

PHOTOCHEMISTRY OF IRGASAN-TRIFLATE : A SIMPLE CONVERSION OF AN AROMATIC HYDROXYL GROUP TO CHLORINE IN THE SYNTHESIS OF POLYCHLORINATED DIPHENYL ETHERS AND POLYCHLORINATED DIBENZOFURANS

Yoon-Seok Chang, Jung-Suk Jang, and Max L. Deinzer*

Department of Chemistry and Department of Agricultural Chemistry
Oregon State University, Corvallis, OR 97331.

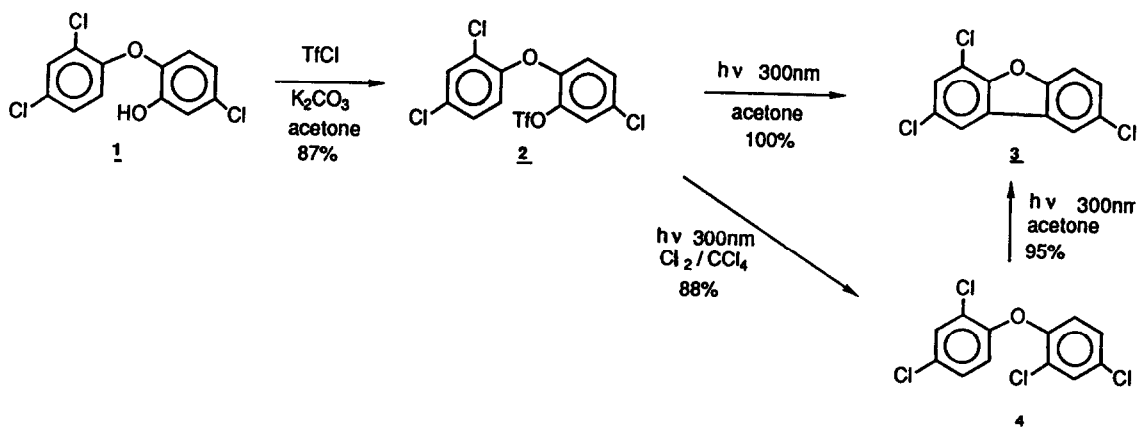
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Abstract: Several chlorophenoxy phenols were converted to their triflates by reaction with trifluoromethanesulfonyl chloride. The triflates undergo triplet sensitized photolytic cyclizations at 300 nm in acetone to give chlorodibenzofurans or singlet state substitution reactions in carbon tetrachloride saturated with chlorine gas to give the corresponding chlorine substituted diphenyl ethers. 2-Chloro-3-hydroxy dibenzofuran was similarly converted to the 2,3-dichlorodibenzofuran. The mechanism for displacement of triflate by chlorine appears to involve chlorine-arene π complexation.

In recent years the polychlorinated dibenzofurans (PCDBFs), along with their dibenzo-p-dioxin counterparts, have been the subject of an intense research effort because of their high toxicity as contaminants in the environment.¹ In connection with our efforts to synthesize polychlorinated diphenyl ethers (PCDPEs) and PCDBFs for mass spectrometric studies² we sought to replace the hydroxyl group of polychlorinated phenoxy phenols (PCPPs) with chlorine. The PCPPs had been prepared previously in this laboratory.³ These compounds also have been isolated from commercial pentachlorophenols as impurities.⁴

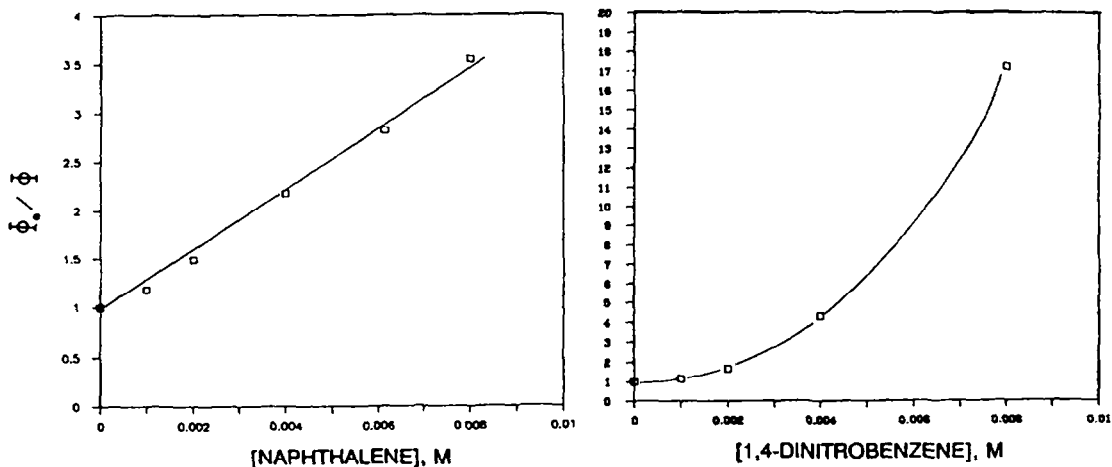
5-Chloro-2-(2,4-dichlorophenoxy)phenol **1**, a commercial pesticide, called Irgasan DP300, CIBA-GEIGY Co., was chosen as the starting material in one example. Irradiation of a degassed 10^{-3} M acetone solution of Irgasan triflate **2**⁵ at 300 nm gave complete conversion to 2,4,8-trichlorodibenzofuran (2,4,8-TrCDBF) **3**⁶. A yield of 88 % of 2,2',4,4'-tetrachlorodiphenyl ether **4**⁷ was obtained when irradiated in chlorine saturated carbon tetrachloride. Compound **4** also could be readily converted to 2,4,8-TrCDBF **3** in acetone solution.

