

posure of lot I to ultraviolet light (Table III), there was a loss of 35.2% of the residues remaining after the 10 days' dark treatment.

After an additional 10 days' exposure of lot II to sunlight (Table III), 77.4% of the residue remaining on lot II after the initial 10-day treatment with ultraviolet light was lost.

When lot III was exposed to ultraviolet light for an additional 10 days (Table III) after the initial 10-day sunlight exposure, a loss of 22.3% of the total residues occurred.

During the 10-day subsequent light exposures, no significant changes occurred in the carbofuran-related degradation products on the plant material other than losses due to temperature effects except with the following compounds: lot I to sunlight, the 3-oxocarbofuran increased from 1.6 to 2.4 ppm and the 7-phenol increased from approximately 0.2 to 2.9 ppm; lot I to ultraviolet light, the 3-oxocarbofuran increased from 1.6 to 2.5 ppm and the 7-phenol increased from approximately 0.2 to 1.5 ppm; lot II to sunlight, the 7-phenol increased from approximately 0.1 to 2.3 ppm and the 3-keto-7-phenol increased from approximately 0.1 to 0.3 ppm.

The presence of ultraviolet light or its absence significantly affected the interconversion of certain of the carbofuran related compounds while increased temperature effects greatly influenced the loss of all residues probably due to volatility from the plant material.

The practical relevance of these findings is that carbofuran and related compounds are removed or decreased

in concentration during the drying of alfalfa by conventional sunlight as well as by artificial ultraviolet light irradiation. Losses of pesticide residues from the plant material probably also occur as volatilization with moisture.

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Photodegradation of Polybromobiphenyls (PBB)

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A series of polybrominated biphenyls (PBB) ranging from 2 to 8 atoms in bromine content was studied in regard to their ultraviolet properties and photochemical reactivity. The compounds containing bromine atoms in positions ortho to the biphenyl linkage were found to have greater ease of debromination in hexane and methanol solutions at wavelengths >290 nm. Debromination at the ortho positions was preferred in all cases. No substitution products were detected in methanol or water-acetonitrile solutions. The sensitizing effect of benzophenone and the slight quenching observed in air-saturated solutions suggest a triplet excited state intermediate.

Recently, polybrominated biphenyls (PBB) have aroused considerable interest among environmental chemists and biologists. This interest is based on the structural similarity of PBBs to the well-known pollutants polychlorinated biphenyls (PCB), combined with the extensive use of PBBs as fire retardants, thereby making their entry into the ecosystem (via sewage, household waste, etc.) a good possibility. Polybrominated biphenyls have not as yet been reported to be present in the environment; however, severe

poisonings of livestock have occurred in the U.S. when feed was accidentally mixed with technical PBB (*Chem. Eng. News*, 1975). Investigations have shown that hexabromobiphenyl preparations induce hepatic porphyria in birds in a manner similar to PCB and HCB (hexachlorobenzene) (Strik and Wit, 1972; Strik, 1973). The toxicity of PBBs and some other biological effects have also been studied (Cecil et al., 1975; Norris et al., 1975).

Degradations of PBBs in the environment may occur either by metabolic (Safe, 1975) or photochemical (Ruza and Zabik, 1975) pathways. Generally, photodegradation of aromatic bromo compounds has received little attention (Maatsura and Omura, 1966; Parkány and Lee, 1974); however, in a recent paper Bunce et al. (1976) reported some mechanistic data on the photolysis of monobromobiphenyls. This study showed that bromobiphenyls follow the same order of photoreactivity as the PCBs (Ruza et al., 1974a) in that cleavage of bromine atoms ortho to

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Table I. Photoproducts of Polybrominated Biphenyls^a

