 3,4-dichlorophenol two isomers of C_{14} -DBF namely 2,3,7,8- and 1,2,7,8-tetrachloroisomers were expected.

^c No attempt was made for the identifications and quantifications of other photoproducts like reductively dechlorinated benzenes (major), polychlorobiphenyls (PCBs), polychlorophenylacetonitriles which have been reported elsewhere¹⁴ for the acetone sensitized and non-sensitized photoreactions of C_{1n} -Bzs (where n= 4-6) in water-acetonitrile mixtures.

^d Calculated from the amounts of the starting chlorobenzene; undecomposed starting chlorobenzene present in a photolyzate being used as an internal standard.

SCHEME



photolyzate is observed. The photoconversions of chlorinated diphenyl ethers containing *o*-chlorine substituent(s) in organic solvents such as methanol and *n*-hexane are well known processes¹⁶. Furthermore, we have conducted irradiation of 2,4,5-Cl₃-DPE (11) (1mM/L) in a mixture of H₂O: CH₃CN (4:6, v/v) for 17 hr and have noticed the appearance of photoproduct 12. This observation confirms the intermediacy of 2,4,5-trichlorodiphenyl ether (11) in the photochemical generation of 12 from tetrachlorobenzene 3 plus phenol (see Scheme). It seems interesting to mention here that the above described photolysis of 11 in water-acetonitrile also proceeds to yield a photoisomerized trichlorodiphenyl ether. Such photo-

isomerization of 11 (and other chlorodiphenyl ethers) has never been reported in the literature¹⁶. Finally, although during the photoreactions of 1,2,4,5-Cl₄-Bz (3) in the presence of 6, the product ortho-hydroxy-PCB 13 could not be detected, but in the case of photolysis of 3 plus 3,4-dichlorophenol for 7 hr some hydroxypolychlorobiphenyls like 2 penta- and 2 tetra-chloroisomers were observable on GC-MS.

Finally, Garå⁸ and associates¹⁷ have shown that the thermochemical ring closure of even 2-hydroxynonachlorobiphenyl (which would lead to the production of octachlorodibenzofuran) does not take place when this biphenyl is injected to a gas chromatograph. Moreover, we^{15,18} have previously concluded that under such GC conditions, the polychlorinated DPEs with o-Cl substituent are not thermally converted into PCDFs. These facts clearly demonstrate that all the PCDFs documented in Table 2 are solely photoproducts.

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