PHOTOCHEMICAL PROCESSES
OF POLYCHLORINATED BIPHENYLS
IN SOLUTION:
PHOTOPRODUCTS AND KINETICS

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ABSTRACT

PHOTOCHEMICAL PROCESSES OF POLYCHLORINATED BIPHENYLS IN SOLUTION: PHOTOPRODUCTS AND KINETICS

by

Luis Octavio Ruzo

A comparison of the photoreactivities of several symmetrical and unsymmetrical tri- and tetrachlorinated biphenyls has revealed differences in the photoproducts obtained and in the kinetic parameters of the excited state.

(1) The photoproducts of eleven polychlorinated biphenyls (PCB) were identified from reactions in cyclohexane and methanol solutions at 300 ± 10 nm. The reactivities of chlorines in the <u>ortho</u> position were found to be greater in all cases than those in <u>meta</u> or <u>para</u> positions Cleavage of halogen to yield dechlorinated PCB and methoxy-substitution in the aromatic rings were the major reaction pathways. Possible mechanisms for both processes are advanced and discussed.

(2) Quantum yields and reaction rate constants were determined for all compounds studied. A correlation between the degree of chlorination, the position of the substituents and the kinetic parameters was observed. PCB containing 2,4 substitution were more reactive than those with 2,3; 2,5; and 2,6 substituted positions. The lowest quantum yields obtained were for PCB with 3,4 and 3,5 chlorination.

(3) The triplet excited state was found to be the reactive intermediate. Its lifetime was measured by quenching methods (Stern-Volmer plots). The reaction and decay rate constants (k_r and k_d) of the triplet were determined. The values were found to correlate well with existing information regarding the geometry, electron distribution and stability of aromatic triplets.

PHOTOCHEMICAL PROCESSES OF POLYCHLORINATED BIPHENYLS IN SOLUTION: PHOTOPRODUCTS AND KINETICS

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Luis Octavio Ruzo

A DISSERTATION

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With the drawing of this love
and the voice of this calling,
we shall not cease from exploration
and the end of all our exploring
will be to arrive where we started,
and know the place for the first time.

T. S. Eliot

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While writing these lines it quickly becomes evident that there's no way to acknowledge everyone's help. The faculty members in my committee, Dr. Peter Wagner and my fellow graduate students have all contributed in some way to the completion of this project.

Totally outside Chemistry, my mother and father have constantly encouraged me and provided their unconditional support. Marlene, who knows better than anyone else how much all this entailed, has been and is now my driving force.

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INTRODUCTION

A. Photochemical Background

1. Environmental Importance of Polychlorinated Biphenyls

Within the last few years a sudden interest has developed in a hitherto relatively unknown class of industrial organochlorine compounds: the polychlorinated biphenyls (PCB).

Traces of these compounds have been reported in environmental samples since 1966.[1] In the following years PCB contamination was found to be almost universal,[2-7] including human milk,[8] human adipose tissue[9] and brain tissue of infants.[10] Little is known about the toxic effects of PCB after long-term exposures, as observed in the endemic poisoning resulting from PCB contaminated rice oil.[11]

Polychlorobiphenyls are prepared commercially from the iron catalyzed chlorination of biphenyl.[12] The product is a complex mixture containing at least sixty different PCB isomers with varying chlorine content.

The characteristic properties of PCB which make them desirable for industrial use are their high dielectric constant and their thermochemical stability up to 900°C. Their stability coupled with the ease with which they are taken up by living organisms and accumulated at higher levels of the food web, has resulted in environmental problems.

At present they are used as dielectric fluids in capacitors and transformers; as industrial fluids in hydraulic systems, gas turbines and vacuum pumps; as plasticisers in adhesives; in textiles, surface coatings, sealants and copy paper; as heat transfer agents, fire retardants and fruit preservers. With such a variety of uses it is not surprising that industrial leaks are largely responsible for the presence of PCB in the ecosystem.

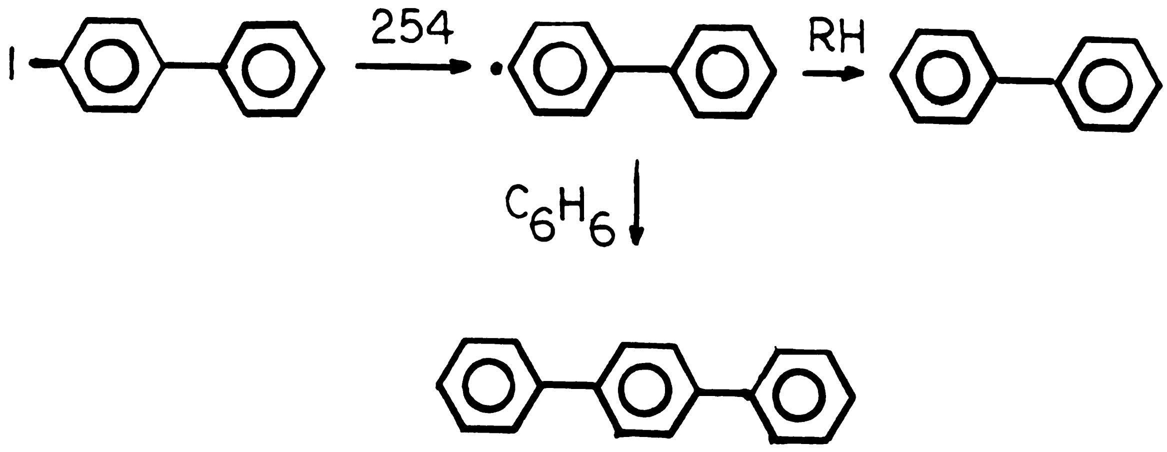
Metabolism and Toxicology. There is evidence that PCB are metabolized slowly in some organisms to their hydroxy derivatives.[13] However, little is known about the efficiency of uptake and excretion and it is considered probable that a steady-state situation exists in some areas.

Even though all the available commercial PCB mixtures (Arochlors) are toxic to some extent, those containing four or less chlorine substitutents have the highest toxicity, as reported in a study of their interaction with tissue culture cells.[14]

2. Photoproducts

At the beginning of our research (1970) no reports existed in the literature concerning the photochemical behavior of PCB. Several chloroaromatics had been studied and in every case either chlorine cleavage with subsequent free radical hydrogen abstraction[15-17] or nucleophilic displacement of chlorine[18-20] occurred.

The photochemistry of iodobiphenyls at 254 nm in benzene and hydrocarbon solvents was reported in 1968.[21] Kharasch found that iodine cleavage resulted in the formation of a biphenylyl radical which could then either attack the solvent to yield terphenyl or abstract hydrogen and from biphenyl.

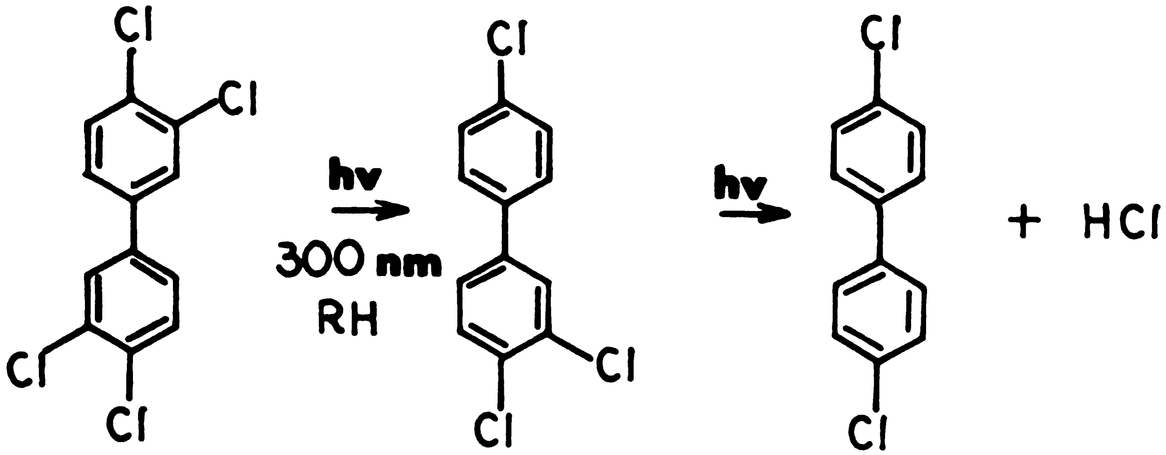


In the presence of oxygen the recombination reaction becomes negligible and p-hydroxybiphenyl is obtained. Further proof of the intermediacy of free radicals is obtained when the reaction is run in the presence of nitric oxide (NO) a known radical scavenger which can inhibit the back reaction, thus the quantum yield of iodobiphenyl reaction increases.

The photolysis of iodobenzene in fluorocarbon solvents at 77°K has been studied by ESR. The results also suggest the formation of free phenyl radicals upon photolysis.[22]

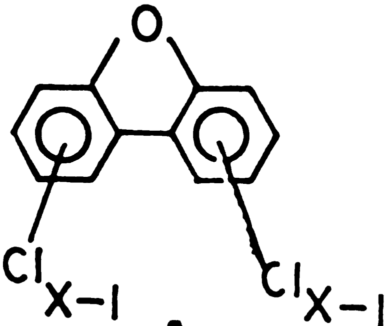
In 1971 the first study of PCB photochemistry appeared in the literature.[23] Dechlorination of 2,2',4,4',6,6'-hexachlorobiphenyl at wavelengths greater than 300 nm in hexane yielded more than ten products containing two to five chlorines per molecule. The individual isomers were not identified beyong establishing their parent peaks (M) from the mass spectra.

Our studies of the photolysis of 3,3',4,4'-tetrachlorobiphenyl showed stepwise dechlorination to be the only reaction undergone by this compound in hexane.[24]

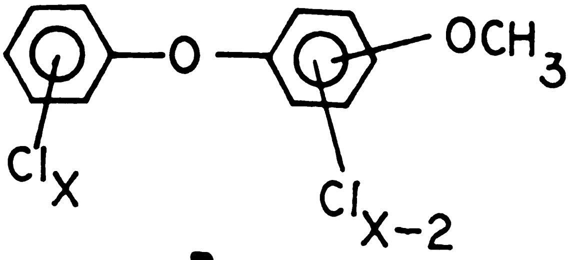


At about the same time 2,2',5,5'-tetrachlorobiphenyl was photolysed in dioxane-water and hydroxy substitution was obtained in addition to small amounts of condensation and reductive dechlorination[25] products. 2,2',5,5'- 3,3',4,4'- and 2,2',6,6'- etrachlorobiphenyls were found to decompose at about the same rate in non-degassed solutions. However, no accurate kinetic values were obtained and no photoproducts were identified beyond their molecular weight.

The photolysis of 2,2',4,4',6,6'-hexachlorobiphenyl in oxygen saturated methanol solution has been found to yield oxygenated, methoxylated and dechlorinated products (A,B,C)[26] in small amounts.



A



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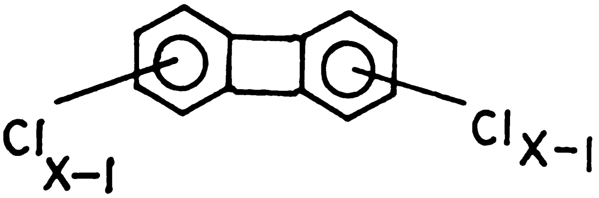
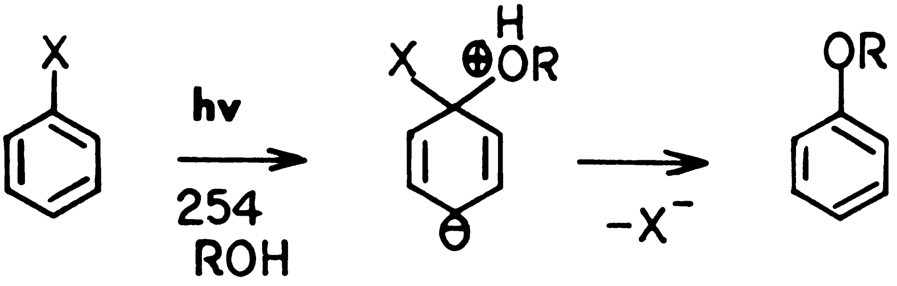


C

These compounds arise from cleavage of <u>ortho</u> chlorines and subsequent radical reactions with oxygen. None of them are observed in degassed solutions.

All these results point to the intermediacy of biphenyl free radicals, either abstracting hydrogen from the solvent, or combining with triplet oxygen to give peroxides and subsequently ethers.

The methoxylated or hydroxylated products observed may be formed in a manner similar to that of several haloaromatic systems studied.[18,27]



$R = CH_3, H$

$X = Cl, Br, I$

The ionic intermediate can be stabilized by electron withdrawing groups <u>ortho</u> or <u>para</u> to X. The reaction usually has a low quantum yield (<0.1) and the preferred course is elimination of X before nucleophilic attack takes place.

Haloterphenyls have also been found to dechlorinate photochemically with subsequent formation of terphenyls and cyclization products.[28]

3. <u>The Excited State of Polychlorinated Biphenyls</u>

In 1933 Adams showed that those derivatives of biphenyl which had substituents above a certain limiting size in the <u>ortho</u> position could be resolved into steroisomers.[29] This phenomenon was explained as a result of restricted rotation of the two benzene rings by interference from the substituent groups.

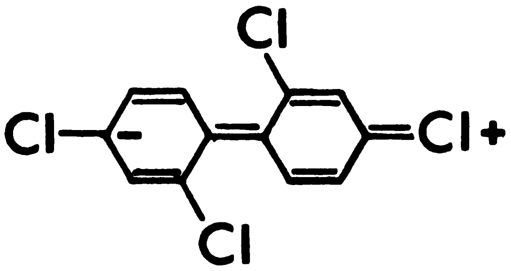
The ultraviolet absorption spectra of several 2,2'-disubstituted biphenyls showed unexpected differences with their benzene analogs.[30] The band maxima in the benzene derivatives corresponded to similar ones in the biphenyl compounds which are displaced toward lower energies. Absorption was nearly additive for the two rings. With 4,4'-dichloro biphenyl the red shift was greater and the band intensity showed a 10^3

fold increase compared to that of 2,2'-dichlorobiphenyl. At the time (1936) no explanation was offered for this phenomenon.

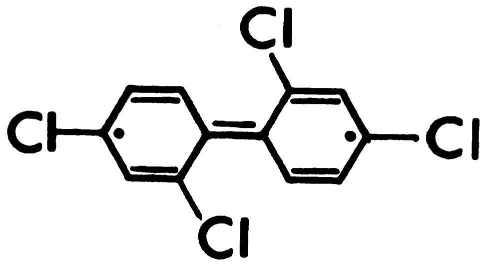
In 1938 the geometry of biphenyl derivatives was studied on the basis of their dipole moments.[31] The carbons 4-1-1'-4' were found to be colinear in a large majority of the compounds studied. X-ray studies confirmed these findings.[32]

The earliest observations with regard to the actual excited state of biphenyls were given by Lewis and Kasha in 1944.[33] The triplet energy (E_t) of several haloaromatics was calculated from their phosphorescence spectra. E_t values were lowest for 4,4'-disubstituted biphenyls (<66 kcal) and highest for the ortho substituted PCB (>70 kcal).

The solution spectrum of biphenyl shows a single structureless band with λ_{max} around 250 nm and ε_{max} of 18,000. Presumably this band represents the 208 nm transition of benzene, which is shifted by conjugation with the chromophoric phenyl substituent. The forbidden benzene transition at 256 nm is probably hidden below the main biphenyl band. The additional weak band displayed at 270-290 nm by some halobiphenyls is probably the result of interactions between the substituent's free electrons in the π system.[34,35] The electron distribution in the excited state can be represented by 1 or 2.



1



2

Thus, if the excited state of PCB is a dipolar or diradical species with coplanar rings and a Cl-Cl' linkage of essentially complete double bond character then the short wave shift in the conjugation band of an ortho chlorinated PCB would arise from an increase in the transition energy resulting from the raising of the triplet energy. The excited triplet is thus shown to be more sensitive to steric effects than the ground state.

On this basis, a correlation may exist between the steric requirements of the triplet and the photochemical lability of the ortho chlorines, relative to that of those in the meta or para positions.

Studies of deuterium isotope effects have been carried out.[36] A molecule such as biphenyl d_{10} would be expected to be closer to planarity than normal biphenyl h_{10} owing to the shorter length of the C-D bond compared to the C-H bond. The extinction coefficient of biphenyl d_{10} reflects the increase in resonance between the rings, in hexane solution a ratio of $\varepsilon_H/\varepsilon_D = 0.96$ has been obtained.[37]

In 1967, Wagner reported the actual triplet energy of biphenyl.[38] He found that there was a 10 kcal difference between the highest energy phosphorescence band at 65.5 kcal and the lowest energy absorption band at 75.5 kcal. This case of non-overlapping emission and absorption spectra is a direct result of the Franck-Condon principle.[39] When the lowest vibrational levels of ground and excited states possess significantly different geometries, true spectroscopic 0-0 transitions are forbidden, and the apparently divergent 0-0 bands observed represent transitions from one vibrationally relaxed state to a vibrationally excited mode of another state. In the case of biphenyl this implies a large difference in geometry between the ground state and the excited triplet. The band at 65.5 kcal in the emission spectrum arises from a transition of the triplet to a vibrationally "hot" ground state. The absorption band at 75.5 kcal would correspond to a transition from the relaxed ground state to a non-equilibrium or "phantom" triplet. The true 0-0 band must lie somewhere between the two values. Quenching experiments relative to benzophenone would indicate an E_t value of 69.5 kcal.

The most stable conformation of ground state biphenyl depends strongly on the medium. The dihedral angle between the rings is 40-50° in the gas phase,[40] 20-25° in solution,[41] and 0° in the crystalline state.[42] Since ortho substituents increase this angle,better quenching could be expected if the excited state was non-planar, and worse quenching if planar. Wagner found that the quenching efficiency of substituted biphenyls was less than expected when quenching a series of ketones.

Other evidence for the planarity of the excited state was provided by Hirota.[43] The S-T* absorption spectra of several compounds in the crystal form was measured in the presence of a "doping" agent, a compound with lower E_t which could trap the excitation. The spectrum of biphenyl thus obtained had a 0-0 band at 65.5 kcal in exact agreement with the highest energy phosphorescence band. That band must arise from a transition between planar conformations of both ground and excited states. Such a transition is a true 0-0 band in the crystal where the dihedral angle is 0°, but not in solution where the conformation of the ground state is twisted.

4. General Mechanistic Scheme and Kinetic Expressions

One advantage liquid-phase photochemistry has over the gas phase is that several kinetic simplifications can be made. Absorption of light by a PCB can produce several excited singlets with many corresponding vibrational levels. In solution, decay to the lowest excited singlet occurs almost instantaneously (10^{-12}sec).[44] Thus, it may be assumed that all singlet processes happen from the lowest singlet (S_1).

