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General Discussion

Photochemical degradation of polyhalogenated biphenyls

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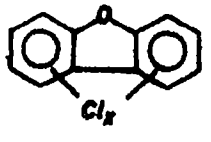
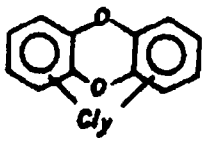
In 1970 it was reported by Vos and coworkers that technical PCB preparations contained toxic, polar components, identified by mass spectroscopy as polychlorinated dibensofurans (1).[1]



x = 4, 5

1



y = 2–8

2

From a chemical point of view these chlorodibensofurans are closely related to the polychlorinated dibensodioxins (2) known as toxic and teratogenic contaminants in chlorophenols and chlorophenoxy acids.

PCB is known to be stable and resistent to chemical and microbial breakdown. Therefore photochemical degradation induced by the UV-content in the sunlight may be a major pathway of decomposition. Last year Safe and Hutzinger gave a report on the photochemical

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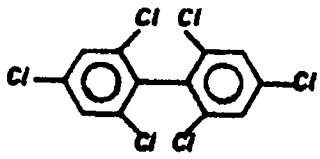
degradation of 2,2',4,4',6,6'-hexachlorobiphenyl (3). Among the products



3

they found one with the molecular weight of 304.[2] This is the calculated molecular weight for tetrachlorodibensofuran (1, x=4).

In subsequent papers the same group has studied the photochemical decomposition of individual PCB's as well as technical PCB preparations. In all cases they obtained polar oxygenated products, but no real effort seems to have been made to separate and identify these products,[3,4] which must be an investigation of great importance.

From work with identifying impurities in pentachlorophenol we had some experience from the separation and identification of as well as reactions with polychlorinated oxygenated aromatics.[5]

We started to investigate the photochemical behaviour of the Cl_6-PCB 3. We used methanol as solvent and a lamp λ_{max} = 290 - 430 nm which is close to the solar radiation, and the sample was irradiated for 30 min.

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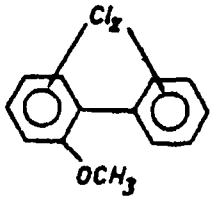
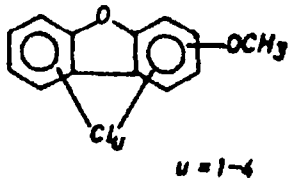
The first separation of the variety of products formed was made by thin layer chromatography, and we could detect at least nine bands. Each band was eluated and the eluate analyzed by means of a combination of gas chromatography - mass spectrometer.

As being reported before we found dechlorination to be one main decomposition pathway. We could identify PCB's with 5,4,3,2 and 1 chlorine. Among the oxygenated products we were able to identify a series of o-methoxy-PCB's (4) and



z = 1-5

4



u = 1-4

5

another group of compounds we consider to be methoxysubstituted chlorodibenzofurans (5).

We discovered that around 80 compounds were formed during this irradiation, and the majority of these were oxygenated chloro-aromatics. We know very little about the toxic, genetic, cancerogenic and teratogenic effects of these compounds.
Flame retardants are in general halogenated compounds and some of them are very closely related to PCB. The consumption of flame retardant is expected to increase significatly. Therefore we feel that special interest must be devoted to these compounds.

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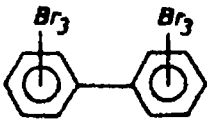
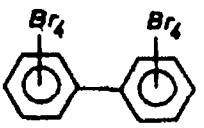
Hexabromobiphenyl (6) is known under the trademark FireMaster BP 6



6



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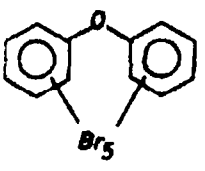
and the octabromo compound 7 as Bromkal 80. In addition to 6 and 7 two polybrominated diphenylethers 8 and 9 have been introduced as flame retardants for polymers. In this connection it must be worth



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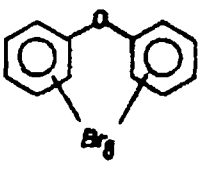

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notice that Suschitzky recently reported that the azadibenzofuran 11 can be prepared in preparative yield by a photochemical cyclisation of the chlorinated ether 10.[6]



10 11

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References

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