Substrate	t_R , min ^b	Product ^c
2-Br	0.68	Biphenyl
3-Br	0.80	Biphenyl
4-Br	0.83	Biphenyl
2,2'-Br ₂	0.98	2-Br
4,4'-Br ₂	1.46	4-Br
2,5-Br ₂	1.16	3-Br
2,6-Br ₂	1.00	2-Br
2,4-Br ₂	1.13	4-Br
2,4,6-Br ₃	1.63	2,4-Br ₂ , 4-Br
2,5,2'-Br ₃	1.67	(Br ₂), 3-Br
2,5,3'-Br ₃	2.07	(Br ₂), 3-Br
2,5,4'-Br ₃	2.08	(Br ₂)
2,2',5,5'-Br ₄	2.86	(Br ₃ , Br ₂), 3-Br
3,3',5,5'-Br ₄	4.39	(Br ₃)
2,5,3',4'-Br ₄	4.04	(Br ₃)
2,4,6,2',5'-Br ₅	4.50	(Br-Br ₁)
2,2',4,4',5,5'-Br ₆	12.50	(Br ₅ -Br ₂)
2,2',3,3',5,5',6,6'-Br ₈	24.60	(Br ₇ -Br ₁)

^a *n*-Hexane and methanol solutions at 300 nm (0.5–2 h).

^b 5% SE-30 column. ^c Parentheses denote products not identified beyond bromine content.

the biphenyl linkage occurs at a faster rate than those of bromine atoms at the meta or para positions. We now report on the rates, photoproducts, and ultraviolet spectra of a number of PBBs containing 2–8 bromine atoms per molecule.

EXPERIMENTAL SECTION

Materials. The isomeric monobromobiphenyls, 2,2'-dibromo-, 4,4'-dibromo-, 2,2',4,4',6,6'-hexabromo-, and 2,2',3,3',5,5',6,6'-octabromobiphenyl are available commercially (Chemical Procurements Laboratories, Inc., and Aldrich Chemical Co.).

Other compounds used were synthesized by coupling reactions between bromoanilines and benzene or bromobenzenes via decomposition of the anilines with amyl nitrite. Solid products were crystallized from ethanol or methanol until gas chromatographic purity (>99%) and stable melting points were obtained. Liquid samples were purified by column chromatography (aluminum oxide, activity I/hexane). 2,2',4,4',5,5'-Hexabromobiphenyl was obtained by purification of a technical flame retardant, fireMaster BP-6 (Sundström et al., 1976a). Authenticity of products was established by mass spectrometry and melting points. Synthesis and characterization of bromobiphenyls are described elsewhere (Sundström et al., 1976b).

Methanol, hexane, and acetonitrile used as solvents were of spectrophotometric grade (Merck, Darmstadt, D.B.R.).

Gas chromatographic investigations were performed on a Hewlett-Packard 5830 A chromatograph equipped with a flame ionization detector and an electronic integrator. For separations two different glass columns (2 m × 2 mm i.d.) were employed, one 5% SE-30 on Chromosorb W (100–120 mesh) and one ca. 0.3% Carbowax on pretreated Chromosorb W (100–120 mesh). The flow rate (helium) was 30 ml/min and detector and injector temperatures were 250 °C. The oven temperature was maintained isothermally at 220 or 250 °C. Retention times of investigated compounds are given in Table I.

Mass spectrometry was carried out on a MAT CH7 Varian apparatus operated at 70 eV ionizing voltage.

Ultraviolet spectra were obtained from a Shimadzu UV 200 double beam spectrometer. Ethanol and hexane were used as solvents.

Photochemical Procedures. Samples of PBB were dissolved in hexane, methanol, or acetonitrile–water (3:2) in concentrations of 10⁻²–10⁻³ M. Two-milliliter solutions