Experiments using mono- and dichlorobiphenyls show that intersystem crossing quantum yields (ϕ_{isc}) increase with increasing number of chlorine substituents.[45] Though small, chlorine has a measurable heavy atom effect (HAE). With iodine and bromine HAE values are greater.[46,47] Such effects on S-T transitions are quite general and are probably the result of spin orbit coupling which causes mixing of singlet and triplet states.[48] The singlet then acquires a small amount of triplet character and the triplet some singlet character, so the transition loses some of its forbidden character. HA effects are responsible for large phosphorescence/fluorescence ratios obtained with haloaromatics.[49] It has also been pointed out that HAE involving π-π^* excited state are quite pronounced since normally negligible amounts of spin orbit coupling are present in symmetrical aromatics.[50]

For kinetic calculations in solution the rate of phosphorescence can usually be ignored since it is much slower than the rates of other triplet processes. The following mechanistic scheme can be written for the photochemical processes of PCB (A) in solvent (SH), with quencher Q.

SCHEME 1

Process	Rate	
$A_o + hv \xrightarrow{I_a} A_1^* \xrightarrow{isc} A_3^*$	I_a (if $\phi_{isc} = 1$)	(1)
$A_3^* \rightarrow A_o$	$K_d [A_3^*]$	(2)
$A_3^* \longrightarrow A\cdot + Cl\cdot$	$K_r [A_3^*]$	(3)
$A\cdot + SH \longrightarrow A - H + S\cdot$		(4)
$S\cdot + S\cdot \longrightarrow S - S$		(5)
$A\cdot + A\cdot \longrightarrow A - A$		(6)
$Cl\cdot + SH \longrightarrow H - Cl + S\cdot$		(7)
$Cl\cdot + A\cdot \longrightarrow A_o$		(8)
$A\cdot + S\cdot \longrightarrow A - S$		(9)
$A_3^* + Q \longrightarrow A_o + Q_3^*$	$K_q [Q][A_3^*]$	(10)

Under steady-state conditions $dA^{*3}/dt = 0$ and the only directly measurable parameter is the quantum yield of reaction. Using the definition of Wagner,[51] the quantum yield for a particular photoprocess i is given by:

$$\phi_i = \phi_{ES}\, \phi_R\, P_i \tag{11}$$

where ϕ_{ES} represents the probability that absorption of light will lead to the required excited states; ϕ_R the probability that the excited state will undergo the primary photoreaction necessary for process i; P_i is the probability that any metastable ground state intermediate will lead to stable product, completing process i rather than forming by-products or reverting to starting material.

Assuming $\phi_{isc} = 1$ for PCB containing three or more chlorines:

$$\phi_i = P_i \frac{K_r}{K_r + K_d} \tag{12}$$

so that ϕ_i becomes the quantum yield of reaction.

When a triplet quencher is used equation 12 becomes:

$$\phi_i = P_i \frac{K_r}{K_r + K_d + K_q(Q)} \tag{13}$$

Dividing equation 12 by equation 13 the familiar Stern-Volmer relationship is obtained:

$$\frac{\phi}{\phi_Q} = 1 + K_q\tau[Q] \tag{14}$$

Where ϕ_Q represents the quantum yield of reaction in the presence of quencher (Q). The lifetime of the triplet (τ) is the reciprocal of the sum of the rates of all the reactions undergone by the triplet.

$$\tau = (K_r + K_d)^{-1} \tag{15}$$

A plot of the relative quantum yield versus quencher concentration is linear with a slope equal to the product $K_q\tau$ and an intercept of 1, if only one excited state is reacting and being quenched.

B. Research Objectives

After we observed that 3,3',4,4'-tetrachlorobiphenyl exhibited unusual characteristics in its ultraviolet spectrum and that it underwent photodecomposition, a set of experiments was designed to elucidate the structure of the resulting photoproducts and the kinetics of PCB photoreactions.

(1) With possible free radical and ionic mechanisms for chloroaromatics, product formation from PCB at wavelengths found in the higher energy end of solar radiation, in alkane and alcohol solvents, can be expected to differ. The nature of the products would be of environmental and chemical interest.

(2) To determine the simple reaction rate constant of PCB upon photolysis in the range 290-310 nm was of interest in order to evaluate their period of permanence in the ecosystem. PCB do not degrade to an appreciable extent, either thermally or metabolically, thus photoreactions remain as the only viable degradation pathway under field conditions.

(3) To determine the effect of the different chlorine substitution patterns in either one or both rings. Chlorination at the <u>ortho</u>, <u>meta</u> or <u>para</u> positions could have different effects on the photochemical processes available to PCB. Excited state lifetimes and reactivities should vary within a series of structurally related PCB. Thus, τ, ϕ_r, K_d, K_r, and ϕ_{isc} needed evaluation.

(4) To determine the possibility of trans-annular effects, leading to abnormalities in the photochemical behavior of PCB.

RESULTS

A. Gas Chromatography

Using COL 1 (apparatus described in exp. sec.) with an oven temperature of 170°C and a nitrogen flow of 8 ml/min, several polychlorinated biphenyls were analyzed and their vpc retention times obtained (Table 1). The values listed were used to identify the photoproducts of I-XI, whose structures are shown in Figures 1 and 2.

Table 1. Gas Chromatographic Retention Times of Polychlorinated Biphenyls in Cyclohexane[a]

PCB	R_t	PCB	R_t	Designation
Monochloro		Trichloro		
2-	0.60	2,4,6-	1.55	(VII)
3-	0.82	2,2',6-	1.65	
4-	0.85	2,2',5-	1.85	
Dichloro		2,4,5-	2.20	(VIII)
2,6-	0.92	2,3',5-	2.45	
2,2'-	1.00	2,4,'-	2.60	
2,5-	1.15	3,4,2'-	2.75	(XI)
2,4-	1.25	3,4,5-	3.60	
2,3-	1.40	3,3',4-	4.30	
3,5-	1.50	Tetrachloro		
3,3'-	1.75	2,2',4,4'-	3.70	(I)
3,4-	1.80	2,2',5,5'-	3.65	(II)
4,4'-	1.95	2,2',3,3'-	4.80	(III)
		2,2',6,6'-	2.30	(IV)
		3,3',5,5'-	5.70	(V)
		3,3',4,4'-	8.90	(VI)
Methoxylated PCB		2,3,4,5-	4.80	(IX)
2,4,4'-Trichloro-2'-methoxy	5.05	2,3,5,6-	3.35	(X)
4,4'-Dichloro-2,2' dimethoxy	6.30			

[a] R_t relative to cyclohexane.

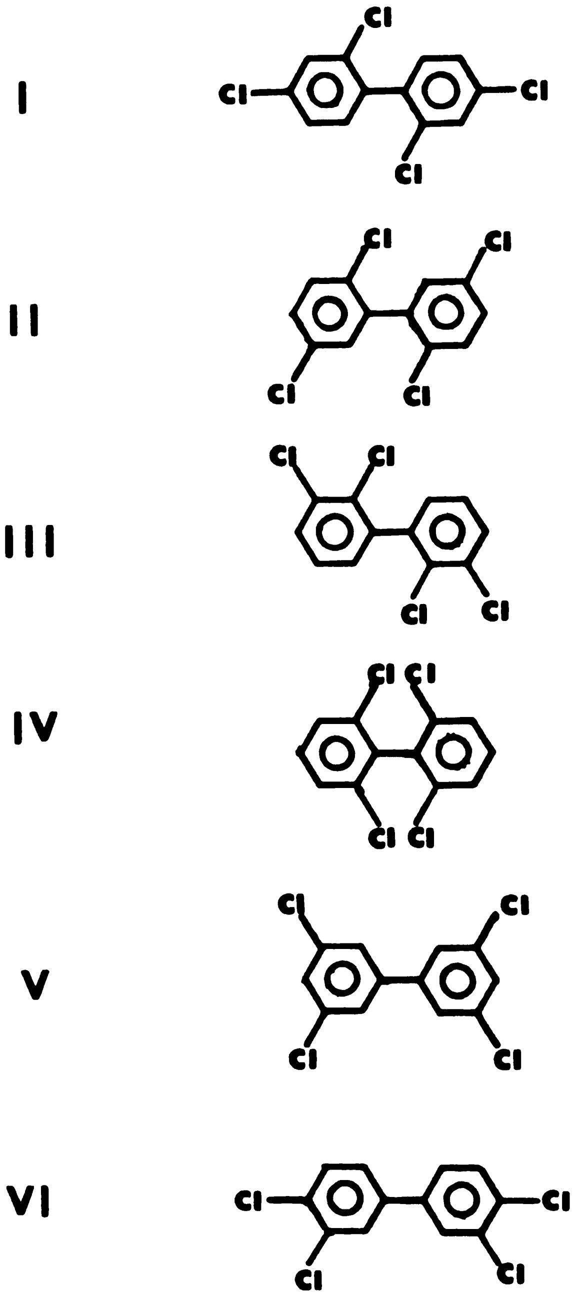
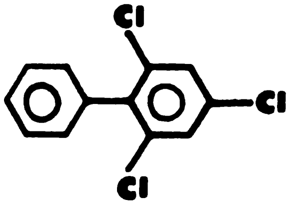
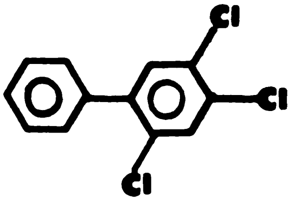


Figure 1. Structures of Symmetrically Substituted Tetrachlorobiphenyls

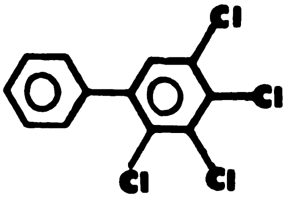
VII



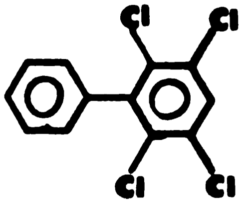
VIII



IX



X



XI

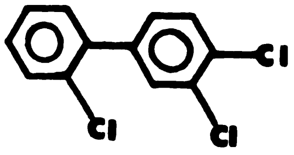


Figure 2. Structures of Unsymmetrical Tri- and Tetrachlorobiphenyls

B. Ultraviolet Spectroscopy

The uv spectra of I-XI were obtained in cyclohexane solution. Scanning was carried out in the 320-220 nm region. Typically PCB solutions were 0.1 - 1.0 x 10^{-4}M except in cases where higher concentrations had to be used in order to obtain the molar absorptivity (ε) in the 280-300 nm region. The values of ε were calculated at 290 nm and at the maximum wavelength of the conjugation band (240-270 nm). In cases where this band disappeared the extinction coefficient was calculated at 255 nm.

Since PCB absorption in the uv conformed to Beer's Law, ε was calculated using equation 17:

$$\log I_0/I = A = \varepsilon bM \tag{17}$$

Those PCB containing para and no ortho chlorines exhibited a band in the 240-270 nm region of greater intensity than that of biphenyl itself. PCB containing ortho chlorines showed decreased intensity relative to that of unsubstituted biphenyl. When only meta chlorines were present the intensity of absorption was similar to biphenyl. Uv spectra are given in Figures 3, 4 and 5. Extinction coefficients are listed in Table 2.

Table 2. Molar Extinction Coefficients of PCB in Cyclohexane Solution

PCB	ε(290 nm)	ε(240-270 nm)	λ_{max}
I	320	10,000	253
II	300	1,200	(255)
III	170	1,500	(255)
IV	50	300	(255)
V	950	18,000	252
VI	6,000	22,000	262
VII	85	4,800	(255)
VIII	1,200	11,800	260
IX	1,100	19,200	260
X	390	2,800	(255)
XI	730	13,100	252
Biphenyl	900	15,000	249

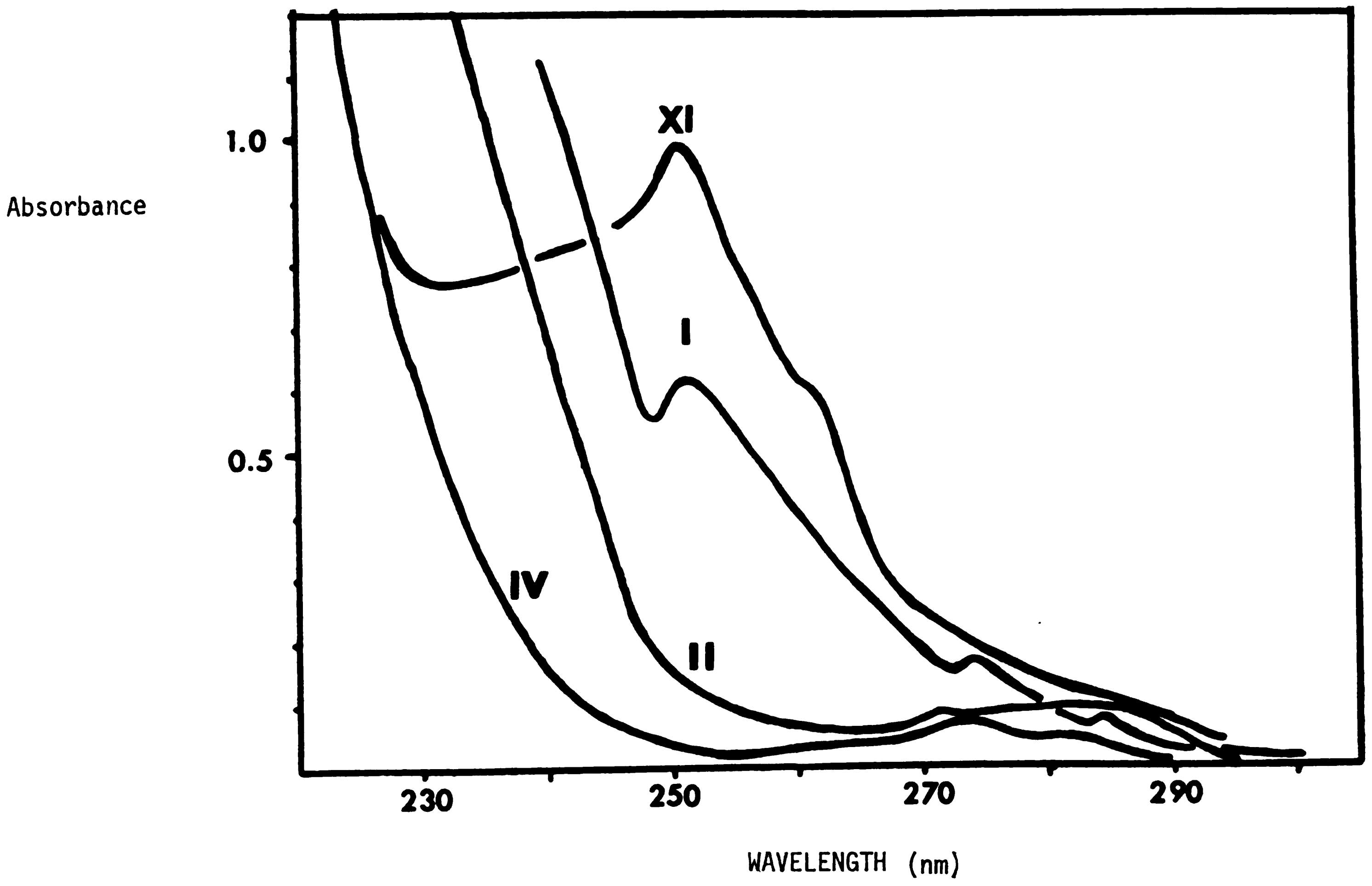


Figure 3. Ultraviolet absorption spectra of 2,2',4,4'- (I), 2,2',5,5', (II), 2,2',6,6'-tetrachlorobiphenyl (III) and 3,4,2'-trichlorobiphenyl (XI)

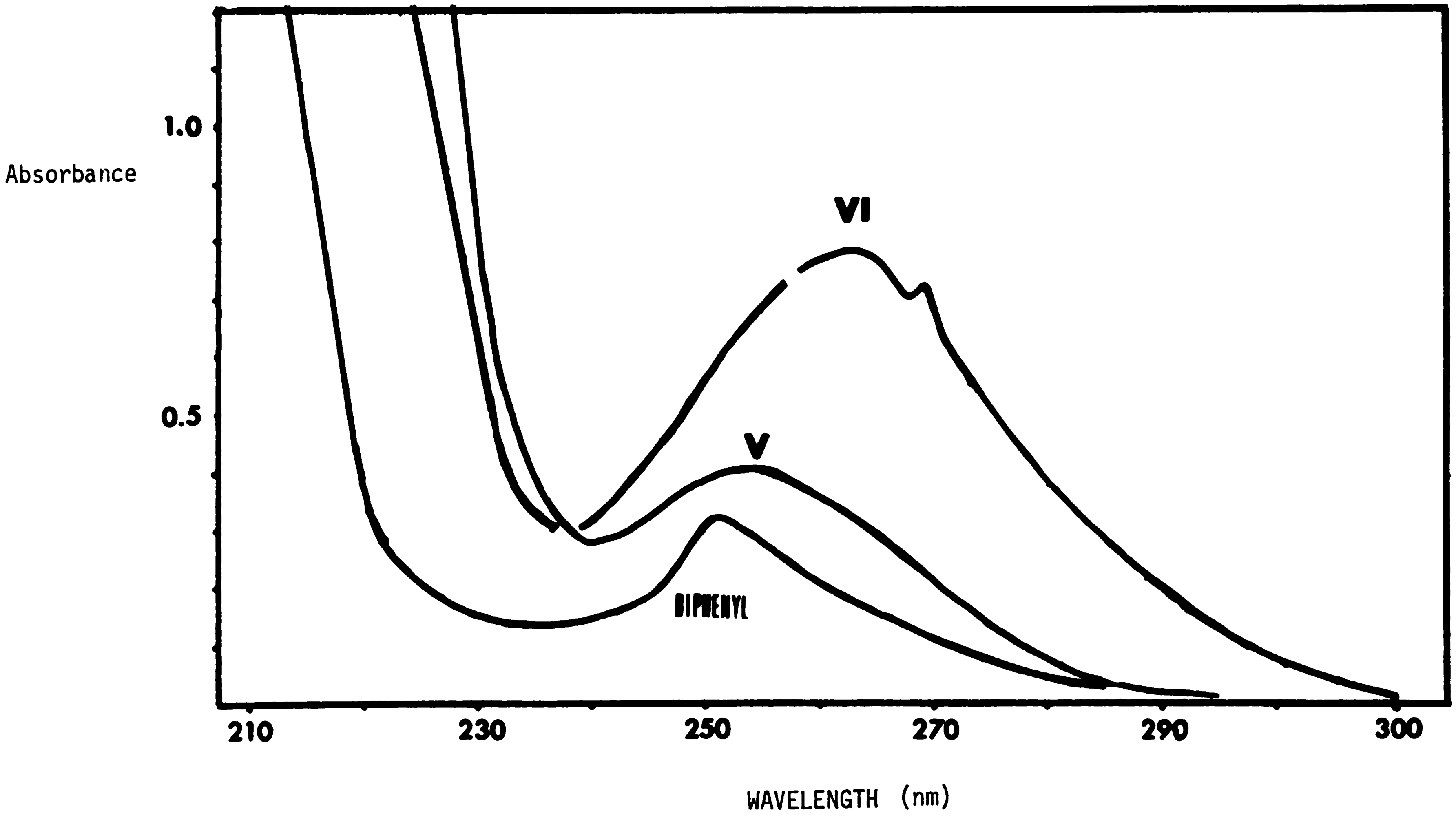


Figure 4. Ultraviolet absorption spectra of 3,3',5;5'-(V) 3,3',4,4'-tetrachlorobiphenyl (VI) and Biphenyl

