Polyhalogenated Biphenyls: Photolysis of Hexabromo and Hexachlorobiphenyls in Methanol Solution

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Polyhalogenated biphenyls have been reported in various biological systems, such as human milk (ACKER and SCHULTE, 1970) and adipose tissue (BIROS et al, 1970). Recently in Michigan several herds of dairy cows were accidentally fed a commercial (Firemaster BP-6) hexabromobiphenyl fire retardant (LASSITER, 1974).

The metabolic pathways of chlorobiphenyls have been reported (SAFE et al, 1973) yielding hydroxylated biphenyls as major products. It was of interest to compare the photoreactivity of hexabromobiphenyl with that of PCB, and to investigate the possibility of photonucleophilic reactions involving the solvent. In a similar manner hydroxybiphenyls have been isolated from PCB photolysis in aqueous media (HUTZINGER and SAFE, 1972).

We have photolyzed 2,2',4,4',5,5'-hexachlorobiphenyl and Firemaster BP-6 in methanol and found them to undergo reductive dehalogenation and ring methoxylation. The reactivity of the brominated biphenyls is far greater than that of the PCB.

METHODS and MATERIALS

Firemaster BP-6 (I) was obtained from Michigan Chemical Co. 2,2',4,4',5,5'-Hexachlorobiphenyl (II) was purchased from Analabs, Inc. 3,3',4,4'-Tetrachlorobiphenyl was synthesized in our laboratory (RUZO et al, 1974).

Methanol solutions ($2X10^{-3}M$) of I and II were photolysed ($\lambda > 286$ nm) for periods of 0.5-2.0 hrs in sealed borosilicate test tubes, using a Rayonette Reactor equipped with Bl RUL 3000 lamps (The Southern N.E. Ultraviolet Co.). Samples were either aerated or degassed by nitrogen flushing. A Beckman GC-65 gas chromatograph interfaced with a DuPont 21-490 mass spectrometer and a PDP-12 (Digital) computer was used for analysis. A 6 ft X 1/8 in stainless steel column packed with 10% DC-200 on Gas Chrom Q (80-100 mesh) with a helium flow of 50 ml/min maintained isothermally at 220 or 250^{o} was used for separation of the photoproducts. The injector and detector temperatures were 280 and 300^{o} respectively.

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Thin-layer chromotagraphy was accomplished by developing with 4:1 benzene-methanol on precoated Silica-Gel F254 plates (EM Reagents).

RESULTS

After 1 hour of irradiation in degassed methanol compound II yielded 2,3',4,4',5-pentachlorobiphenyl and 3,3',4,4'-tetrachlorobiphenyl. These were identified from their mass spectra and by comparison with an authentic sample of 3,3',4,4'-TCB. The molecular ions appeared at m/e 324 and 290 respectively. The pentachlorobiphenyl showed the expected M+2, M+4, M+6, M-8, M+10, M-35 and M-70 signals. The tetrachlorobiphenyl showed a retention time and mass spectrum identical with that of a standard (R_t 13 min).

After one hour of irradiation approximately 10% of I had reacted to give 70% tetrachlorobiphenyl and 30% pentachlorobiphenyl. The rapid loss of ortho chlorines in biphenyl systems is well supported in the literature (L.O. RUZO et, 1974). It has been postulated that the excited PCB triplet is planar and can thus be stabilized from the para position and destabilized by ortho substituents. 2,4,-disubstituted biphenyls such as II combine both effects and show greatest reactivity.

Compound I after 45 minutes of irradiation (70% reacted) yielded as major products penta- and tetra-bromobiphenyls with retention times of 25 and 16 minutes respectively. These showed characteristic mass spectra (M at 544 and 466 m/e). Compound I also yielded >1% methoxylated product. A compound with M^+ at m/e 526 identified tentatively as dimethoxy tetrabromobiphenyl was observed after separation of the reaction mixture by preparative thin layer chromatography followed by gas chromatographic analysis (R_t 16 min).

By measuring the amounts of I and II reacted it is observed that the brominated biphenyl is about seven times as reactive as its chloro counterpart, an increase in reactivity which can be attributed to its lower bond energy. Over similar time periods dark controls did not show reaction.

When I and II were irradiated in aerated solution the rates of reaction decreased considerably (~50%), as would be expected with a triplet intermediate.

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