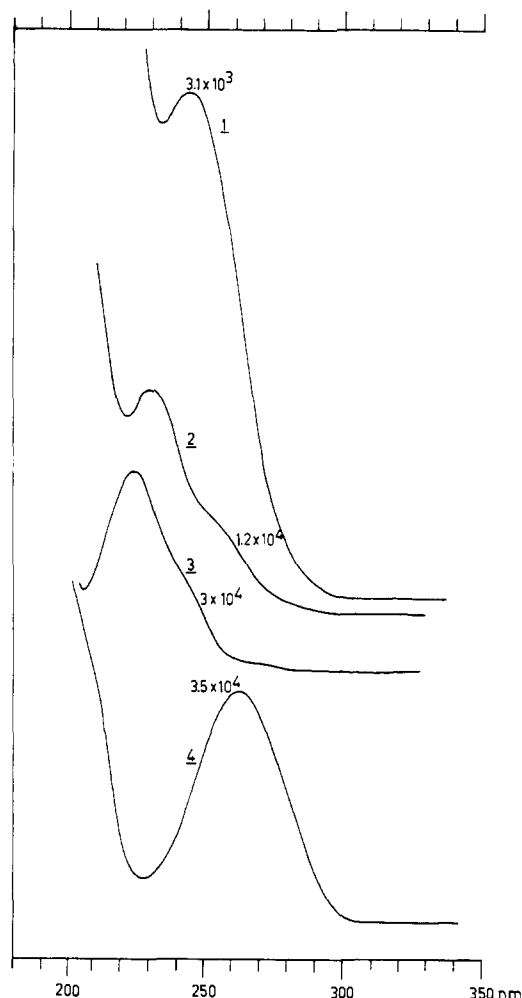


Figure 1. Ultraviolet spectra of (1) 2,4-dibromo-, (2) 2,4',5-tribromo-, (3) 2,2',3,3',5,5',6,6'-octabromo-, and (4) 4,4'-dibromobiphenyl. Extinction coefficients are indicated.

were photolyzed during 0.5–3 h using a Rayonette reactor (New England Ultraviolet Co.) equipped with RUL 3000 lamps (peak output 290–310 nm) and a “merry-go-round” apparatus to ensure equal exposures of samples to the radiation. The PBB solutions were degassed by nitrogen bubbling (2 h) at 0 °C or air-saturated in a similar manner (1 h).

RESULTS

Ultraviolet Spectroscopy. The uv spectrum of unsubstituted biphenyl features two important absorption maxima, one at 202 nm and a second at 242 nm, the latter referred to as the K band. The 242-nm band is attributed to the conjugated biphenyl system with the contributions of both phenyl rings. The effect of various substituents on the K band has been reported (Pickett et al., 1936; Beaven, 1958); the meta and para substituents cause a bathochromic shift and ortho groups cause a shift to lower wavelengths with a diminished ϵ value. It is generally accepted that in the highly hindered ortho-substituted biphenyls there is considerable hindrance to free rotation which results in the loss of coplanarity between the two phenyl rings. The polybrominated biphenyls showed spectra in accordance with previous findings (Figure 1). 4,4'-Dibromobiphenyl showed a K band with λ_{max} at 263 nm. Increased substitution by bromine at the 2, 2', 6, and 6' positions caused this band to disappear and the spectra exhibited a series of weak absorption maxima between 270 and 300 nm. These signals have been attributed to for-

bidden transitions to an excited state with increased contributions from homopolar structures (Gillam and Stern, 1957). The absorption of even the most highly ortho-substituted PBB at 310 nm is sufficient for photoreaction (Table I).

The reactivity of *o*-bromobiphenyl has been previously reported (Bunce et al., 1976) to be greater than the meta or para isomers. Our present findings support this characteristic behavior. The ultraviolet spectra show that the steric effect which prevents coplanarity is present in *o*-bromobiphenyls and this can be used as a basis for hypothesizing a planar excited state by which a driving force is provided for cleavage of ortho substituents.

Photoreactivity. Hexane solutions of PBB irradiated at 300 nm gave in virtually quantitative yield the corresponding debrominated biphenyls, identified when possible by comparison of their gas chromatographic properties with authentic compounds of known structure. In all cases the major products observed arose from loss of bromine atoms from the 2 or 2' positions of the biphenyl system. For all the dibromo isomers studied the monobromobiphenyl obtained could be conclusively identified. 2-Bromobiphenyl was observed as a product only from 2,2'- and 2,6-dibromobiphenyl. In all other cases loss of the bromine in the 2 position gave 3- or 4-bromobiphenyl as products. 2,4,6-Tribromobiphenyl yielded only 2,4-dibromo- and 4-bromobiphenyl; no 2,6-dibromobiphenyl was observed.

Although not all necessary standards were available to identify the photoproducts of the higher brominated species, their retention times and mass spectra suggested the same stepwise debromination process occurred as with the di- and tribromo isomers. The retention times of bromobiphenyls on gas chromatography followed the same pattern as the PCBs (Hutzinger et al., 1974), i.e. for compounds with the same number of halogen substituents the retention time was shortest for the isomer with the most substituents in the 2 and 6 positions of the biphenyl ring (Table I). 2,2',4,4',5,5'-Hexabromobiphenyl yielded several products, among them 4,4'-dibromobiphenyl, but again, no 2,2'-dibromobiphenyl could be detected. The higher brominated products from this hexabromobiphenyl had retention times consistent with penta-, tetra-, and tribromobiphenyls. 2,2',3,3',5,5',6,6'-Octabromobiphenyl gave as one of its photoproducts 3,3',5,5'-tetrabromobiphenyl indicating the primary loss of all four 2, 2', 6, and 6' bromines.