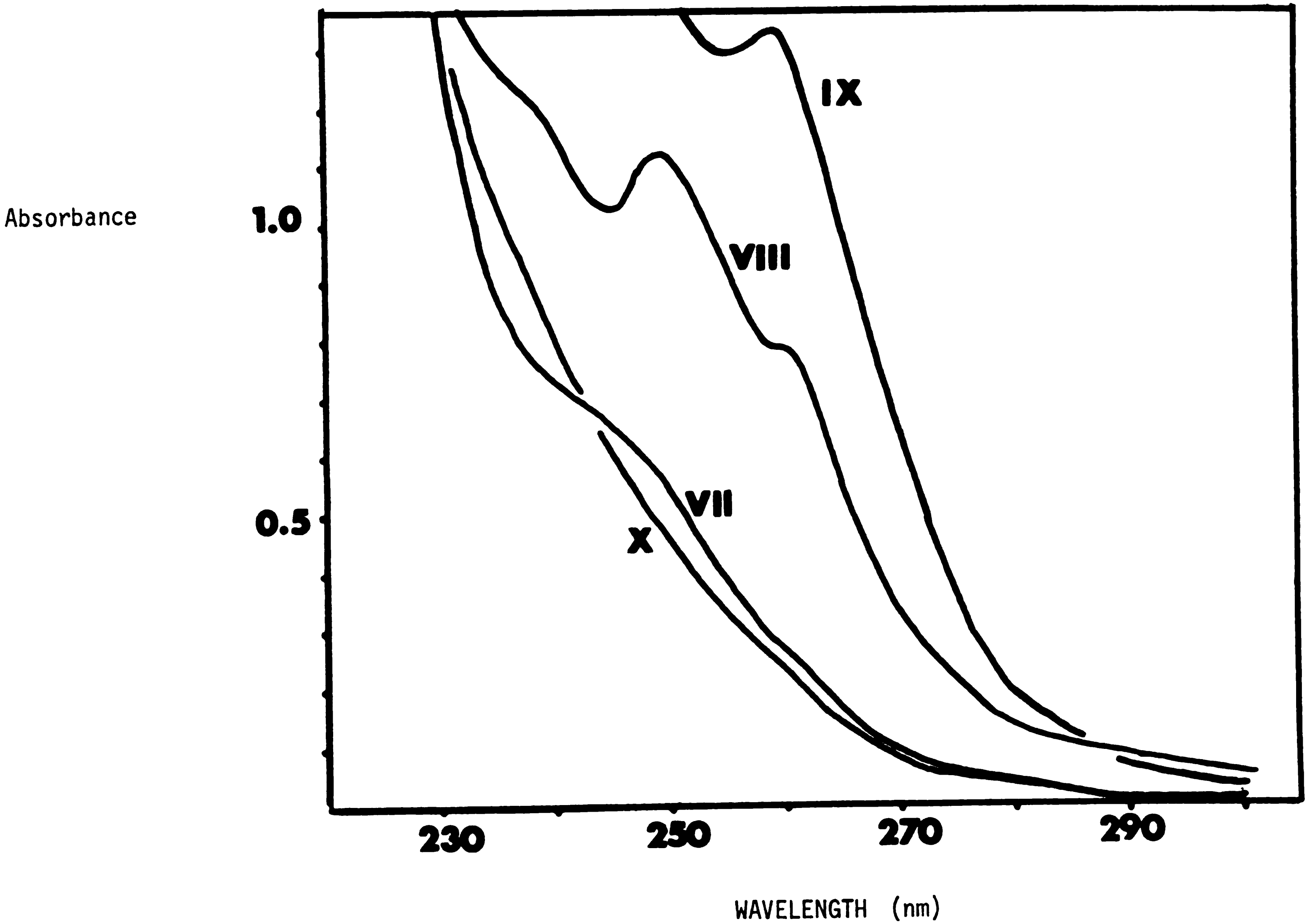


Figure 5. Ultraviolet absorption spectra of 2,4,6- (VII), 2,4,5- (VIII) trichlorobiphenyls and 2,3,4,5- (IX), 2,3,5,6- (X) tetrachlorobiphenyls

C. Photoproducts

In all photolyses described the photoproducts obtained were identical in both degassed and non-degassed solutions. Hydrogen chloride gas was observed by the introduction of indicator paper into the reaction vessel and by its characteristic odor. Dark controls were employed in each case and no reaction was observed in these over the photolysis time period. All reactions were carried out by irradiation between 290-310 nm. In all cases mass balances based on reacted PCB were obtained. Photoproducts and their mass spectra parent peaks (M) are shown in Tables 3-9. Simplified vpc traces of photolyzed PCB in cyclohexane are given in Figures 11 and 12. The mass spectra of the photoproducts of 2,2',4,4'-tetrachlorobiphenyl (I) are shown in Figures 6-10. Photoproducts arising from I-XI exhibited fragmentation patterns dependent only on the number of chlorines present.

1. <u>2,2',4,4'-Tetrachlorobiphenyl (I)</u>. Irradiation of a 0.01M cyclohexane solution for 25 hours yielded three products with vpc R_t at 0.8, 1.9 and 2.6 minutes. By comparison with PCB standards available (Table 1) and their mass spectra these were identified as 4-chlorobiphenyl (<1%), 4,4'-dichlorobiphenyl (70%) and 2,4,4'-trichlorobiphenyl (29%). Photolysis of I in methanol solution gave additional methoxylated products (<5% of I reacted).

Comparison of their vpc retention times with known samples and mass spectrometric analysis identified them as 2,4,4'-trichloro-2'-methoxybiphenyl and 2,2'-dimethoxy-4,4'-dichlorobiphenyl. A compound of formula $C_{12}H_7Cl_2(OCH_3)$ was observed in <1% yield. Mass spectral data is shown in figures 6-10.

Photolysis of I in acetone and toluene solutions yielded the same products as in cyclohexane.

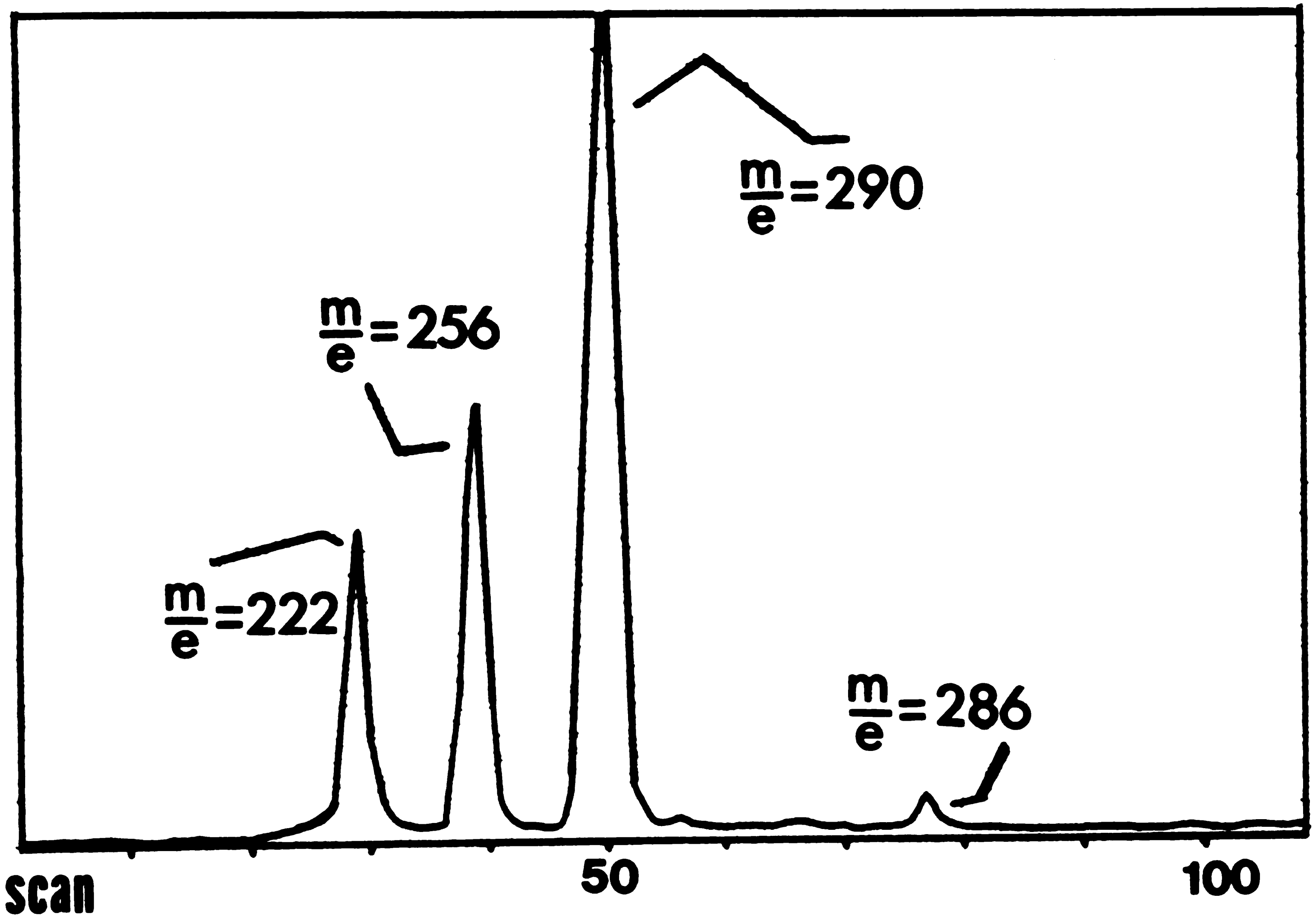


Figure 6. Vpc-ms separation of the photoproducts of 2,2',4,4'-Tetrachlorobiphenyl (I) in Methanol

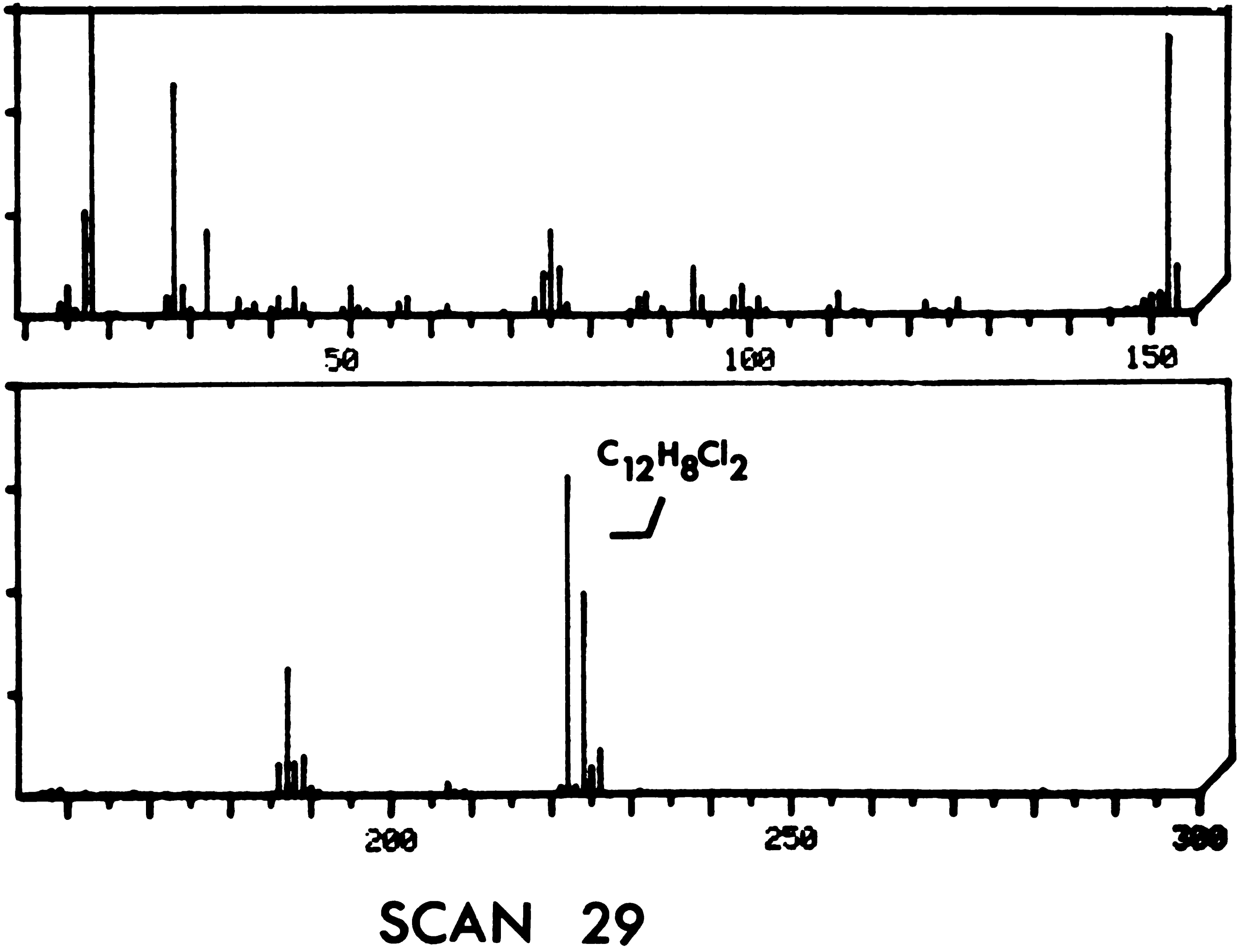
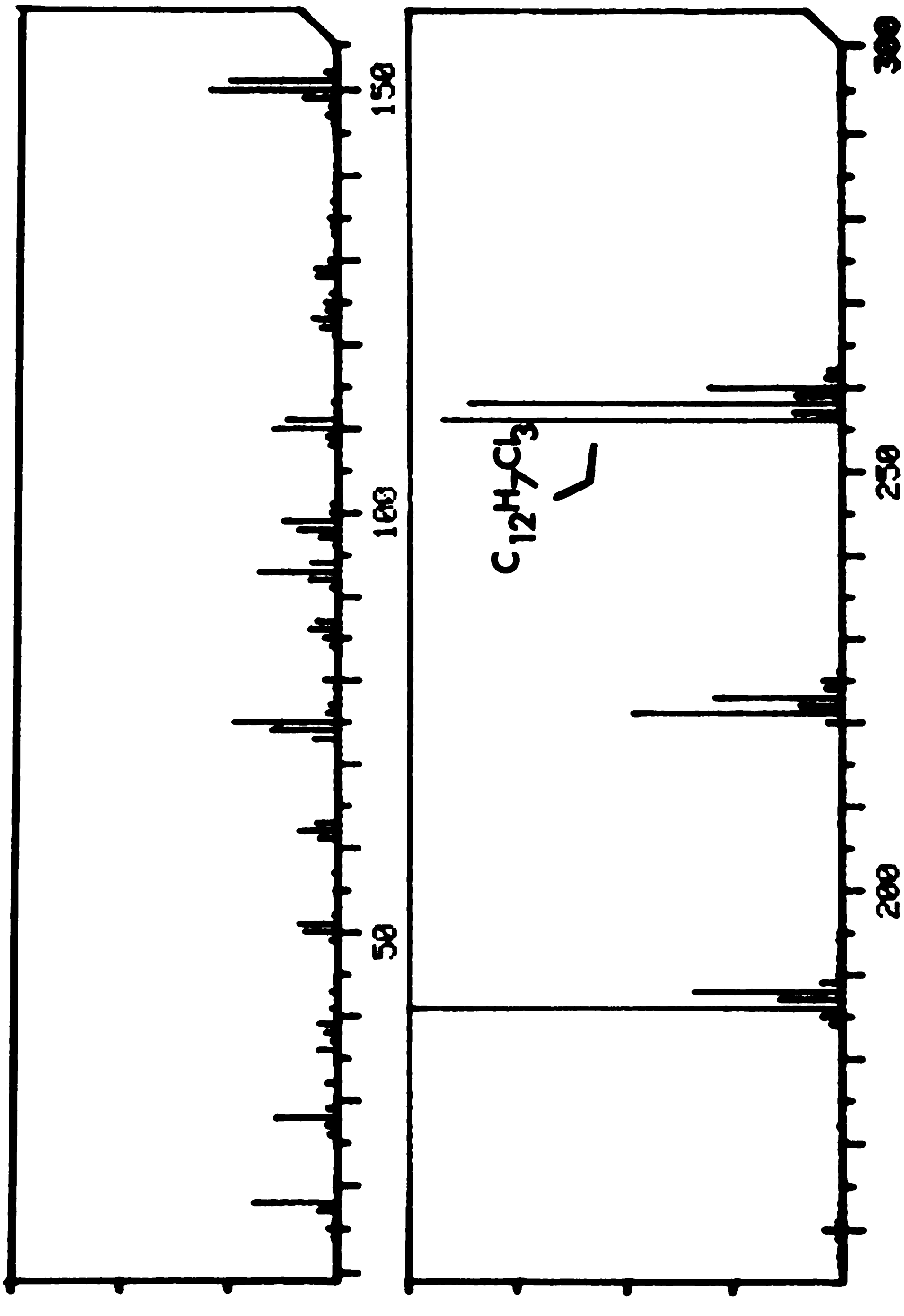


