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FORMATION OF CHLORODIBENZOFURANS BY IRRADIATION OF CHLORINATED DIPHENYL ETHERS

Åke Norström, Kurt Andersson and Christoffer Rappe
Department of Organic Chemistry, University of Umeå
S-901 87 Umeå, Sweden

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Introduction

The contamination of various products by the highly toxic chlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) has been the subject of much concern in recent years. Owing to stricter regulations and improved processing, the levels of these contaminants have now decreased.[1,2,3] However, another side of the problem is the formation of PCDDs and PCDFs from less toxic substances under environmental conditions, for example by photodegradation and biodegradation. Up to now very limited interest has been shown in this aspect of the problem.

Polyhalogenated 2-phenoxyphenols, found as contaminants in commercial polychlorinated phenols,[4,5] were found to undergo both a photochemical and a thermal ring closure yielding PCDDs.[6] In the present paper we report that irradiation of polychlorodiphenyl ethers - other abundant impurities in commercial polychloro phenols - results in the formation of PCDFs, and in one case this could be used as a synthetic method.

Experimental

NMR spectra were recorded on a Varian model A-60 spectrometer using TMS as an internal standard. Mass spectra were recorded using a LKB Model 9000 instrument equipped with a Pye Unicam Model 84 GC.

n-Hexane for the photolysis was technical grade purified by treatment with 7 % fuming sulphuric acid, distilled in an all-glass apparatus and checked for impurities using EC/GC and UV.

2,2',4,4'-Tetrachlorodiphenyl ether I was synthesized according to Derichs and Stumpf,[7] who found the product to be the 2,2',6,6'-Cl_4 isomer. However, the GC-pure product (1 % OV - 17, 190° C, 40 ml N_2/min m.p. 86-8° C, yield 51 %, was analyzed by NMR, solvent CCl_4. The spectra consisted of three peaks with a signal ratio 1:1:1 (δ 6.75 (d) $J = 9.0$ Hz; $\delta = 7.17$ (q), $J = 9.0$ and 3.0 Hz; $\delta = 7.46$ (d), $J = 9.0$ Hz). The mass spectrum had a molecular ion at m/e = 306 with the typical cluster of four chlorine atoms.

2,4,4'-Trichlorodiphenyl ether II was synthesized according to a method by Crowder et al.[8] 0.23 g (0.01 mole) of sodium was dissolved in 60 ml of methanol and 1.63 g (0.01) of 2,4-dichlorophenol was added, followed by 3.85 g (0.01 mole) of 4,4'-dichlorobiaryliodomium chloride, prepared according to Behringer *et al.*[9] After refluxing for 24 hrs, the methanol was evaporated and the residue dissolved in ether and H_2O. The aqueous phase was extracted with ether, and the combined ether phases washed successively with 2 N NaOH and H_2O and then dried over $MgSO_4$. Evaporation of the ether and two recrystallizations from n-butanol yielded 0.8 g (30 %), m.p. 51-52° C, only one component according to GC (1 % APM, 11° for 2 min - 40°/min - 210°). The mass spectrum gave a molecular ion at m/e = 272 and the typical cluster for three chlorine atoms.

Irradiation of 2,4,4'-trichlorodiphenyl ether II. 0.10 g of 2,4,4'-trichlorodiphenyl ether was dissolved in 100 ml of n-hexane. Nitrogen was bubbled through for 10 minutes, and thereafter the solution was irradiated for 30 min using a Hanau Q 80 UV-lamp (λ_{max} = 290-430 nm) equipped with a quartz condenser. After evaporation of the solvent, the residue was recrystallized twice from n-butanol, yielding 0.017 of white crystals, m.p. 183-5° C. Mixed melting point and GC-analyses (1 % OV-17 and 1 % APM at 190° C) showed the product to be identical with an authentic sample of 2,8-dichlorodibenzofuran prepared according to Gilman et *al.*[10] Yield 20 %. The degradation was followed by GC and the 2,8-isomer seems to be the only Cl_2-dibenzofuran formed.

Irradiation of 2,2',4,4'-tetrachlorodiphenyl ether I. This experiment was performed as outlined for the Cl_3-ether. The reaction was followed by GC-analyses (1 % APM, 190° C, 40 ml N_2/min) and the photodegradation products identified by GC/MS. The reaction was found to follow the degradation scheme outlined in Fig. 1. Already after 15 minutes of irradiation the photoproducts III and IV were the main components in the photolysate, and after 30 minutes only traces of the starting material I could be detected.

Discussion

The photochemistry of the unsubstituted, alkyl- and alkoxysubstituted ethers has recently been studied,[11,12] and the reaction was found to result in dibenzofurans.[12,13] Up to now, no report concerning the photochemistry of the chlorinated diphenyl ethers has been published. Hutzinger _et al._[11] have studied the photochemical degradation of 2,8-Cl_2- and Cl_8-dibenzofuran.[7] They found the reductive dechlorination to be main reaction pathway.

We have found that the photochemical breakdown of polychlorinated diphenyl ethers can follow two competitive pathways: dechlorination and ring closure to chlorinated dibenzofurans see Fig. 1. Ruzo _et al._[14] have shown that in the photochemical degradation of PCBs the _o_-chlorine is preferentially lost, and the same seems to be the case for the chlorinated diphenyl ethers. It is possible that the two competitive pathways may have their first intermediate in common, but this question has not been studied yet.

The photochemical formation of the highly toxic PCDFs from the much less toxic diphenyl ethers can be a reaction of environmental significance. The polychlorinated diphenyl ethers are found as impurities in commercial chlorophenols, which are widely used as fungicides and herbicides. It is therefore recommended that the level of chlorinated diphenyl ethers in chlorophenols should be minimized.

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Fig 1