Polychlorinated Biphenyls: Photolysis of 3,4,3′,4′-tetrachlorobiphenyl and 4,4′-dichlorobiphenyl in Solution

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INTRODUCTION

We wish to report the photoproducts of 3,4,3',4'-tetrachlorobiphenyl and 4,4'-dichlorobiphenyl in hexane solution at 300 nm.

The photolysis of 2,4,6,2',4',6'-hexachlorobiphenyl has been studied (1), but isomeric composition of the products has not been determined. Polychlorinated biphenyls have been found in the environment and are known to be toxic and resistant to microbial breakdown (2), therefore, photodecomposition may prove to be their major breakdown pathway.

In our study we have found that there is stepwise dechlorination upon photolysis and the products have been identified.

METHODS & MATERIALS

4,4'-Dichlorobiphenyl was obtained from Aldrich Chem. Co. 3,4,3',4'-tetrachlorobiphenyl was prepared by reacting 3,4-dichloro-1-iodobenzene in ether solution with magnesium metal to form the Grignard reagent and coupling was accomplished using cupric chloride. This is a modification of the procedure used by Tsutsui (3). The overall yield was 40% of theory. The product was characterized by its melting point and spectrometric methods (NMR, UV IR, Mass spec.).

10 mg of 3,4,3',4'-Tetrachlorobiphenyl in 10 ml of redistilled n-hexane and 10 mg 4,4'-dichlorobiphenyl in 10 ml n-hexane (spectrograde) were photolyzed in the ultraviolet (λ>286 nm, λmax 310 nm) for 36 hours and 150 hours respectively, in sealed borosilicate test tubes, using a Rayonette reactor equipped with RUL 3000, B1 lamps (The Southern N.E. Ultraviolet Co.).

Using an LKB 900 GC-mass spcetrometer equipped with a 6 ft stainless steel column of 3% OV-210 on gas chrom Q, temperature programmed 140-190°C the products were resolved and their mass spectra obtained.

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The products were also separated using a 6 ft stainless steel column of 3% Apiezon L on gas chrom Q, flow rate 35 $\frac{ml}{min}$ at 220°C for the dichlorobiphenyl and 240° for the tetrachlorobiphenyl irradiated solutions.

RESULTS

The retention times for the photoproducts of 3,4,3',4'-tetrachlorobiphenyl and 4,4'-dichlorobiphenyl were found to be identical with those of standards. The three peaks obtained (240°) with 3,4,3',4'-tetrachlorobiphenyl with retention times 5.27, 10.86, 22.83 min corresponded to those of standard 4,4'-dichlorobiphenyl (5.27 min) and 3,4,3',4'-tetrachlorobiphenyl (22.83 min). Mass spectrometry revealed a tetrachlorinated biphenyl at 22.83 min (m/e 290), a trichlorinated biphenyl at 10.86 min (m/e 256) and a dichlorinated one at 5.27 min (m/e 222). From these data and the fact that no photochemical rearrangements of chlorinated biphenyls have been observed we conclude that the peak at 10.86 min corresponds to 3,4,4'-trichlorobiphenyl and that 3,4,3'-trichlorobiphenyl is not formed in the reaction since no 3,3'-dichlorobiphenyl is found among the products.

The two peaks obtained from the 4,4'-dichlorobiphenyl photolysis with retention times 4.17 min and 9.60 min (220°C) corresponded with standard samples of 4-chlorobiphenyl and starting material.

SUMMARY

The large difference in retention times for the photoproducts of 3,4,3'4'-tetrachlorobiphenyl can be explained on the basis of their chlorine content and the effect of vicinal chlorosubstitution as observed by V. Zitko and coworkers (4).

The absence of biphenyl among the photoproducts of 4,4'-dichlorobiphenyl was not surprising since 4-chlorobiphenyl (λmax 203, 253) does not absorb at the wavelength of irradiation (λ>286), 4,4'-dichlorobiphenyl exhibits only marginal absorption at this wavelength (λmax 201, 259, 286) this explains the low yield of 4-chlorobiphenyl obtained (appx. .1%). The greater reactivity at the meta position may be the result of bond weakening due to steric interactions with the chlorine atom at the para position. Rate studies may provide an answer to this problem.

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