Figure 7. Ms scan of 4,4'-Dichlorobiphenyl



SCAN 39

Figure 8. Ms scan of 2,4,4'-Trichlorobiphenyl

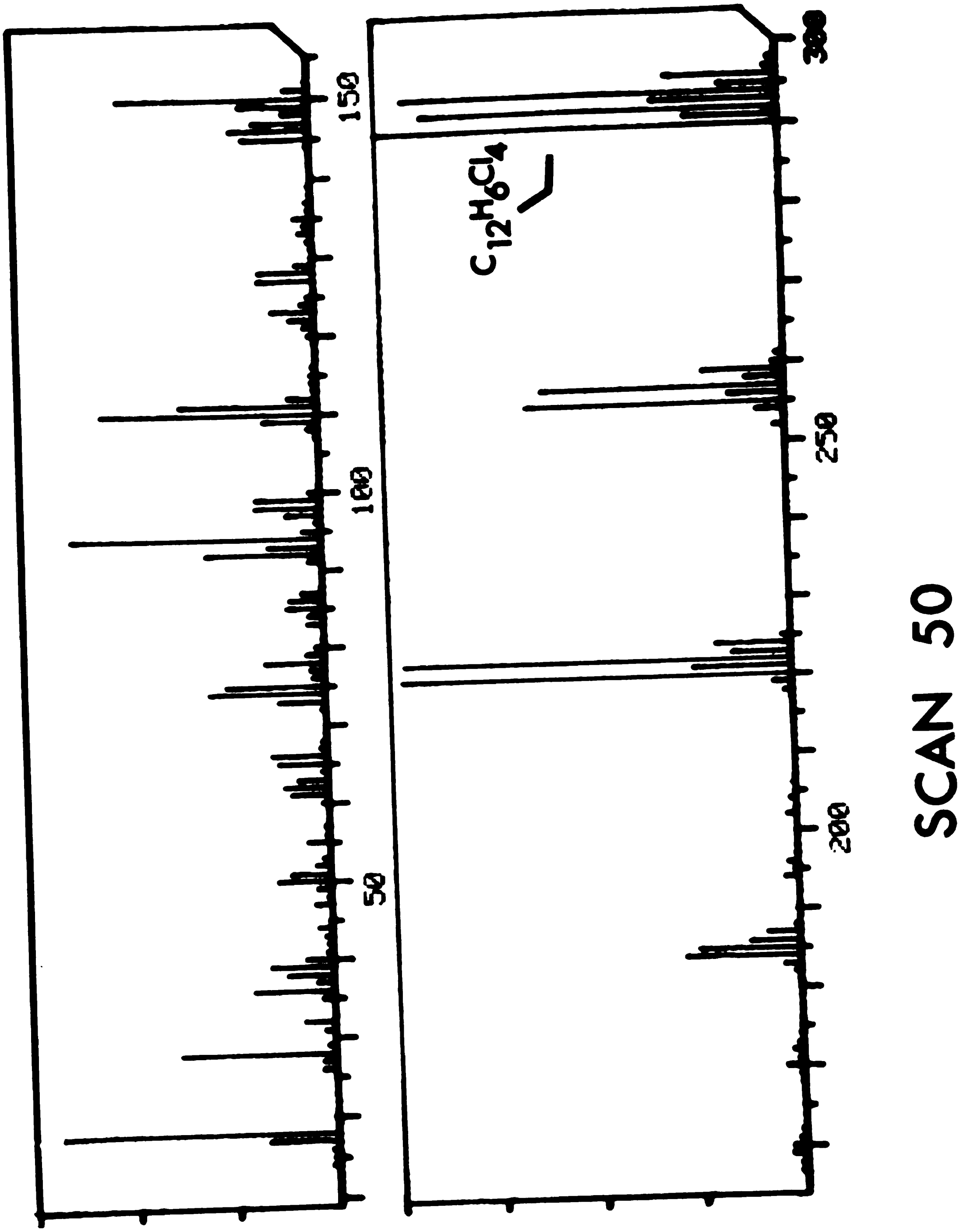


Figure 9. Ms scan of 2,2',4,4'-Tetrachlorobiphenyl (I)

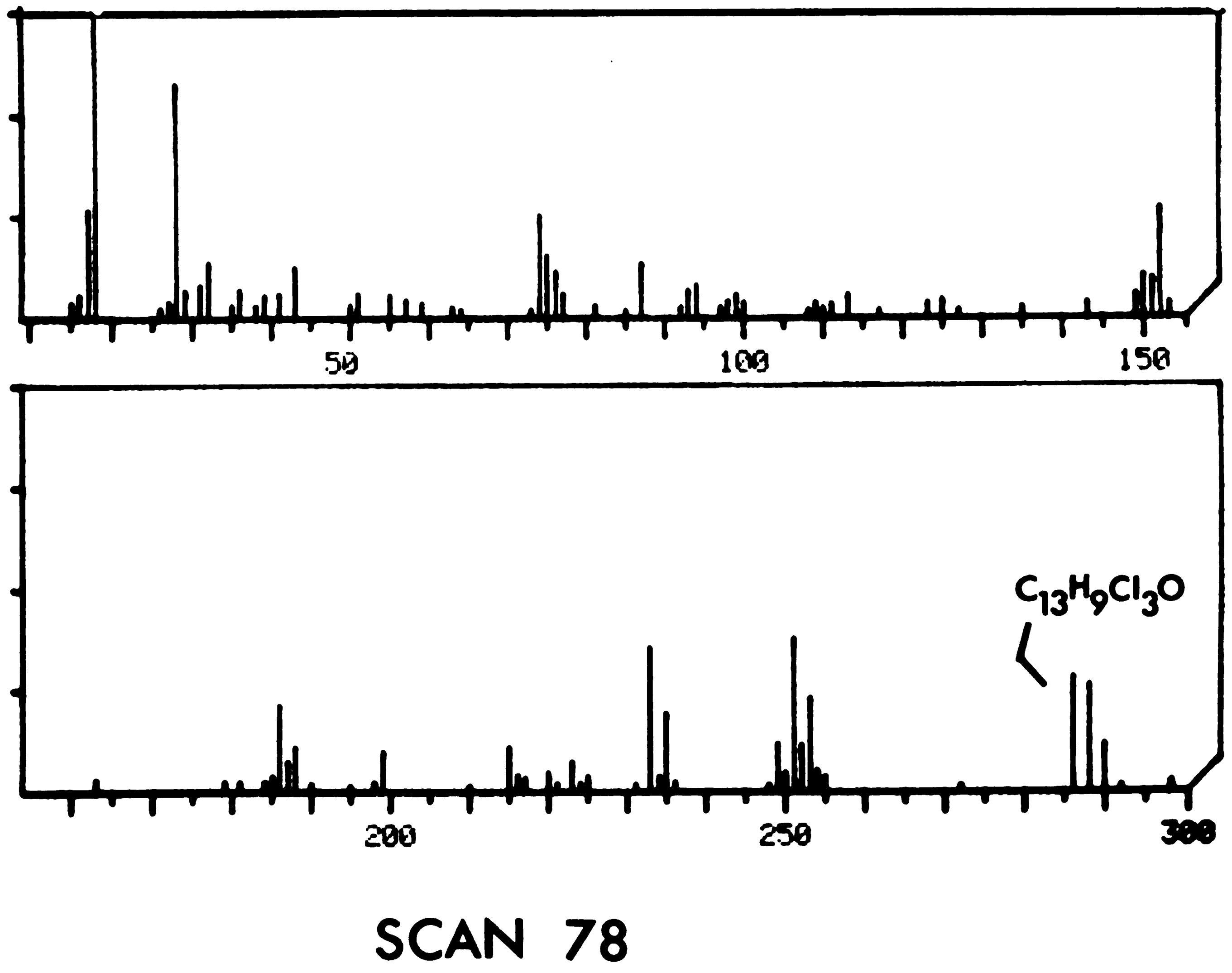


Figure 10. Ms scan of 2,4,4'-Trichloro-2'-methoxybiphenyl

2. 2,2',5,5'-Tetrachlorobiphenyl (II). Irradiation of a 10^{-3}M solution for 30 hours yielded three products with R_t at 0.8, 1.8 and 2.5 minutes. Comparison with standards and mass spectra identified them as 3-chlorobiphenyl (<1%) 3,3'-dichlorobiphenyl (69%) and 2,5,3'-trichlorobiphenyl (30%).

Photolysis of II in methanol yielded additional methoxylated products which were not identified beyond their empirical formulas (Table 4).

3. 2,2',3,3'-Tetrachlorobiphenyl (III). Irradiation of a 10^{-3}M cyclohexane solution for 40 hours yielded four products with R_t at 0.8, 1.8, 2.9 and 3.1 minutes. The photoproducts were identified as 3-chlorobiphenyl (<1%), 3,3'-dichlorobiphenyl (63%), 2,2',3-trichlorobiphenyl (11%) and 2,3,3'-trichlorobiphenyl (25%). The methoxylated products obtained in methanol are listed in Table 5.

4. 2,2',6,6'-Tetrachlorobiphenyl (IV). Irradiation of a 10^{-3}M cyclohexane solution for 40 hours yielded two products with R_t at 1.0 and 1.65 minutes. These were identified as 2,2'-dichlorobiphenyl (<1%) and 2,2',6-trichlorobiphenyl (99%). In methanol solution an additional product with formula $C_{12}H_6Cl_3(OCH_3)$ in less than 1% yield was obtained.

5. 3,3',5,5'-Tetrachlorobiphenyl (V). Irradiation of a 10^{-3}M cyclohexane solution for 120 hours yielded one product with R_t at 3.80 minutes. Its mass spectrum showed a parent peak at m/e 256. No standard was available that matched the vpc retention time and m/e value. It was concluded that the product was 3,3',5-trichlorobiphenyl. No additional products were obtained in methanol.

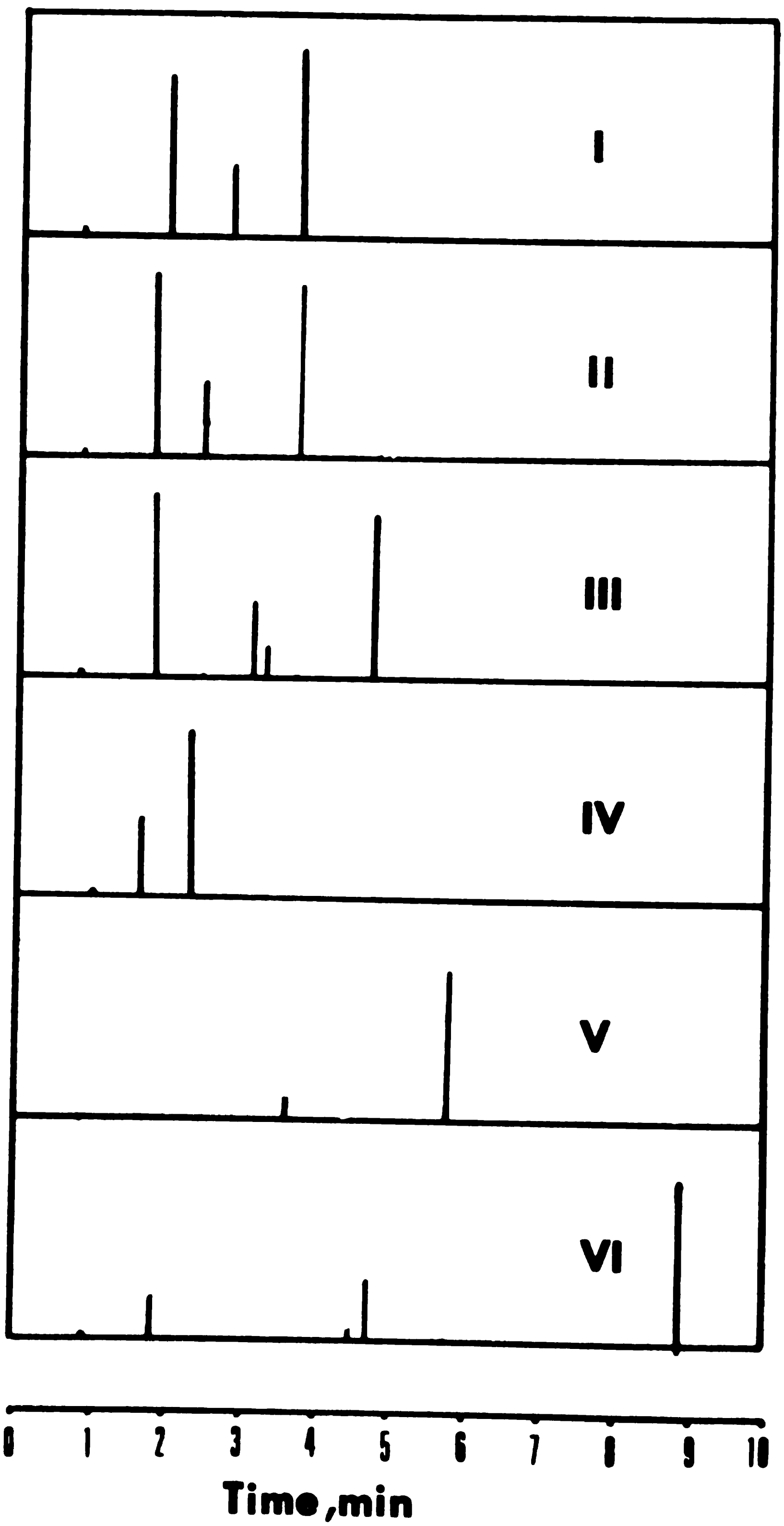


Figure 11. Vpc Traces of 2,2',4,4'- (I), 2,2',5,5'- (II), 2,2',3,3'- (III), 2,2',6,6'- (IV), 3,3',5,5'- (V) and 3,3',4,4'-Tetrachlorobiphenyls (VI).

Table 3. Photoproducts of 2,2',4,4'-Tetrachlorobiphenyl (I) in Cyclohexane and Methanol Solutions

Products (Cyclohexane)	m/e	Products (Methanol)[a]	m/e
2,4,4'-Trichlorobiphenyl	256	2,4,4'-Trichlorobiphenyl	256
4,4'-Dichlorobiphenyl	222	4,4'-Dichlorobiphenyl	222
4-Chlorobiphenyl[b]	188	4-Chlorobiphenyl[b]	188
		$C_{12}H_6Cl_3(OCH_3)$	286
		$C_{12}H_6Cl_2(OCH_3)_2$	282
		$C_{12}H_7Cl_2(OCH_3)$[b]	252

[a] Combined methoxylated products constitute <5% of total product formation.

[b] Product constitutes <1% of total product formation.

Table 4. Photoproducts of 2,2',5,5'-Tetrachlorobiphenyl (II) in Cyclohexane and Methanol Solutions

Products (Cyclohexane)	m/e	Products (Methanol)[a]	m/e
2,3',5-Trichlorobiphenyl	256	2,3',5-Trichlorobiphenyl	256
3,3'-Dichlorobiphenyl	222	3,3'-Dichlorobiphenyl	222
3-Chlorobiphenyl[b]	188	$C_{12}H_6Cl_3(OCH_3)$	286
		$C_{12}H_6Cl_2(OCH_3)_2$[b]	282

[a] Combined methoxylated products constitute < 3% of total product formation.

[b] Product constitutes < 1% of total product formation.

Table 5. Photoproducts of 2,2',3,3'-Tetrachlorobiphenyl (III) in Cyclohexane and Methanol Solutions

Products (Cyclohexane)	m/e	Products (Methanol)	m/e
2,2',3-Trichlorobiphenyl[b]	256		
2,3,3'-Trichlorobiphenyl	256	2,3,3'-Trichlorobiphenyl	256
3,3'-Dichlorobiphenyl	222	3,3'-Dichlorobiphenyl	222
3-Chlorobiphenyl[b]	188		
		$C_{12}H_6Cl_3(OCH_3)$	286
		$C_{12}H_6Cl_2(OCH_3)_2$	282

[a] Combined methoxylated products constitute <3% of total product formation.

[b] Products constitutes <1% of total product formation.

Table 6. Photoproducts of 2,2',6,6'-Tetrachlorobiphenyl (IV) in Cyclohexane and Methanol Solutions

Products (Cyclohexane)	m/e	Products (Methanol)	m/e
2,2',6-Trichlorobiphenyl	256	2,2',6-Trichlorobiphenyl	256
2,2'-Dichlorobiphenyl	222	2,2'-Dichlorobiphenyl	222
		$C_{12}H_6Cl_3(OCH_3)$[a]	286

[a] Product constitutes <1% of total product formation.

Table 7. Photoproducts of 3,3',5,5'-Tetrachlorobiphenyl (V) in Cyclohexane and Methanol Solutions

Products (Cyclohexane)	m/e	Products (Methanol)	m/e
3,3',5-Trichlorobiphenyl	256	3,3',5-Trichlorobiphenyl	256
		3,3'-Dichlorobiphenyl[a]	222

[a] Produce constitutes < 1% of total product formation.

Table 8. Photoproducts of 3,3',4,4'-Tetrachlorobipnehyl (VI) in Cyclohexane and Methanol Solutions

Products (Cyclohexane)	m/e	Products (Methanol)	m/e
3,4,4'-Trichlorobiphenyl	256	3,4,4'-Trichlorobiphenyl	256
3,3',4-Trichlorobiphenyl	256		
4,4'-Dichlorobiphenyl	222	4,4'-Dichlorobiphenyl	222
4-Chlorobiphenyl[a]	188	4-Chlorobiphenyl[a]	188
		$C_{12}H_6Cl_3(OCH_3)$[a]	286

[a] Product constitutes < 1% of total product formation.

6. 3,3',4,4'-Tetrachlorobiphenyl (VI). Preliminary studies of the photodecomposition of VI in n-hexane[24] showed the formation of 4-chlorobiphenyl, 4,4'-dichlorobiphenyl and 3,4,4'-trichlorobiphenyl. Better separation was later obtained with a S.C.O.T. column (COL1) uncovering a small (2%) of 3,3',4-trichlorobiphenyl. In cyclohexane after 100 hours irradiation 4-chlorobiphenyl (1%), 4,4'-dichlorobiphenyl (40%), 3,3',4-trichlorobiphenyl (6%), and 3,4,4'-trichlorobiphenyl (53%) were obtained. In methanol solution less than 1% trichloromethoxybiphenyl was formed.

7. 2,4,6-Trichlorobiphenyl (VII). Irradiation of a 10^{-3}M solution in cyclohexane for 25 hours yielded two products with R_t at 1.3 and 0.8 minutes. Vpc and ms data identified them as 2,4-dichlorobiphenyl (85%) and 4-chlorobiphenyl (15%).

8. 2,4,5-Trichlorobiphenyl (VIII). Irradiation of a 10^{-3} M cyclohexane solution for 20 hours yielded two products with R_t at 0.8 and 1.8 minutes, corresponding to 4-chlorobiphenyl (2%) and 3,4-dichlorobiphenyl (98%).

9. 2,3,4,5-Tetrachlorobiphenyl (IX). Irradiation of a 10^{-3}M cyclohexane solution yielded after 20 hours one product with R_t at 3.5 minutes, corresponding to 2,4,5-trichlorobiphenyl (95%) and another at 1.8 minutes corresponding to 3,4-dichlorobiphenyl (5%).

10. 2,3,5,6-Tetrachlorobiphenyl (X). Irradiation of a 10^{-3}M cyclohexane solution for 70 hours yielded a trichlorobiphenyl (50%) and a dichlorobiphenyl (50%) which was identified as 3,5-dichlorobiphenyl. The trichlorinated product can be assumed to be 2,3,5-trichlorobiphenyl.

11. 3,4,2'-Trichlorobiphenyl (XI). Irradiation of a 7 x 10^{-3}M cyclohexane solution for 20 hours yielded only 3,4-dichlorobiphenyl (R_t 1.8).