Scheme 1



Photolysis of PCDFEs in acetone resulting in its cyclization to form PCDBFs has been known as the major photoconversion pathway.⁸ However, the detailed mechanism for conversion is still obscure. It was proposed⁹ that acetone acts as a triplet photosensitizer due to its high triplet energy ($E_T = 79 - 82 \text{ kcal/mol}$)¹⁰ and that the excited triplet state of the substrate is responsible for the cyclization via single electron transfer. The yield of photoproduct **3** was low in other organic solvents¹¹ and the formation of **3** in acetone was quantitatively quenched in the presence of triplet quencher, naphthalene, for which the Stern-Volmer plot was linear. Particularly efficient nonlinear quenching was also observed with 1,4-dinitrobenzene, in which a secondary process is involved such as electron transfer or singlet energy quenching (Figure 1). In this case the ortho-triflate group is much superior to the other ortho-chlorine as a leaving group during cyclization.

Figure 1

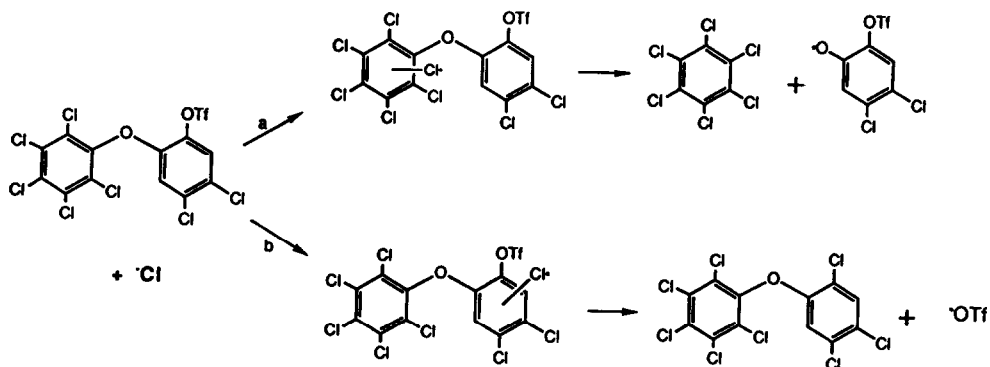


Traditional chlorination reagents¹² including SOCl_2 , POCl_3 , PCl_3 and $(\text{C}_6\text{H}_5)_3\text{PCl}_2$ ¹³ for substituting a chlorine for a hydroxyl group are often used, but the conditions involve high temperatures. Conversion of the hydroxyl group to an amino functionality via diethylphosphate¹⁴ followed by diazotization and chlorination¹⁵ is also well known. In the latter steps dechlorination or hydrogen atom abstraction are often observed. The preparation of **4** from the photolysis of **2** in Cl_2/CCl_4 solution is a new and milder procedure for this transformation.

The mechanism of this photolytic chlorine-substitution may include π -complexation between the triflate compound and chlorine atom followed by ipso substitution. It has been found that in the typical photolytic chlorination condition the chlorine atom forms a π -molecular complex with arenes. Electron-poor arenes that have lower π -basicities than benzene form weaker Cl^+ /arene π -complexes and these π -complexes can rearrange to σ -molecular complexes followed by ipso

substitution.¹⁶ Ipeo substitution of bromine or iodine (X=Br, I) by chlorine is well known.¹⁷ In some cases chlorine atom can also be captured on the other benzene ring to undergo displacement of chlorinated phenoxy radical bearing the triflate group to give a polychlorobenzene (Scheme 2, pathway a).

Scheme 2



The experiments also were carried out with the chlorine-37 enriched compound and significant loss of chlorine-37 excess was observed (from 95% to 65%) (Entry 5 of Table 1). This provides additional evidence for π -complexation prior to the ipso substitution. Table 1 shows some transformations of hydroxy compounds to the corresponding chloro compounds.

Table 1. Photolysis of Triflates in Cl_2/CCl_4 at 300 nm

Entry	Triflates	Photo Products	Yield (%)* PCDFEs
1		+ 8:1	88
2		+ 15:1	75
3		+ 12:1	42
4		+ 13:1	40
5			91

* The yields and ratios were determined by HPLC with a 254 nm UV detector.

A typical experimental procedure for the chlorine substitution reaction is as follows. A hydroxy compound is dissolved in acetone and anhydrous potassium carbonate is added. The mixed solution is stirred with a magnetic bar at room temperature and trifluoromethanesulfonyl chloride solution in acetone is slowly added. After completion of the reaction, the product is isolated by a silica-gel column. The triflate compound is dried and redissolved (usually, 10^{-2} M concentration) in carbon tetrachloride solution saturated with chlorine gas and photolyzed in a pyrex tube at 300 nm for 1 - 2 hours. The solution is concentrated down and chromatographed on a preparative silica TLC plate or on a HPLC column.

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5. ^1H NMR (400MHz, CD_3COCD_3) δ 7.69(dd,2H), 7.47(td,2H), 7.28(d,1H), 7.08(d,1H)
6. ^1H NMR (400MHz, CD_3COCD_3) δ 8.24(d,1H), 8.19(dd,1H), 7.73(d,1H), 7.71(dd,1H), 7.51(t,1H)
7. ^1H NMR (400MHz, CD_3COCD_3) δ 7.67(d,2H), 7.42(dd,2H), 7.07(d,2H)
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