The reaction pathways of the PBBs are partly analogous to those reported for the chlorobiphenyls, i.e. a series of tetrachlorobiphenyls was found to yield dechlorinated compounds arising from loss of chlorine ortho to the biphenyl linkage upon photolysis in hexane and methanol solutions (Ruzo et al., 1974b). However, the corresponding methoxylated products observed in the chlorobiphenyl photolyses in methanol were not detected in the photolysis of PBBs in the same solvent. When 2,4-dibromo- and 2,3',4',5-tetrabromobiphenyl were photolyzed in acetonitrile-water solution it was shown that debromination also was the major reaction. The possible presence of polar material in the form of hydroxylated species was investigated by thin-layer and gas chromatography before and after treatment with diazomethane. No differences in the chromatographic patterns were observed thus excluding the presence of phenolic compounds.

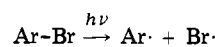
Examination of the nonvolatile residues obtained after the photolyses in hexane showed that dimerization reactions giving rise to quaterphenyls were occurring to a small extent (<5%). The products are thus analogous to

Table II. Photoreactivity of Polybrominated Biphenyls in Hexane Solution

X substrate	Concn, M	ϵ (310 nm) ^a	% re-acted	Rel rate ^b
2,2',4,4',5,5'-Br ₆	2.5×10^{-3}	88.0	55	24.4
2,5,2'-Br ₃	3.0×10^{-2}	1.3	13	20.4
2,2'-Br ₂	6.1×10^{-2}	1.6	10	20.0
2,2',3,3',5,5',6,6'-Br ₈	1.1×10^{-3}	436.0	94	18.2
2,5,4'-Br ₃	1.2×10^{-2}	20.0	19	17.1
2,6-Br ₂	2.1×10^{-2}	3.3	17	15.5
2,4,6-Br ₃	1.5×10^{-2}	5.3	52	14.7
2,4,6,2',5'-Br ₅	4.0×10^{-3}	27.5	37	14.4
2,5-Br ₂	2.0×10^{-2}	6.0	43	11.1
2,5,3'-Br ₃	2.0×10^{-2}	9.0	8	10.9
2,5,3',4'-Br ₄	2.1×10^{-3}	47.6	56	7.1
2,4-Br ₂	3.1×10^{-2}	3.9	13	6.7
2,2',5,5'-Br ₄	1.3×10^{-2}	6.9	24	2.5
4,4'-Br ₂	3.0×10^{-3}	33.4	25	1.0
3,3',5,5'-Br ₄	1.2×10^{-3}	38.2	48	0.7

^a In hexane solution. ^b Rate calculated from zero-order expression relative to the 4,4'-Br₂ isomer.

those found in other aryl halide systems (Pinhey and Rigby, 1969; Stevens, 1971) and explicable in terms of intermediate aryl radicals.



Reaction Rates. The reactions of PBBs appear to proceed from triplet excited states, as might be expected for heavy-atom compounds. Thus, rates are retarded slightly in air-saturated solutions as compared to degassed solutions, and benzophenone (0.2 M) sensitizes the reactions.

As seen in Table II PBB isomers containing ortho bromine atoms are photolyzed more efficiently than other isomers, suggesting a steric effect of the bromine atoms analogous to the effects found in the photolyses of PCBs (Ruzo et al., 1974b). Thus, 4,4'-dibromo- and 3,3',5,5'-tetrabromobiphenyl exhibit the lowest disappearance rates in spite of their considerably higher ϵ values at around 300 nm. After adjustment for incomplete absorption of radiation by the ortho-substituted PBBs the largest rates were observed for 2,2',4,4',5,5'-hexabromobiphenyl (Table II). The reaction rates do not appear to be dependent on the total number of bromine substituents.

The values shown in Table II are averages of several runs relative to the disappearance rate of 4,4'-dibromobiphenyl. The rates were calculated from the zero-order expression:

$$M_0 - M_t = kt$$

where M_0 and M_t are the molar concentrations at times 0 and t and k is the zero-order rate constant. The values were then adjusted according to the absorbance of the solution in the 290–310 nm region.