Table 9. Photoproducts of Unsymmetrical PCB (VII-XI) In Cyclohexane Solution

PCB	Products	m/e
VII	2,4-Dichlorobiphenyl	222
	4-Chlorobiphenyl	188
VIII	3,4-Dichlorobiphenyl	222
	4-Chlorobiphenyl	188
IX	3,4,5-Trichlorobiphenyl	256
	3,4-Dichlorobiphenyl	222
X	2,3,5-Trichlorobiphenyl	256
	3,5-Dichlorobiphenyl	222
XI	3,4-Dichlorobiphenyl	222

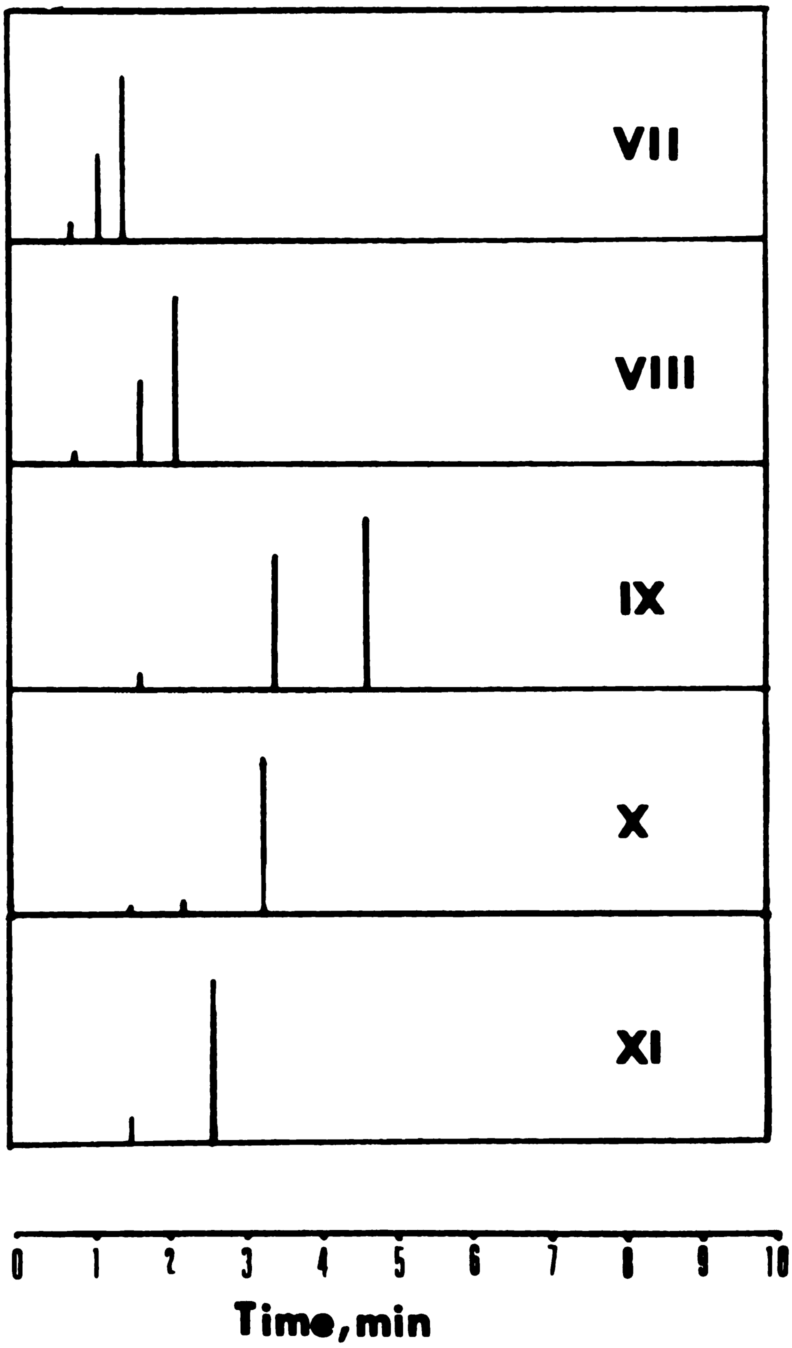


Figure 12. Vpc Traces of 2,4,6- (VII), 2,4,5- (VIII) and 3,4,2'- (XI) Trichlorobiphenyls and of 2,3,4,5- (IX) and 2,3,5,6- (X) Tetrachlorobiphenyls

D. Reaction Rate Constants and Quantum Yields

1. Rate Constant Determination. The photoreactions of PCB were found to be 0 order when >99% of the incident light was absorbed. Equation 19 gives the rate constant for a 0 order reaction (k):

$$(PCB)^{\circ} - (PCB)^{t} = k\ t \qquad (18)$$

where t is the time of irradiation and (PCB) is the substrate concentration at 0 and t times. Calculating the amount reacted at several time periods of irradiation of degassed PCB solutions, a plot of substrate reacted vs time elapsed with a slope equal to k can be obtained. Plots for I-VI are shown in Figures 13-15. The k values are given in Table 10.

For compounds VII-XI one point rate constants were determined, (Table 11). The k values obtained in cyclohexane were found to be slightly lower than those in methanol solution.

The largest k values were obtained for PCB containing ortho-para chlorination (I, VII-IX, XI). Compounds with ortho-meta chlorination showed intermediate k values (II-IV,X), and those with meta-para substitution,(V-VI) the lowest.

2. Quantum Yield Determinations. Absolute quantum yields of reaction (ϕ_r) where determined for I-XI. Degassed cyclohexane solutions of PCB containing internal standard were irradiated in parallel with actinometer solutions at 300 ± 10 nm. After irradiation each tube was analyzed for PCB reacted by vpc. Values for ϕ_r are given in Tables 10 and 11.

The quantum yields obtained correlated will with the rate constants. The extremely low values of ϕ_r found for V and VI by necessity must contain a relatively large error and were calculated basically for comparison purposes.

Table 10. Reaction Rate Constants(k) and Quantum Yields (ϕ_r) for PCB in Cyclohexane

PCB	k, 10^{-9}M $\sec^{-1}$	ϕ_r
I	74.5	0.100
II	7.4	0.010
III	5.0	0.007
IV	3.8	0.006
V	1.2	0.002
VI	2.8	0.005

Table 11. One Point Reaction Rate Constants(k) for Unsymmetrically Substituted PCB in Cyclohexane Solution

PCB	k, 10^{-9}M $\sec^{-1}$	ϕ_r
VII	14.0	0.02
VIII	42.4	0.05
IX	29.3	0.04
X	6.0	< 0.01
XI	12.0	0.02

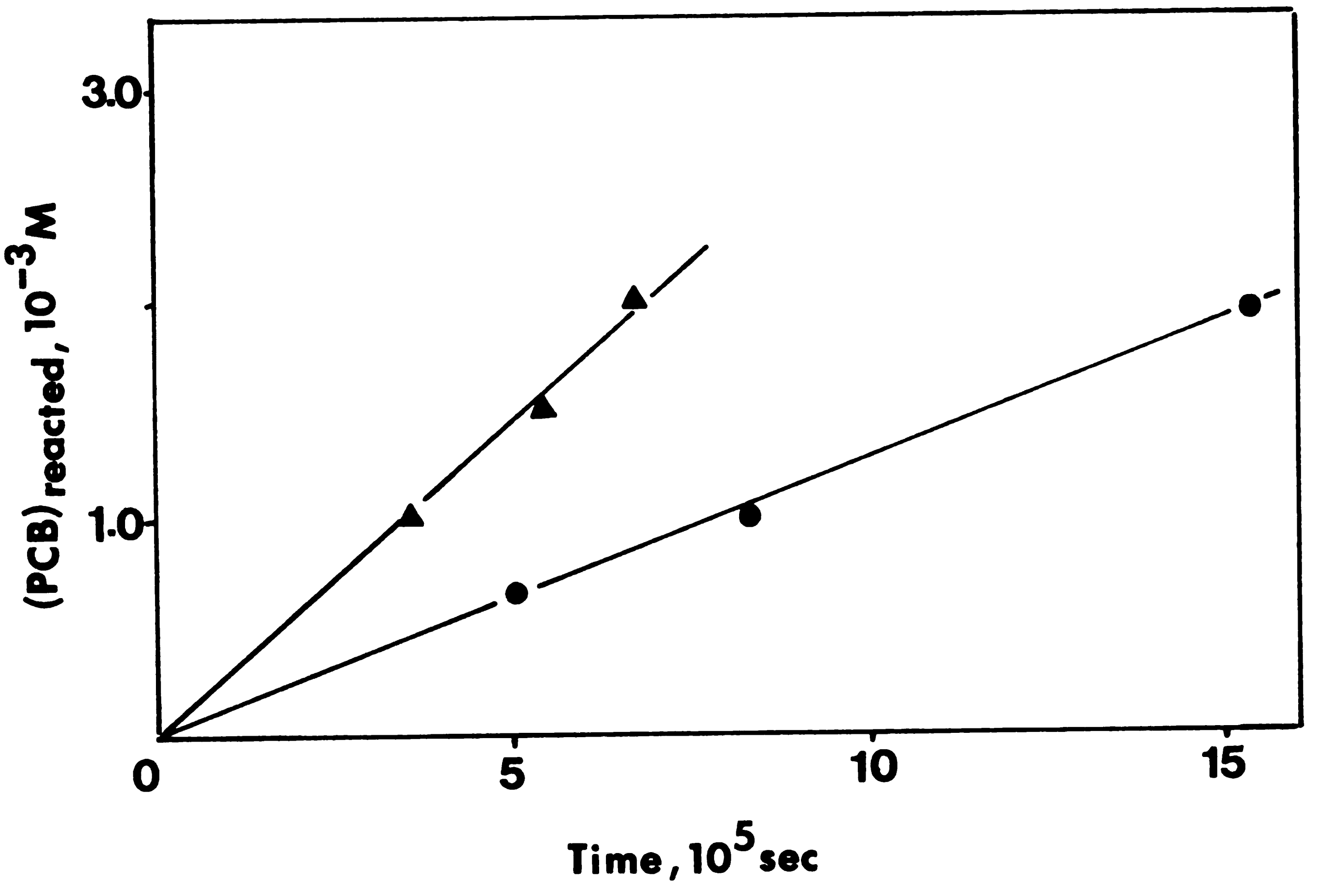


Figure 13. Reaction Rate Constants in Cyclohexane of 3,3',4,4'- (VI) ▲ and 3,3',5,5-' (V) ● Tetrachlorobiphenyls

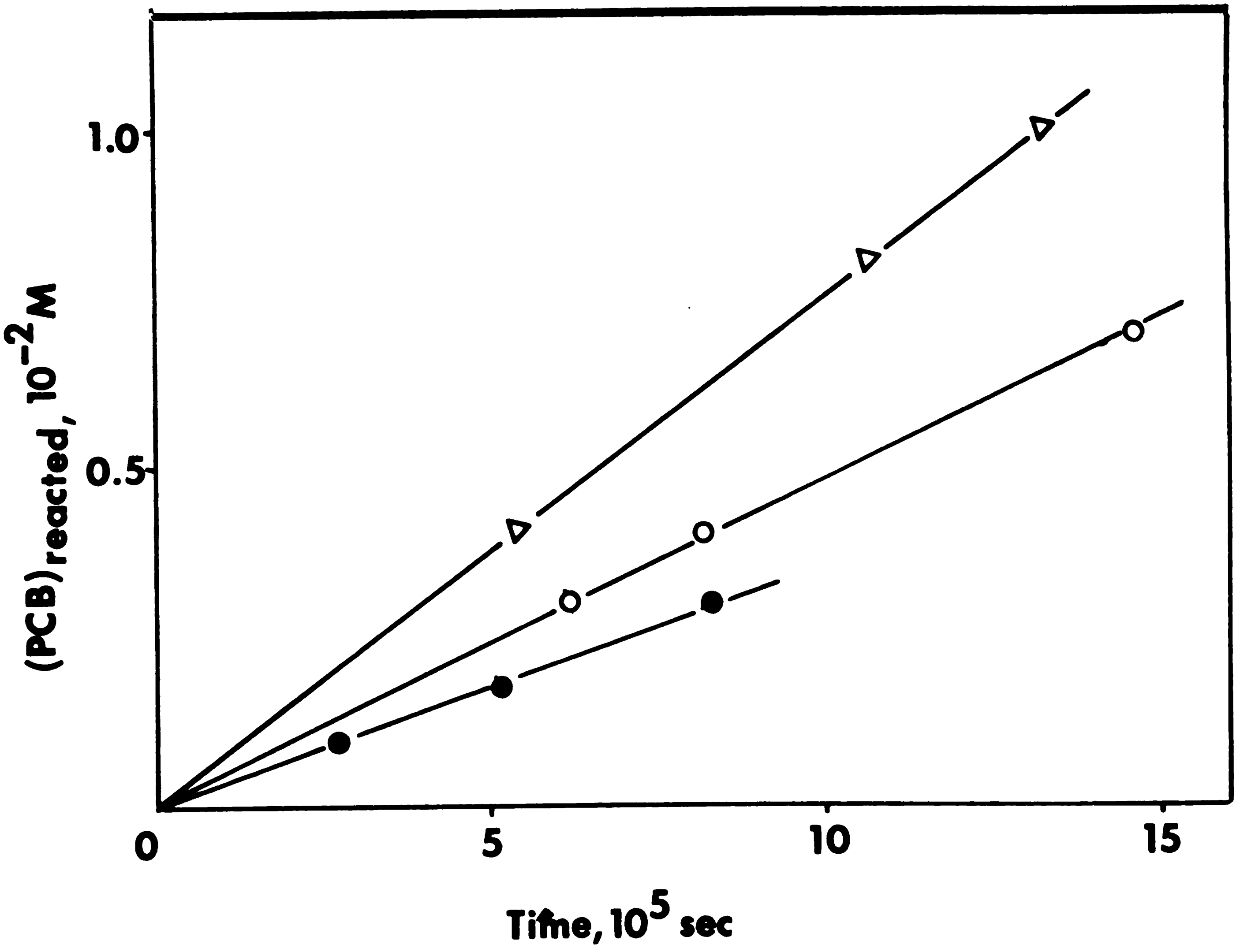


Figure 14. Reaction Rate Constants in Cyclohexane of 2,2'-5,5'- (II) △, 2,2',3,3'- (III) ○ and 2,2',6,6'- (IV) ● Tetrachlorobiphenyls

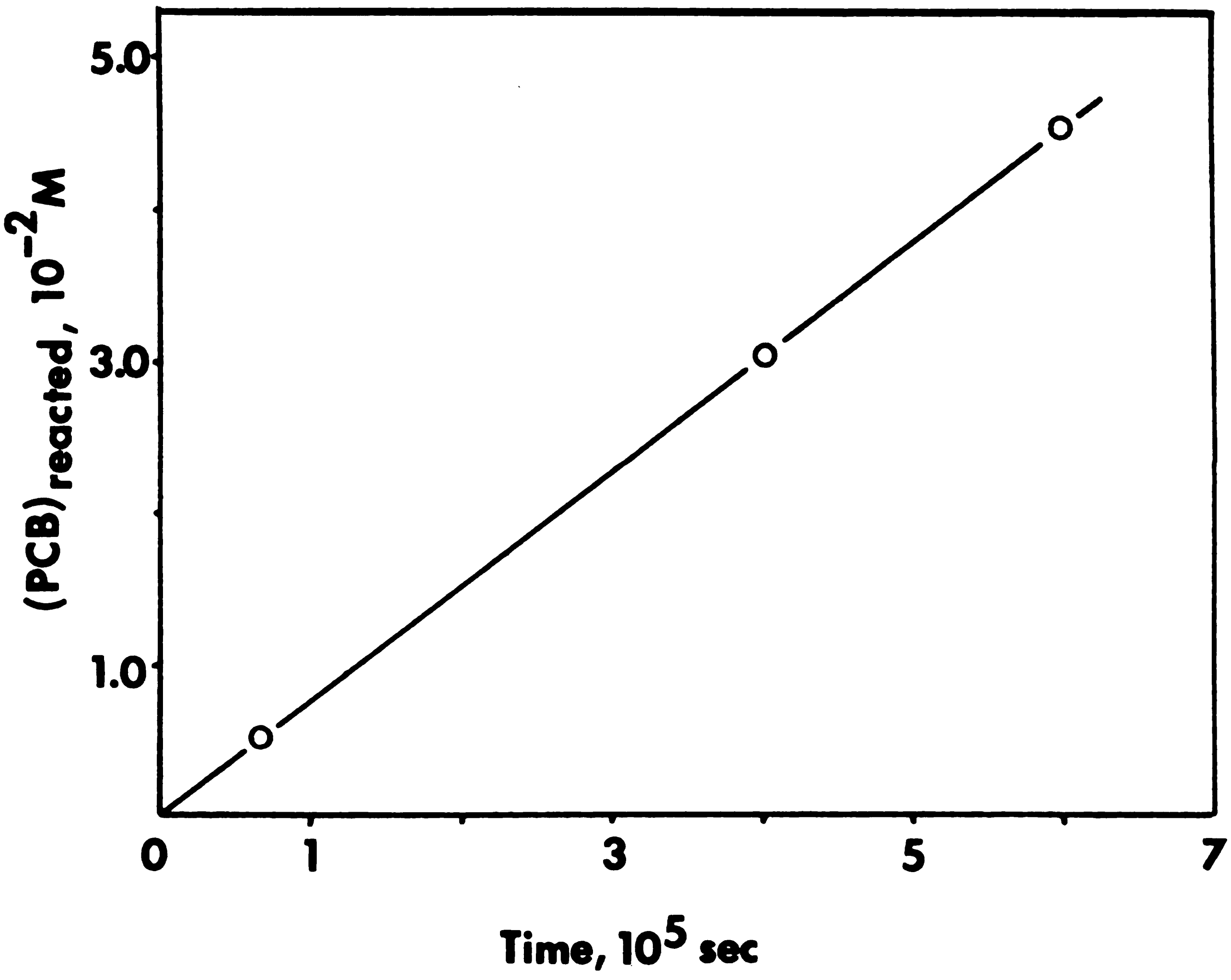


Figure 15. Reaction Rate Constant in Cyclohexane of 2,2',4,4'-Tetrachlorobiphenyl (I)

E. Quenching Studies. Lifetime of Triplet.

In order to determine the lifetime of the excited state of I-VI quenching of the dechlorination reaction was attempted with isoprene (E_t = 60 kcal/mole) and benzyl (52 kcal/mole). Both compounds proved inefficient, either because of high E_t value or strong absorption in the region of irradiation. 1.3-Cyclohexadiene (E_t = 50 kcal/mole) was found to be appropriate for the systems under study.

Degassed solutions containing PCB and internal standard with varying quencher concentrations were irradiated in parallel at 300± 10 nm to 20% PCB conversion. Vpc analysis of PCB reacted permitted the calculation of relative quantum yields, $\phi°/\phi$. The Stern-Volmer plots obtained were linear with unity intercepts (Figures 14-17). The slopes are equal to $k_q\tau$. The diffusion rate constants in cyclohexane and methanol are known,[52] however, some change is expected in their value at 30°C, according to the Debye equation[53] which shows k_q to be temperature dependent.

$$k_q = \frac{1}{4} (2 + d_1/d_2 + d_2/d_1)\ 8RT/3 \times 10^3\eta \qquad (19)$$

where $d_1 = d_2$, $R = 8.31 \times 10^7$ ergs/mole deg K and η is the viscosity in gr sec^{-1} cm^{-1}. In cyclohexane at 303°K $k = 0.81 \times 10^{10} M\ sec^{-1}$ and in methanol 1.3×10^{10} M sec^{-1}. Using these values the excited state lifetimes were calculated (Table 12). The τ values were the same in both solvents within experimental error.

