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PREPARATION OF CHLORINATED DIPHENYL ETHERS FROM BIARYLIODONIUM SALTS

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The manufacture and use of various types of halogenated aromatics as polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), chlorinated phenols and their derivatives, and other chlorinated or brominated aromatics have caused many different environmental problems. Most of these technical products are more or less complex isomeric mixtures and many by-products have been identified. For example, highly toxic chlorinated dibenzofurans (PCDFs) have been found in commercial PCBs.[1,2] The chlorinated phenols and their derivatives have been subjected to many studies and several types of contaminants have been found,[3,4] some of them in amounts of more than 1 %.

We recently studied one class of contaminants the polychlorinated diphenyl ethers (PCDEs). Photolysis of PCDEs yielded the highly toxic PCDFs in good yield[5,6] and this could be of environmental significance. PCDEs are also highly suitable starting materials for the synthesis of PCDFs via a palladium(II) acetate promoted cyclisation reaction.[7] Carbon-13 chemical shifts have been determined for 14 isomeric PCDEs.[8]

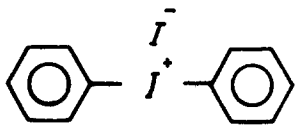
Sundström and Hutzinger[9] have published an extensive review article of the methods hitherto used for the synthesis of PCDEs. In this paper we present the synthesis of a number of PCDEs from readily available biaryliodonium salts via coupling with the appropriate chlorophenol. We are now continuing this work

with new halogenated biaryliodonium salts.

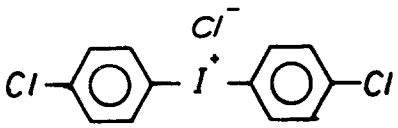
Experimental

Mass spectra were recorded using a LKB 9000 instrument equipped with a Pye Unicam Model 84 GC. The gas-chromatographic analyses were performed on a Pye Unicam Model 64 GC with flame ionisation detector. An all-glass column, 1.5m x 4mm, was used, filled with 1% Apiezon M on 80/100 mesh Chromosorb W-AW--DMCS and operated at 120° for 2 min, then programmed at 40°/min up to 210° to attain separation of the solvent peak and the iodobenzene. PMR was recorded in a few cases on the products to determine the correct structure of the biaryliodonium salts. Melting points are uncorrected.

Biaryliodonium iodide(I) and 4,4'-dichlorobiaryliodonium chloride(II) were prepared according to Beringer.[10]



I



II

For the coupling reactions, the process of Crowder[11] was followed with some modifications. In a typical run, 10 mmoles of sodium was dissolved in 60 ml methanol p.a. and equimolar amounts of the chlorophenol and the biaryliodonium salt were added. 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 were successively washed with 2M NaOH and H_2O and then dried. Evaporation of the solvent and distillation in vacuo or recrystallisation gave the yields reported in Table 1. All products were >99% pure by GC. Mass spectra of the compounds showed an intense molecular ion with a typical chlorine cluster. The fragmentation consists of subsequent loss of chlorine and the typical fragment m/e=63 which is probably COCl. Isomers with one ring unsubstituted gave an intense fragment at m/e=77 (C_6H_5) and isomers with a p--chlorine as the only substituent at one ring gave an intense fragment at m/e==111 (C_6H_4Cl).

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Table I

Biaryliodonium salt[a)]	Chlorophenol	Diphenyl ether	Yield % recryst from	m.p. b.p. (mm)
I	4-chloro	4-chloro	82	-
			-	130-2 (10)
II	4-chloro	4,4'-dichloro	63	-
			-	158-60 (10)
I	2,4-dichloro	2,4-dichloro	44	-
			-	160-2 (10)
II	2,4-dichloro	2,4,4'-trichloro	30	51-2
			n-BuOH	-
II	3,4-dichloro	3,4,4'-trichloro	40	-
			-	196-8 (10)
I	2,4,6-trichloro	2,4,6-trichloro	46	52-4
			n-BuOH	-
II	2,4,6-trichloro	2,4,4',6-tetra-chloro	52	88-90
			EtOH	-
I	2,4,5-trichloro	2,4,5-trichloro	40	59-61
			n-BuOH	-
II	2,4,5-trichloro	2,4,4',5-tetra-chloro	35	62-4
			EtOH	-
I	3,4,5-trichloro	3,4,5-trichloro	44	51-3
			n-BuOH	-
II	3,4,5-trichloro	3,4,4',5-tetra-chloro	39	65-7
			EtOH	-
I	2,3,5,6-tetra-chloro	2,3,5,6-tetra-chloro	36	94-6
			toluene	-
II	2,3,5,6-tetra-chloro	2,3,4',5,6-penta-chloro	65	96-8
			EtOH	-
I	2,3,4,5,6-penta-chloro	2,3,4,5,6-penta-chloro	41	139-42
			toluene	-
II	2,3,4,5,6-penta-chloro	2,3,4,4',5,6-hexa-chloro	36	146-7
			toluene	-

a) I = difenyliodonium iodide
II= di-(4-chlorofenyl)-iodonium chloride