The rapid photolysis of PBB in hexane solution at wavelengths available at the lower end of sunlight radiation indicates the environmental significance of such nonbiological degradative processes. Since PBBs are nearly insoluble in water the bulk of these materials which may be carried in environmental waters is probably dissolved or suspended in liquid fats, in soap or detergent micelles, or absorbed on microparticulates. Hydrogen abstraction reactions can readily occur in these systems. It is also of interest to note that there is a strong similarity between the photochemical processes undergone by PBBs and PCBs in that steric factors determine the reactivity in both series and that the greater reactivity of the former (Ruzo and Zabik, 1975) will render them less persistent in the environment.

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Insect Growth Regulators. Analogues of TH-6038 and TH-6040

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A number of analogues of the insect growth regulators TH-6038 (1) and TH-6040 (2) were synthesized and tested against four species of insects. The effects of selective replacement of oxygen by sulfur in 1 and 2, as well as of various other structural modifications of these compounds, were determined. Although none of the new compounds were as active as 2, several effectively inhibited larval development of all insects tested, and one compound, *N*-(4-chlorophenyl)-*N'*-(2,6-difluorobenzoyl)thiourea, inhibited reproduction of female house flies when administered in their diet at a concentration of 1%.

Chemicals capable of selectively disrupting the development of immature insects have become of ever increasing interest over the past several years. Two such compounds, 1-(4-chlorophenyl)-3-(2,6-dichlorobenzoyl)urea (TH-6038, Thompson-Hayward 6038, 1) and 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea (TH-6040, Thompson-Hayward 6040, Dimilin, 2) are noteworthy for several reasons. (1) They are effective against a broad spectrum of insect larvae (Wellinga et al., 1973a,b). (2) They are not only chemically dissimilar to the previously developed insect growth regulators, i.e. juvenile hormone mimics, but they are also biologically dissimilar in that they are lethal to a variety of insects at all larval stages. Thus they are effective against the feeding stages of some crop pests whereas juvenile hormone mimics may control the pests only after considerable feeding damage has been done. (3) They have the ability to effectively sterilize adult females of several insect species (Moore and Taft, 1975; Taft and Hopkins, 1975; also unpublished results from our laboratories).

The antifertility property of 1 and 2 has been of limited utility, however, because of the ability of the insects to rather rapidly regain fertility after exposure to the chemicals is terminated (Robbins et al., 1976; McHaffey, 1976). During the development of compounds 1 and 2, the Philips-Duphar group thoroughly examined the effects of

different substituents on the aromatic rings and also of substitution of nitrogen (Wellinga et al., 1973a,b), but they did not report chemosterilant activity of these compounds. We became interested in whether minor modifications in the structures of 1 and 2 might moderate the biological activities in this or any other respect and, accordingly, synthesized analogues wherein the oxygen atoms of 1 and 2 were individually replaced by sulfur atoms (3-6). We also prepared the trifluoro analogue 7, the sulfonylurea 8 (replacement of C=O of 2 by SO₂), the carbamate 9 (replacement of NH of 1 by O), the benzoxazole derivative 11 (construction of an *O*-aryl bond in 2), and the related compounds 7, 10, and 12.

After this work was complete, Yu and Kuhr (1976) reported the synthesis and activity against seedcorn maggot larvae (*Hylemya platura* (Meigen)) of several 1-phenyl-3-benzoylureas and thioureas, including three compounds reported in this paper (5, 6, and 7). Our melting points are in good agreement with those reported.

MATERIALS AND METHODS

Syntheses of new compounds are outlined in Scheme I and are described in the Experimental Section; most were based on analogies in the literature. Worthy of note are the one-step synthesis of 2,6-difluorobenzene-sulfonyl chloride 20, and the different behaviors of the two benzoyl isothiocyanates, 15 and 16, with 4-chlorophenol and aluminum chloride. The benzoxazole 11 was prepared by two independent methods to ensure a correct structural assignment.

The larval test systems for the yellow fever mosquito, *Aedes aegypti* (L.), the confused flour beetle, *Tribolium confusum* Jacquelin duVal, the house fly, *Musca domestica*

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