Table 12. Lifetimes of the Triplet Excited States of Polychlorinated Biphenyls

PCB	solvent	$k_q\tau$	τ, 10^{-8} sec
I	methanol	101.4	0.78
I	cyclohexane	68.8	0.85
II	methanol	87.1	0.67
III	methanol	100.1	0.77
IV	methanol	91.0	0.70
IV	cyclohexane	76.9	0.95
V	methanol	248.3	1.91
V	methanol	286.0	2.20

F. Intersystem Crossing Quantum Yields (ϕ_{isc})

The sensitized isomerization of cis → trans piperylene was used to determine isc for several PCB. Reproducible results were only obtained for 3,3',4,4'-tetrachlorobiphenyl (VI) indicating a value of unity by comparison with benzophenone. The sensitized phosphorecence of biacetyl gave better results allowing the calculation of isc for I, III, V and VI.

Benzene solutions of PCB and biacetyl were degassed and their phosphorescence emission at 512 nm compared with that of benzene solutions of benzophenone/biacetyl. In all cases $\phi_{isc} = 1$ (Table 16). At 25°C PCB I-VI did not fluoresce or phosphoresce.

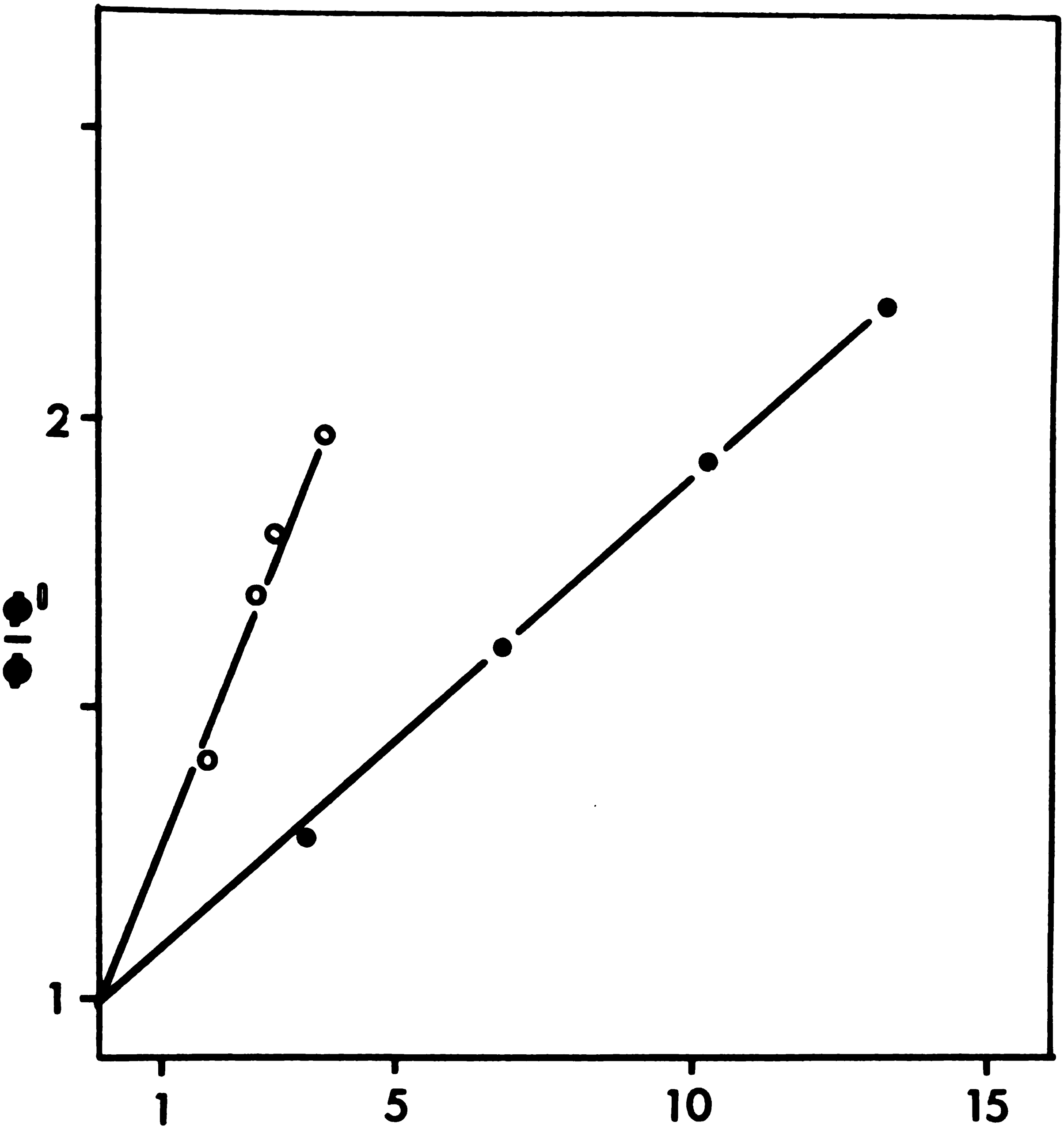


Figure 16. Stern-Volmer plots of 3,3',5,5'- (V) ○ and 2,2',6,6'- (IV) ● Tetrachlorobiphenyls using 1,3-Cyclohexadiene in Methanol

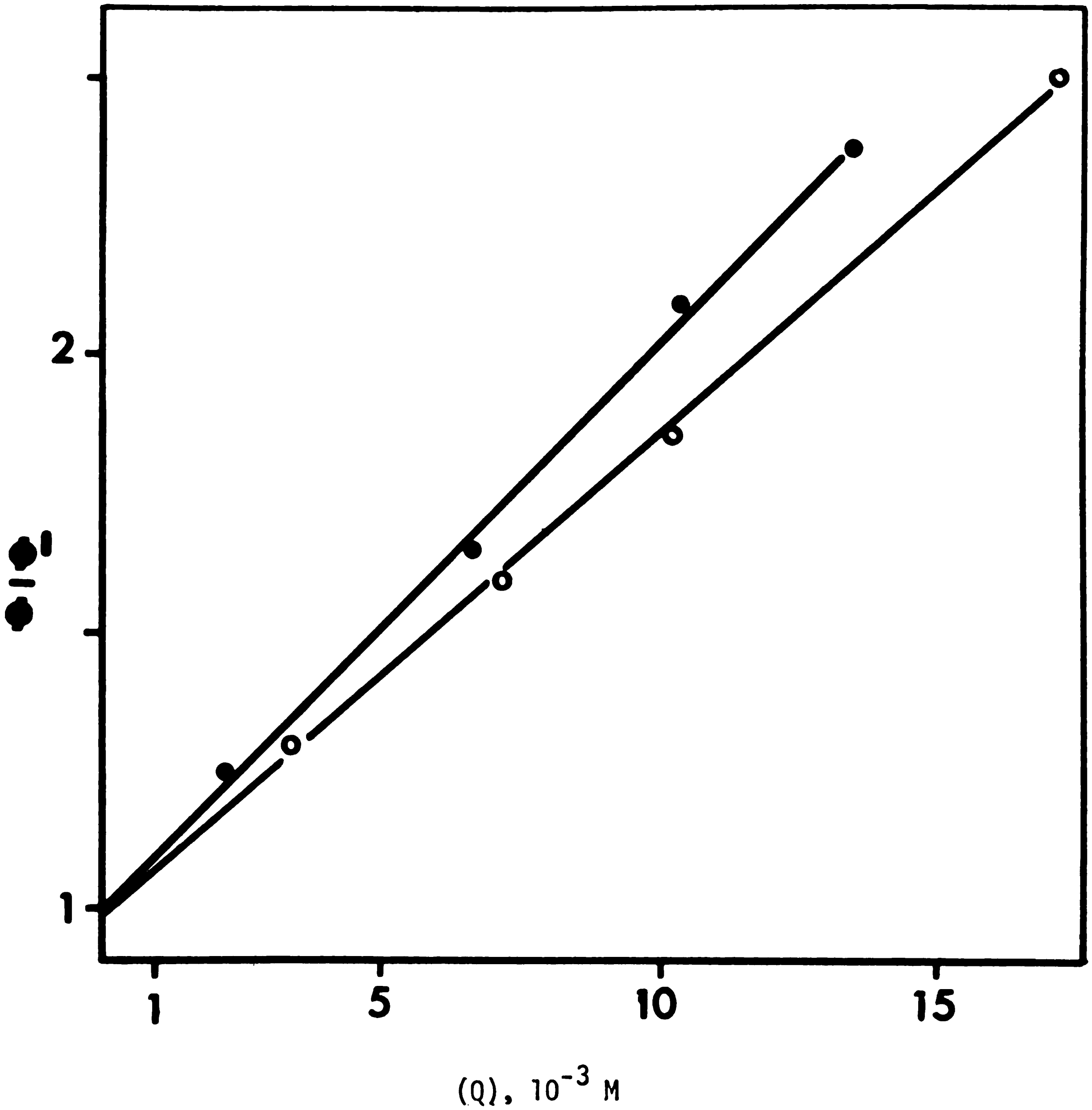


Figure 17. Stern-Volmer plots of 2,2',4,4'- (I) ● and 2,2',5,5'- (II) ○ Tetrachlorobiphenyls using 1,3-Cyclohexadiene in Methanol

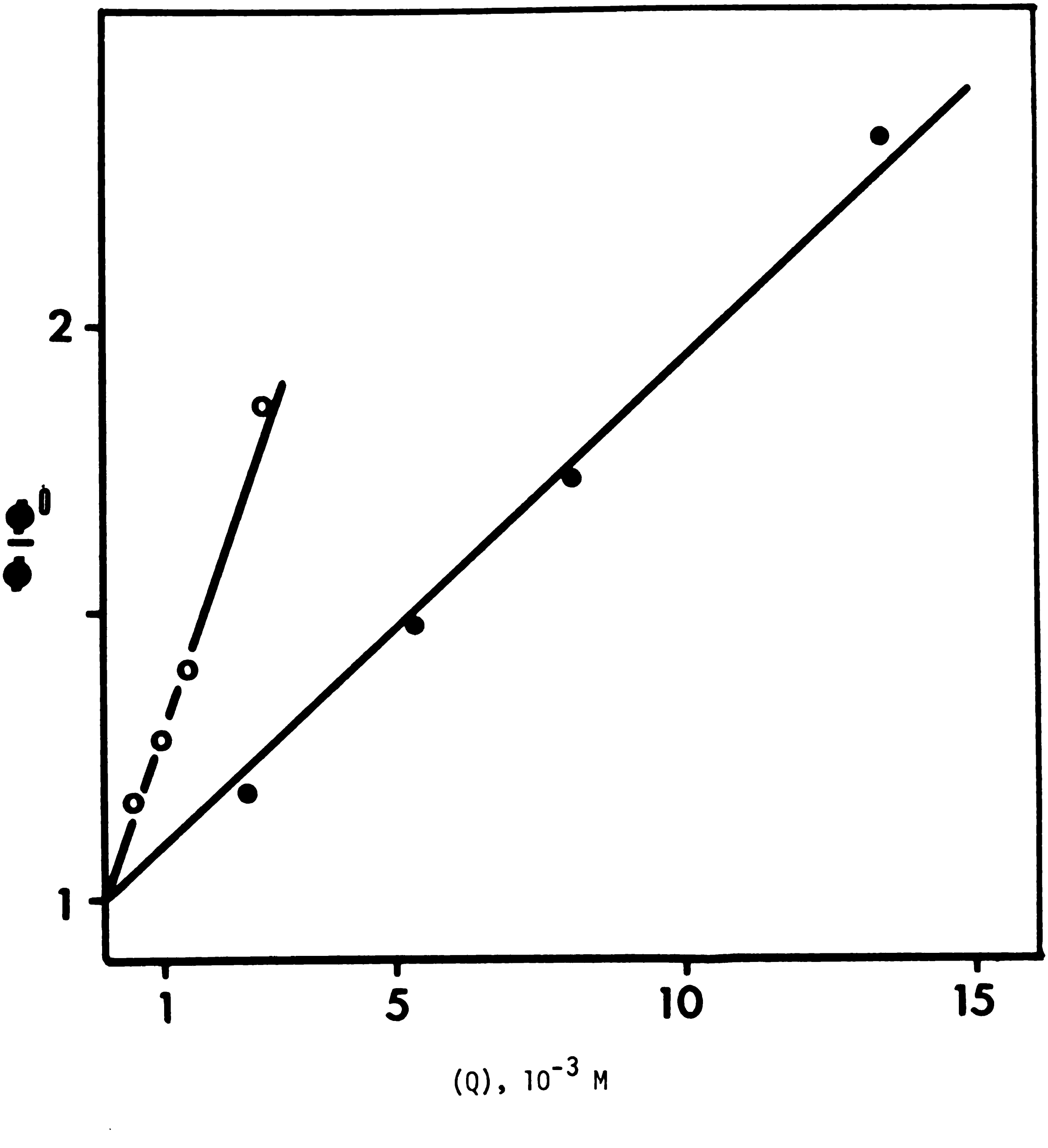


Figure 18. Stern-Volmer plots of 3,3',4,4'- (VI)○ and 2,2',3,3'- (III)● Tetrachlorobiphenyls using 1,3-Cyclohexadiene in Methanol

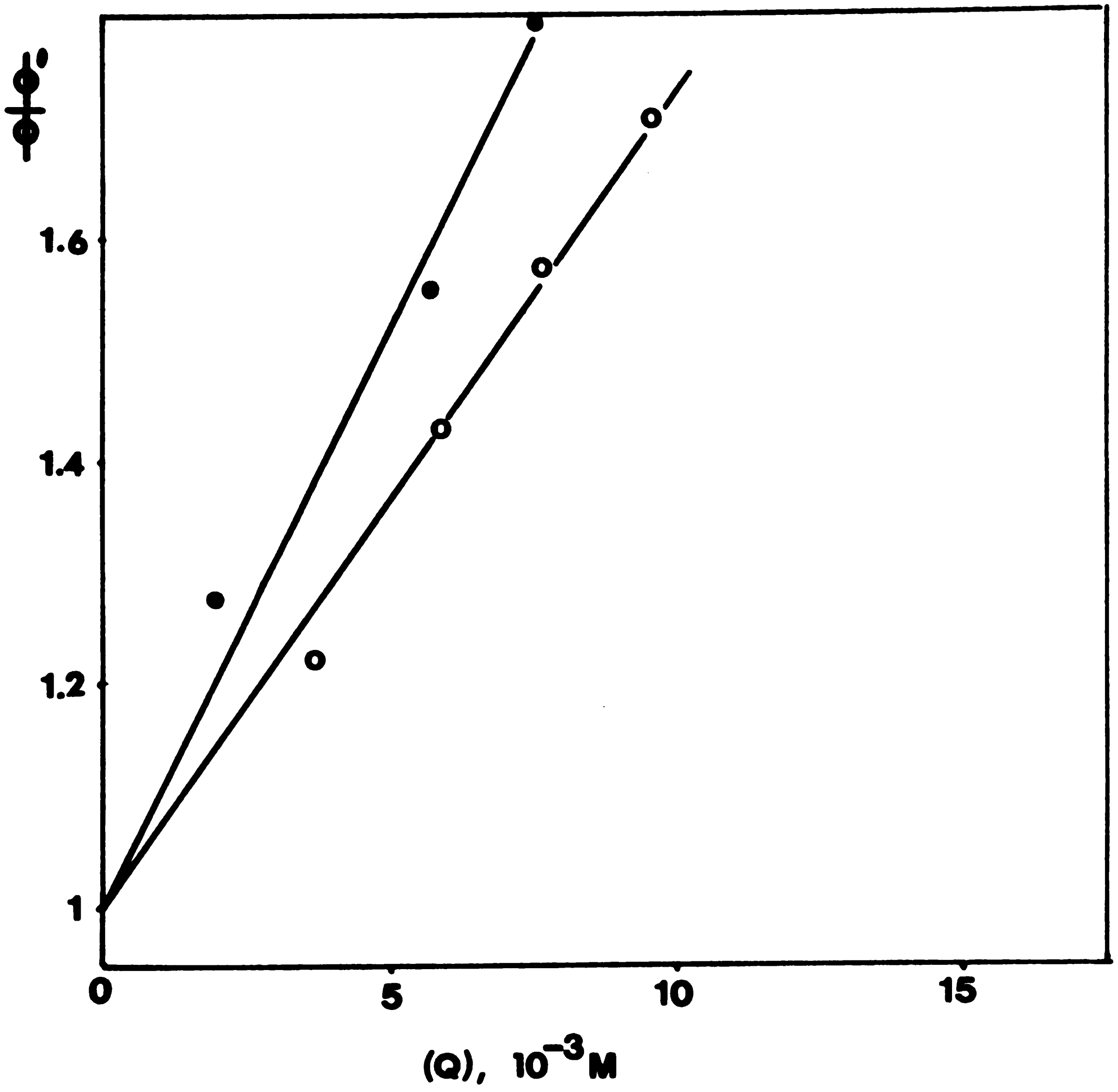


Figure 19. Stern-Volmer plots of 2,2'-6,6'- (IV) ● and 2,2',4,4'- (I) ○ Tetrachlorobiphenyls using 1,3-Cyclohexadiene in Cyclohexane

Table 13. Intersystem Crossing Quantum Yields of Selected Polychlorobiphenyls

PCB	ϕ_{isc}
I	1.00 ± 0.01
III	0.97 ± 0.03
V	0.99 ± 0.02
VI	0.99 ± 0.00

G. Reaction (k_r) and Decay (k_d) Rate Constants of the PCB Triplet.

Using equations 20 and 21 and the values obtained for the quantum yield of reaction and the triplet lifetime, the rate constants of decay and reaction of I-VI were calculated (Table 17).

$$\tau^{-1} = k_d + k_r \qquad (20)$$

$$\phi_r = \phi_{isc}\, k_r\, (k_d + k_r)^{-1} \qquad (21)$$

Table 14. Summary of Triplet State Reactivities of Polychlorinated Biphenyls

PCB	ϕ_r	τ, 10^{-8} sec	$1/\tau$, 10^7 sec^{-1}	k_r, 10^7 sec^{-1}	k_d, 10^7 sec^{-1}
I	0.100	0.78	12.82	1.282	11.54
II	0.010	0.67	14.92	0.149	14.77
III	0.007	0.77	12.99	0.091	12.90
IV	0.006	0.70	14.28	0.086	14.20
V	0.002	1.91	5.23	0.010	5.22
VI	0.005	2.20	4.54	0.023	4.52

DISCUSSION

A. Ultraviolet Spectroscopy and the Excited State of Biphenyl

In general, when halogen atoms are associated to an aromatic system there is a shift of the π-π^* absorption region towards the red. This is attributed to interactions between the lone-pair orbitals associated with the halogen atoms, and the aromatic π orbitals (resonance effect). The electronic transitions of lowest energy are still π-π^*, but the upper orbital now has both C-C and C-X antibonding character, and the photodissociation of either bond is possible.

The small bathochromic shifts obtained in the uv spectra of PCB in methanol point to the expected π-π^* transition. 4,4'-Dichlorobiphenyl shows λ_{max} at 259 nm in cyclohexane and 261 nm in methanol. The absorption resulting from this transition tails out to 310 nm for I-XI, its intensity depending on the degree and position of the chlorine substituents.

The extinction coefficient of the 249 nm band of biphenyl absorption (ε = 18000) indicated the probability of a particular transient species forming. As shown in figures 3-5 that band's ε decreases considerably in the presence of <u>ortho</u> chlorines and increases with <u>para</u> chlorination. This effect must be the result of successful inhibition of planarity of the triplet observed in other systems,[32,33] and of an increase in the double bond character of the C1-C1' bond by electron donation from the <u>para</u> position.

From this data it could be predicted that in any photoreaction of PCB the driving force would be enhanced by the destabilizing effect of the <u>ortho</u> chlorines and the stabilizing effect of the <u>para</u> chlorines on the excited state.

B. Reaction Mechanism

With the exception of most fluoroaromatics the primary process in haloaromatics involves cleavage of the C-X bond to yield radicals. In some of the early experiments the presence of free halogen atoms was observed from transient spectra due to formation of ClO, BrO, IO, following the flash photolysis of the halogenated compound.[16b]

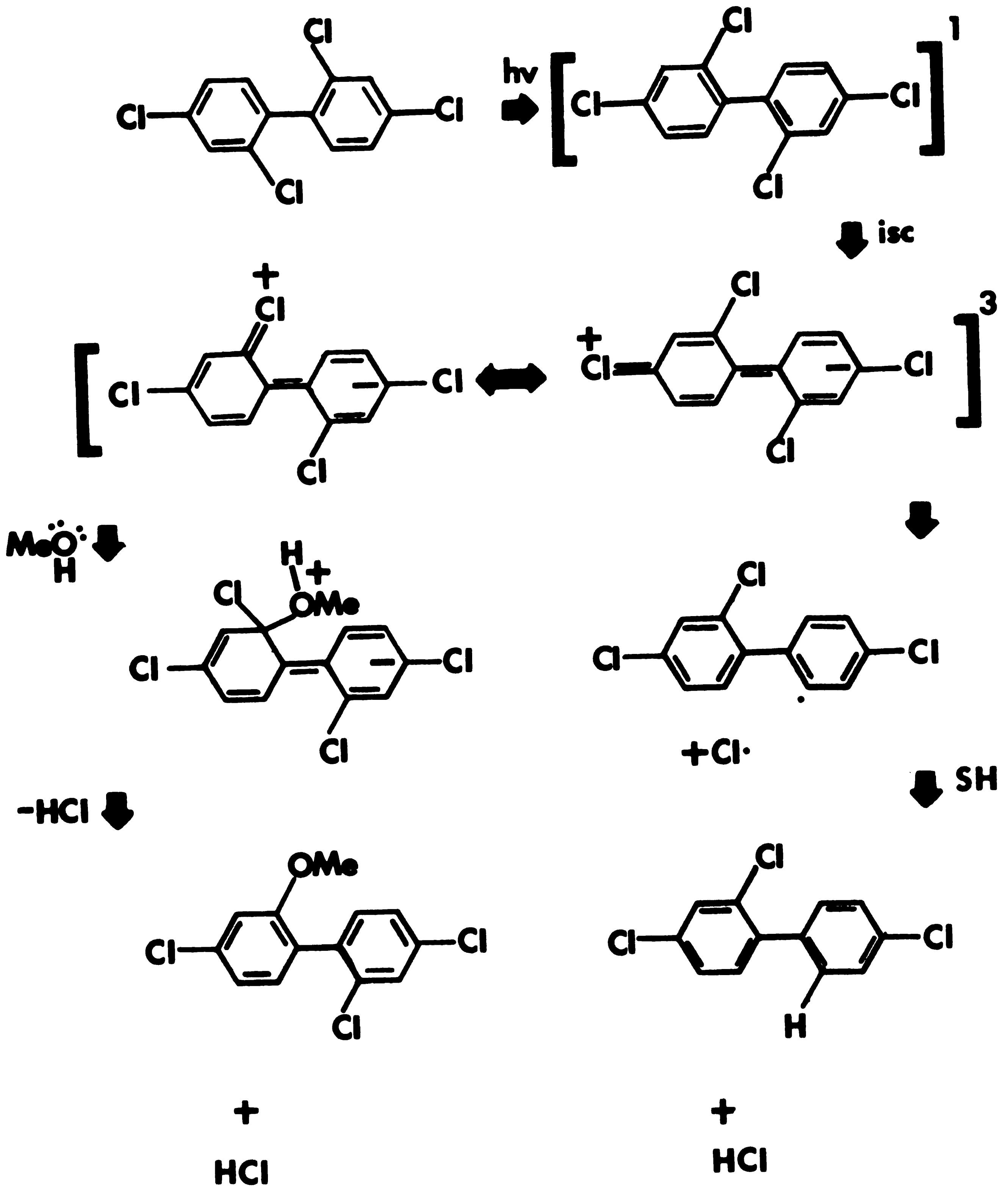
The formation of dechlorinated PCB in hydrogen donating solvents such as cyclohexane and methanol points to the presence of a free radical species capable of hydrogen abstraction. Cleavage of the C-Cl bond (83 kcal/mole) in the triplet yields a phenyl radical in a primary rate determining step. Formation of HCl was detected during irradiation in keeping with such a mechanism.

As shown in the results section it is preferentially the ortho chlorines that cleave. Some meta cleavage was also observed (III), but could be considered negligible compared to ortho dechlorination. In the absence of ortho substituents meta dechlorination occurs preferentially (VI, VIII, IX). These results point to the importance of steric and resonance effects in determining the course of the reaction.

Dechlorination in I-VI was in a stepwise manner, chlorine cleaving first on one ring, then in the same position in the other ring. In none of the cases studied was one ring dechlorinated preferentially over the other.

The methoxylated products obtained in methanol solution most likely arise from nucleophilic attack of the solvent with intermediacy of an ionic species stabilized by charge delocalization over the biphenyl system.

SCHEME 2



Since no methoxylation occurs at the para position it must be concluded that bond weakening of the ortho chlorine plays an important part in this process. Attack of the nucleophile can be visualized as occurring on an already partially ionized C-Cl bond, where carbon has developed a partial positive and chlorine a partial negative charge. This weakening of the bond would not occur at the para carbon-chlorine position since it does not destabilize the excited state.

The mechanistic pathways for reductive dechlorination and photonucleophilic substitution are outlined in Scheme 2 for 2,2',4,4'-tetrachlorobiphenyl at 300 nm.

C. Photochemical Mechanism

1. The following mechanistic scheme can be drawn from our results:

$$^{o}(\text{P-Cl}) \xrightarrow[I_a]{h\nu} {}^{1}(\text{P-Cl})^{*} \xrightarrow[\text{isc}]{100\%} {}^{3}(\text{P-Cl})^{*} \qquad (22)$$

$$^{3}(\text{P-Cl})^{*} \xrightarrow[k_d]{} (\text{P-Cl}) \qquad (23)$$

$$^{3}(\text{P-Cl})^{*} \xrightarrow[k_r]{} \text{products} \qquad (24)$$

where $^{o}(\text{P-Cl})$, $^{1}(\text{P-Cl})^{*}$ and $^{3}(\text{P-Cl})^{*}$ represent the PCB in its ground, excited singlet and excited reactive triplet states. The quanta absorbed in the initial excitation step are represented as I_a.

Normal kinetic analysis yields expressions 25-29.

$$\frac{-d\ ^{o}(\text{P-Cl})}{dt} = I_a - k_d\ ^{3}(\text{P-Cl})^{*} \qquad (25)$$

$$\frac{-d\ {}^{3}(\mathrm{P{-}Cl})^{*}}{dt} = 0 = k_d\ {}^{3}(\mathrm{P{-}Cl})^{*} + k_r\ {}^{3}(\mathrm{P{-}Cl})^{*} - I_a \qquad (26)$$

$${}^{3}(\mathrm{P{-}Cl})^{*} = I_a/(k_d + k_r) \qquad (27)$$

$$\frac{-d\ {}^{o}(\mathrm{P{-}Cl})}{dt} \cdot (I_a)^{-1} = \phi_r \qquad (28)$$

$$\phi_r = 1 - \frac{k_d}{k_d + k_r} \qquad (29)$$

Expression 29 indicates that the quantum yield of reaction is independent of concentration and is determined only by k_r and k_d.

Further manipulation of (29) leads to expression (30):

$$\phi_r = \phi_{isc}\ k_r\ (k_d + k_r)^{-1} \qquad (30)$$

Equation (30) allowed direct calculation of the reaction rate constant for the excited state. This is the same expression normally employed for calculation of kinetic parameters in photoprocesses of triplet ketones when isc approaches 100%.[54]

The linearity of the Stern-Volmer plots[51] and the absence of fluorescence from tetrachlorobiphenyls indicate the existence of only one reactive excited state, a triplet. Whether it is the lowest (T_0) or one of the higher energy triplets has not been determined in this investigation.

2. Reactivity of the Excited State. Evidence for reactivity of the triplet can be obtained directly from the quantum yield and lifetime measured. Since the lifetimes have been found to be the same in polar

and non-polar solvents, it can be assumed that the excited species is not polar and a diradical might provide a more accurate representation of its electron distribution.

The lifetimes obtained for I-VI (Table 12) show little variation among the ortho chlorinated compounds. However, 3,3',5,5'- and 3,3',4,4'-tetrachlorobiphenyls show values greater by a factor of three than those of I-IV. Apparently two ortho chlorines are sufficient to decrease the amount of inter-ring conjugation to an appreciable extent. The stabilizing effect of para chlorination only slightly affects the lifetime.

Quantum yields give a more dramatic demonstration of the substituent effects as shown in tables 10 and 11. The value of ϕ_r for 2,2'4,4'-tetrachlorobiphenyl (0.100) is greater by a factor of 10-50 than those obtained for II-VI. The unsymmetrical PCB VII-IX and XI also show larger values. The lowest values obtained are for those compounds containing no ortho chlorines (V and VI). It is clear that the reactivity of PCB could at least partially be explained on the basis of the "ortho" effect, however, the large difference between the 2,4 and 2,3 substituted PCB could not be explained without calculation of the k_d and k_r values. The ratios of decay/reaction for six PCB triplets are listed below.

PCB	k_d/k_r
I	9
II	100
III	120
IV	150
V	520
VI	200

In all cases decay is preferred to reaction, however this tendency grows more pronounced in the order 2,4 - 2,3 - 3,4 - 3,5 substitution. In compounds having 2,4 substitution the reaction becomes a competitive path to reversion to the ground state.

Transannular effects are shown to be present in the reaction of 3,4,2'-trichlorobiphenyl (XI) to yield 3,4-dichlorobiphenyl ($\phi_r = 0.02$). This quantum yield is the smallest of those obtained for 2,4 PCB, but still greater than those of the rest, the highest of which is 0.01 (II). It can be concluded that the driving force for the reaction is greatest when both the ortho and para chlorines are on the same ring and that the rates increase when the effects arise from both rings.

D. Environmental Significance

Since PCB are thermally and biologically non-degradable, their presence in the environment, either by misuse or accidental leakage, constitutes a long-term problem. Photochemical degradation is shown to be a major if not the only degradation pathway, since solar radiation of the wavelength required is present.

The prevalent substitution patterns of tetrachlorobiphenyls found in Arochlor 1242 and 1248 (42 and 48% chlorine respectively) are 2,5; 2,3; 2,4; and 3,4[10]. Of these the only ones that can be degraded with relative ease are the 2,4 substituted isomers.

The photochemical introduction of biological "handles", which make metabolic degradation possible, is shown to take place in methanol and in water. Methoxy and hydroxy groups are introduced rather slowly, this detracts from their environmental significance. Furthermore, since PCB introduction in the aquatic environment usually takes place in the presence of other hydrophobic substances (oils), contact with the potential nucleophile, water, would be minimized.

E. Summary

The involvement of steric and electronic effects in the biphenyl system is well supported. Triplet reactivities showed a marked sensitivity toward the degree and position of chlorine substituents. Greater quantum yield and rate constants of reaction are characteristic of 2,4 substitution while the reverse is true for 3,4 or 3,5 patterns. The triplet lifetimes were found to be dependent on substituent positions as well.

The photoproducts of PCB reactions arose through the same excited state *via* dechlorination and/or nucleophilic substitution.

F. Further Experiments

The following experiments are examples of possible ways towards acquiring more information on PCB photochemistry:

1. Solid state photolysis of individual isomers could be carried out in soils containing environmental triplet sensitizers such as mercury salts and quinones.

2. The effect of chlorine substituents in haloterphenyls, one ring apart could be studied to determine the extent of transannular effects from the *para* position on one ring to the *ortho* in another.

3. Other electron donating substituents could be examined to study their effects on triplet lifetime and reactivity.

EXPERIMENTAL

PART I. MATERIALS AND PROCEDURES

A. Preparation and Purification of Materials

Purity is of critical importance in determining photochemical rate constants, since even small amounts of quenching or sensitizing substances can have large effect on slow rates. Determination of the properties of the excited state such as lifetime, and intersystem crossing can be affected. Therefore all the compounds used in the photolyses described were carefully checked by vpc after purification to insure against such occurrences.

1. Polychlorinated Biphenyls

a. 2,2',4,4'-Tetrachlorobiphenyl (I). 2,4-Dichloroaniline was diazotised and upon addition of potassium iodide it yielded 2,4-dichloroiodobenzene (85% yield).[57] 2,4-Dichloroiodobenzene (10g, 0.036 mole) was dissolved in 50 ml of refluxing dimethyl formamide (DMF) and copper powder (10g, 0.16 mole) was added with stirring over a two hour period. The mixture was refluxed under nitrogen for 20 hours.[58] The reaction mixture was then poured into 400 ml of ice water and allowed to stand overnight under refrigeration. Vacuum filtration yielded a brown solid which was then extracted with 200 ml of boiling acetone.

The undissolved residue was filtered off and discarded. The acetone extract was concentrated to 30 ml in the rotary evaporator and upon cooling a yellow precipitate formed. This solid was recrystallized twice from ethanol and the white crystals obtained were dried under vacuum. The yield was 4.1 g (78% of theory). The melting point was 44-45°C. The nmr spectra showed signals at δ 7.25 (2H, multiplet) and 7.50 (1H, triplet). The mass spectrum showed a parent peak at m/e 290.

M + 2, M + 4, M + 6 and M + 8 peaks were present. Fragments were observed at m/e 255, 220, 185 and 150 corresponding to dechlorinated species. Vpc analysis (COL1) showed a single peak and the sample was considered to be > 99.9% pure.

b. 2,2',5,5'-Tetrachlorobiphenyl (II). Preparation was analogous to that of I. The crude product was recrystallized from acetone and ethanol. The white crystals were dried under vacuum and their melting point determined (86-87°C). The yield was 4.2 g (80% of theory). The nmr spectrum showed a multiplet at δ 7.35. The mass spectrum was similar to that of I. Vpc analysis analysis showed a single peak (COL1).

c. 2,2',3,3'-Tetrachlorobiphenyl (III). Preparation was analogous to the ones previously described. The white crystals obtained after recrystallization from ethanol and acetone were dried and sublimed (50°C, 0.2 mm). Their melting point was 120-121°C. The nmr spectrum showed multiplets at δ 7.18 (2H) and 7.42 (1H). The mass spectrum had the same fragmentation patterns as those of I and II. The compound was found to be pure by vpc (COL1).

d. 3,3',5,5'-Tetrachlorobiphenyl (V). Using the same method white crystals were obtained which melted at 168-169°C. The yield was 4.8 g (91% of theory). Its nmr spectrum showed a coincidental singlet at δ 7.50. Its mass spectrum was in agreement with its structure, showing the presence of four chlorines and the biphenyl skeleton. Only one peak was detected by vpc.

e. 2,2',6,6'-Tetrachlorobiphenyl (IV). All attempts to prepare this compound failed. Ullman coupling of 2,6-dichloroiodobenzene yielded only unreacted starting material. Photochemical coupling in benzene[21] at 300 nm yielded only 1,3-dichlorobenzene and

2,6-dichlorobiphenyl. Compound IV was finally obtained from Analabs, Inc. (North Haven, Conn.). The sample was recrystallized twice from ethanol and its mass spectrum checked for authenticity. Vpc analysis showed a single peak (COL1).

f. 3,3',4,4'-Tetrachlorobiphenyl (VI). This compound was prepared using a modified form of the procedure described by Tsutsui.[59] 3,4-dichloroiodobenzene was obtained from Pfaltz and Bauer, Inc., Flushing, N. Y.) and 15 g (.055 moles) of it reacted with 1.3 g of magnesium metal (0.055 mole) in refluxing anhydrous ether (50 ml). One hour after the magnesium was consumed 4 g (0.03 mole) of copper (II) chloride was added and refluxing continued for 2 hours. The product was extracted with 100 ml of ether and the extract concentrated to 20 ml. Upon cooling a white solid precipitated. Upon recrystallization from ethanol and vacuum drying the melting point was determined (179-180°C). The nmr spectrum showed signals at δ 7.80 (1H) and 7.61 (2H). The mass spectrum was similar to that of I-V. Vpc analysis showed one peak (COL1).

g. 2,4,6-Trichlorobiphenyl (VII) was obtained commercially (Analabs) and purified as described above.

h. 2,4,5-Trichlorobiphenyl (VIII) was obtained from Analabs and recrystallized from ethanol until pure by vpc.

i. The same procedure described in (h) was used for all other PCB samples obtained from Analabs, Inc.

j. 2,4,4-'Trichloro-2'-methoxybiphenyl. 2,4-Dichloroiodobenzene and 2-methoxy-4-chloroiodobenzene (Aldrich) in equimolar amounts were coupled with copper powder in DMF in a manner analogous to I. The reaction yielded 28% I, 51% trichloromethoxybiphenyl and 8% dichlorodimethoxybiphenyl. These products were separated by vpc (COL 5) and identified by vpc-mass spectrometric techniques. The mixture was used as standard for the identification of the photoproducts obtained from compound I in methanol.

k. 2,2',4-Trichloro-4'-methoxybiphenyl. Preparation was analogous to that of I. 2,4-Dichloroiodobenzene and 2-chloro-4-methoxyiodobenzene (Aldrich) in equimolar amounts were coupled using copper powder in DMF to yield I (24%), 2,2'-dichloro-4,4'-dimethoxybiphenyl (11%), and 2,2',4-trichloro-4'-methoxybiphenyl (56%).

These products were identified using gas chromatography-mass spectrometry (COL5) and the mixture used as standard for identification of the photoproducts of I in methanol.

2. Solvents

a. Benzene (J. T. Baker, Chem. Co., GC-Spectrophotometric Quality) was washed with concentrated sulfuric acid until the acid layer no longer turned yellow. It was then washed with sodium hydroxide, saturated sodium chloride and distilled water. After drying over sodium sulfate it was distilled from P_2O_5. Only the center cut (70%) was retained.

b. Toluene (Fisher Scientific Co.) purification was similar to that of benzene.

c. Cyclohexane (Burdick and Jackson Labs., Glass Distilled) purification was similar to that of benzene.

d. n-Hexane (Burdick and Jackson Labs., Glass Distilled) was fraction distilled twice.

e. Methanol (Burdick and Jackson Labs., Glass Distilled) was fraction distilled twice over magnesium metal.

f. Ethanol (Commercial Solvents Co., Absolute) was used as received.

g. Acetone (Burdick and Jackson Labs., Glass Distilled) was used as received.

3. Quenchers

a. cis-1,3-Pentadiene (cis-piperilene, Aldrich Chem. Co.) was passed through alumina followed by distillation. Pure by vpc (COL2).

b. trans-1,3-Pentadiene (Aldrich) was used as received.

c. 1,3-Cyclohexadiene (Aldrich) was used as received.

d. Biacetyl (Aldrich) was fraction distilled.

4. Sensitizers

a. Benzophenone (J. T. Baker) was recrystallized three times from ethanol.

b. Valerophenone (Aldrich) was fraction distilled.

5. Internal Standards

a. Hexadecane (Aldrich) purification was similar to that of benzene.

b. Octadecane (Aldrich) was recrystallized from ethanol.

c. Eicosane (Matheson, Coleman and Bell) was used as received.

d. Docosane (Matheson, Coleman and Bell) was used as received.

B. Photolysis Procedures

1. Preparation of Samples

Class A volumetric flasks and pipettes were used exclusively to make up photolysis solutions.

Stock solutions of PCB and internal standards in various solvents used were prepared in 25 ml volumetrics. For quantum yield determinations (PCB) concentrations ranged from 0.05M to 0.200M to insure absorption of 99.9% of the impinging light in the 290-310 nm range. For triplet lifetime measurements two stock solutions were prepared in each case. One contained PCB in 10^{-2}M concentration with an adequate concentration of internal standard and the other contained quencher (1,3-cyclohexadiene). One milliliter of PCB solution was then pipetted into each of five 10 ml volumetrics and 1,2,4,6, or 8 ml portions of quencher solution added. The flask was then filled to the mark with solvent. From each of these solutions three exactly 3 ml portions were withdrawn *via* a 10 ml syringe and injected into 13 x 100 mm Pyrex culture tubes which had been drawn into small capillaries about 2 cm from the open end to facilitate sealing after degassing.

For photoproduct identification 10^{-3}M solutions of I-XI were photolyzed in a 50 ml round bottom flask equipped with a magnetic stirrer and then concentrated for analysis.

2. Degassing

In order to remove dissolved oxygen, sample tubes were attached to a vacuum line over no. 00 one-holed rubber stoppers on individual stopcocks. The solutions were slowly frozen above liquid nitrogen and then immersed before opening to the vacuum. A minimum vacuum of 0.01 mm was attained before closing the stopcocks and allowing the tubes to thaw. After the fourth freezing and evacuation the tubes were sealed off with a torch.

In cases where only rough estimates of rate constants and quantum yields were needed, the solvents were placed in a ultrasonicator for 0.5 hours and then nitrogen was bubbled through for an additional 0.5 hours.

3. Irradiation

Sample tubes were irradiated in parallel on a rotating merry-go-round apparatus[60] to insure that the same amount of light impinged each sample, for quantum yield determinations and quenching studies.

The light source used was a Rayonette Reactor (The Southern N.E. Ultraviolet Co.) fitted with RUL 3000 lamps having a peak output energy (90%) at 300± 10 nm (Figure 20). The light output was continuous over > 80 hour periods (Figure 21). The irradiation chamber temperature was 30°C.

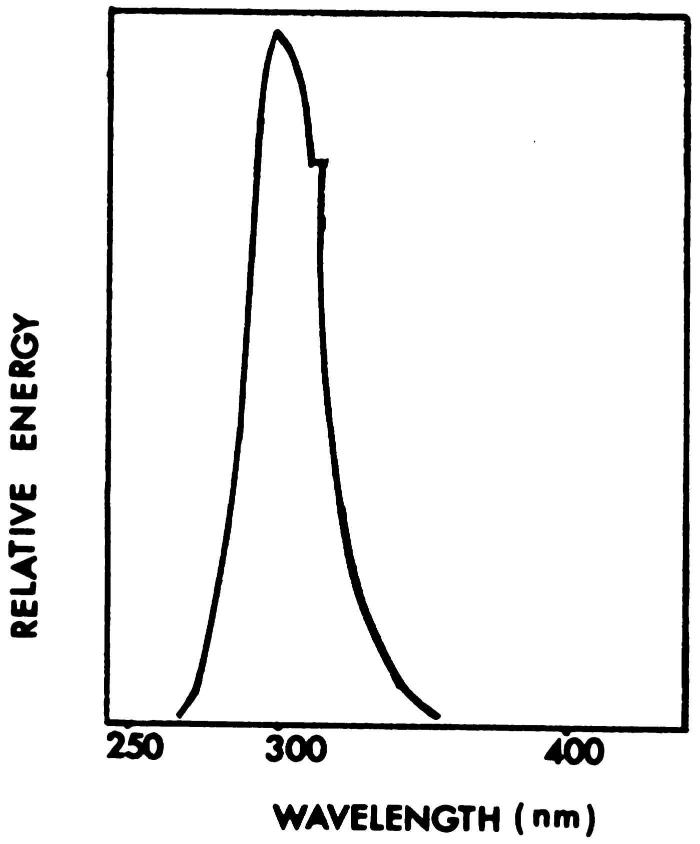


Figure 20. Energy output distribution of RUL3000 UV lamps

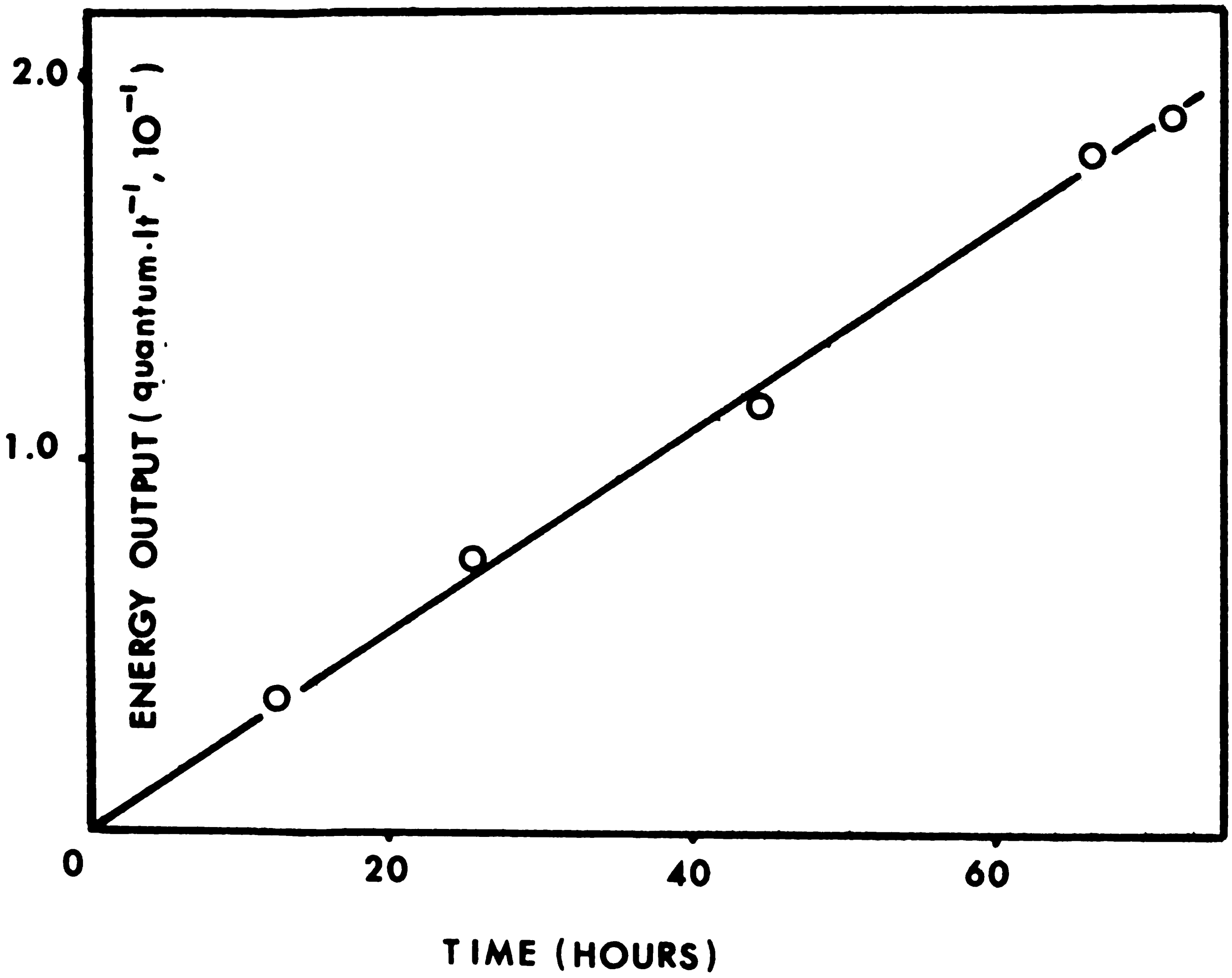


Figure 21. Energy output of RUL 3000 lamps

C. Analysis of Photolysate

1. Instruments

All analyses for photoproducts were made in the following instruments equipped with flame ionization detectors.

VPC-1 Varian Aerograph, model 1400 with Sargent recorder.

VPC-2 Beckman, model GC-65 with Beckman recorder and disc integrator.

VPC-3 Beckman, model GC-4 with Bristol Dynamaster recorder and disc integrator Model 202.

A variety of vpc columns were utilized, as designated below.

COL-1 50' x 1/16" o.d. 0.02" i.d. stainless steel S.C.O.T. (Support Coated Open Tubular) SE-30 column (Perkin-Elmer) Used at temperatures in the 150-210°C range, nitrogen flow 6-8 ml/min.

COL-2 32' x 1/8" stainless steel column containing 25% 1,2,3-tris-(2-cyanoethoxy)propane on 60/80 chromosorb P. Used at temperatures in the 40-60°C range.

COL-3 6' x 1/8" glass column containing 3% OV-210 on 60/80 mesh Gas Chrom Q. Used at temperatures in the 130-200°C range.

COL-4 6' x 1/8" stainless steel column containing 3% Apiezon L on 60/80 mesh Gas Chrom Q.

COL-5 6' x 1/8" stainless steel column containing 15% QF-1, 10% DC-200 on Gas Chrom Q. (60/80 mesh).

Mass spectra were obtained from a DuPont 21-490 apparatus interfaced with VPC-2 (COL1 and 5) or the sample was introduced by direct probe.

2. Product Identification

Photoproducts were identified primarily by their vpc retention times, mass spectra and comparison to authentic standards. The photolysate of

I-XI always contained starting materials and dechlorination products. Their retention times (R_t) increasing with greater chlorine content and amount of vicinal substitution. The detector response did not vary appreciably for PCB containing 2-4 chlorines.

Using COL-1 the methoxylated products obtained in methanol had only slightly greater R_t than their chlorinated counterparts. Using COL-5 much better separation was obtained.

In the case of 2,2',4,4'-tetrachlorobiphenyl enough conversion occurred so that an nmr spectra of the major photoproduct, 4,4'-dichlorobiphenyl, could be obtained. The nmr matched that of an authentic sample (δ 7.31, coincidental singlet).

3. Standardization

Vpc detector response was checked for linearity using varying concentrations of PCB. To determine the remaining PCB concentration after photolysis the vpc area ratio $(PCB)_t/(PCB)_o$ was multiplied by the initial concentration. The use of an internal standard insured that the injections were the same.

D. Actinometry

1. Quantum Yields of Reaction (ϕ_r)

All sample tubes for which quantum yields were measured had PCB concentrations sufficient for complete absorption of the incident light. Cis-trans isomerizations of cis-piperilene were employed to monitor the light output. Actinometer tubes containing 0.05-0.10 M concentrations of benzophenone and 0.1-0.2 M cis-piperilene in benzene solution were prepared as described before and irradiated in parallel with the sample tubes.

The triplet state of benzophenone formed quantitatively from the singlet (100% isc), is completely quenched by piperilene, the excited piperilene then decays to both cis and trans isomers in a known ratio.[61] The light intensity (Einstein lt^{-1}) I_a can be calculated from the following relationship:

$$I_a = (\text{pip}^{3*}) = (\underline{\text{cis}}\ \text{pip})_0 \ \ln(0.555/0.555\text{-}\%\ \underline{\text{trans}}) \qquad (31)$$

Due to the length of time some samples had to be irradiated, specially those with very small quantum yields, several sets of actinometer tubes had to be used in series.

2. Intersystem Crossing Quantum Yields (ϕ_{isc})

Measurement of isc was attempted by comparison of the benzophenone and PCB sensitized isomerization of cis-piperilene. Only compound VI yielded reproducible results, indicating 100% isc. Probably radical reactions with the quencher resulted in marked variance of the results.

Measurement of isc was successfully accomplished by sensitizing the phosphorescence of biacetyl (512 nm) with either benzophenone (isc = 1) or PCB. The intensities obtained were compared to each other and the ratio provided a direct measure of intersystem crossing in PCB. After each measurement the degassed sample was aerated and a 0 intensity reading obtained. All phosphorescence studies were carried out in an Aminco Spectrofluorophotometer.

E. Ultraviolet Spectroscopy

Uv spectra were obtained from a Beckman DB-G grating spectrophotometer. Solutions 0.1-5.0 x 10^{-4}M in I-XI were prepared in cyclohexane and scanned from 320-220 nm. The sample was contained in a standard 1 cm quartz cell.

EXPERIMENTAL

PART II. KINETIC DATA

A. Reaction Rate Constants for Polychlorinated Biphenyls in Cyclohexane Solution .

General Comments: $(PCB)^o$ refers to the starting tetrachlorobiphenyl concentration. $(PCB)^t$ is the concentration at time t. The concentration of PCB is plotted vs time to obtain the rate constant (k) from the slope. C_n is the internal standard. Every figure given for $(PCB)^o$ - $(PCB)^t$ is the average of at least two simultaneously irradiated samples. Correlation values were obtained by the least squares method.

Table 15. Reaction Rate Constants for Polychlorinated Biphenyls (I-VI) in Cyclohexane Solution

Part A. 2,2',4,4'-Tetrachlorobiphenyl[a]

$(PCB)^o$,M	$(PCB)^t$,M	$(PCB)^o-(PCB)^t$,M	time,10^5sec
0.190	0.185	0.005	0.67
0.190	0.160	0.030	4.02
0.190	0.145	0.045	6.00

[a] 0.100 M C_{20} standard used. Correlation 1.0000

Part B. 2,2',5,5'-Tetrachlorobiphenyl[a]

$(PCB)^o$,M	$(PCB)^t$,M	$(PCB)^o-(PCB)^t$,M	time,10^5sec
0.078	0.074	0.004	5.40
0.078	0.070	0.008	10.70
0.078	0.068	0.010	13.30

[a] 0.100 M C_{20} standard used. Correlation 1.0000

Part C. 2,2',3,3'-Tetrachlorobiphenyl[a]

$(PCB)^o$,M	$(PCB)^t$,M	$(PCB)^o-(PCB)^t$,M	time,10^5sec
0.079	0.076	0.003	6.12
0.079	0.075	0.004	8.20
0.079	0.072	0.007	14.60

[a] 0.100 M C_{20} standard used. Correlation 0.9999

Part D. 2,2',6,6'-Tetrachlorobiphenyl[a]

$(PCB)^o$,M	$(PCB)^t$,M	$(PCB)^o-(PCB)^t$,M	time,10^5sec
0.045	0.044	0.001	2.70
0.045	0.043	0.002	5.20
0.045	0.042	0.003	8.30

[a] 0.050 M C_{22} standard used. Correlation 1.000

Part E. 3,3',4,4'-Tetrachlorobiphenyl[a]

$(PCB)^o$,M	$(PCB)^t$,M	$(PCB)^o-(PCB)^t$,M	time,10^5sec
0.012	0.011	0.001	3.6
0.012	0.0105	0.0015	5.4
0.012	0.010	0.002	6.8

[a] 0.010 M C_{22} standard used. Correlation 0.9980.

Part F. 3,3',5,5'-Tetrachlorobiphenyl[a]

$(PCB)^o$,M	$(PCB)^t$,M	$(PCB)^o-(PCB)^t$,M	time,10^5sec
0.0230	0.0225	0.0006	5.0
0.0230	0.0220	0.0010	8.3
0.0230	0.0210	0.0020	15.3

[a] 0.020 M C_{22} standard used. Correlation 0.9986.

B. Quantum Yield of Reaction for Polychlorinated Biphenyls in Cyclohexane Solution

General Comments: $(PCB)^o$ and $(PCB)^t$ represent the initial and final concentrations of starting material, as determined by vpc analysis. C_n represents the internal standard used in each case. I_a (light absorbed) values were obtained from cis-piperilene actinometry as described previously and are averages of at least two tubes per period. All quantum yield (ϕ_r) determinations required several sets of actinometer tubes irradiated in series.

Table 16. Quantum Yields of Reaction for I-VI.

Part A. 2,2',4,4'-Tetrachlorobiphenyl[a]

$(PCB)^0$,M	$(PCB)^t$,M	$(PCB)_{reacted}$,M	I_a,E lt^{-1}	ϕ_r
0.190	0.144	0.046	0.456	0.101
0.150	0.105	0.045	0.456	0.100

[a] 0.100 M C_{20}.

Part B. 2,2',5,5'-Tetrachlorobiphenyl[a]

$(PCB)^o$,M	$(PCB)^t$,M	$(PCB)_{reacted}$,M	I_a,E lt^{-1}	ϕ_r
0.078	0.073	0.005	0.456	0.011
0.120	0.116	0.004	0.456	0.009

[a] 0.100 M C_{20}.

Part C. 2,2',3,3'-Tetrachlorobiphenyl[a]

$(PCB)^o$,M	$(PCB)^t$,M	$(PCB)_{reacted}$,M	I_a,E lt^{-1}	ϕ_r
0.079	0.076	0.003	0.456	0.007
0.095	0.091	0.004	0.456	0.008

[a] 0.100 M C_{20}.

Part D. 2,2',6,6'-Tetrachlorobiphenyl[a]

$(PCB)^o$,M	$(PCB)^t$,M	$(PCB)_{reacted}$,M	I_a,E lt^{-1}	ϕ_r
0.045	0.042	0.003	0.502	0.006
0.090	0.087	0.003	0.502	0.006

[a] 0.100 M C_{20}.

Part E. 3,3'5,5'-Tetrachlorobiphenyl[a]

$(PCB)^o$,M	$(PCB)^t$,M	$(PCB)_{reacted}$,M	I_a,E lt^{-1}	ϕ_r
0.0230	0.0218	0.0012	0.626	0.002
0.0115	0.0104	0.0011	0.626	0.002

[a] 0.010 M C_{22}.

Part F. 3,3',4,4'-Tetrachlorobiphenyl[a]

$(PCB)^o$,M	$(PCB)^t$,M	$(PCB)_{reacted}$,M	I_aE, lt^{-1}	ϕ_r
0.012	0.010	0.002	0.537	0.004
0.024	0.022	0.002	0.330	0.006

[a] 0.010 M C_{22}.

C. Quenching

Relative quantum yields of reaction for I-VI were measured as a function of quencher concentration for use in the Stern-Volmer quenching plots. Conversions (PCB reacted) were kept below 20% to insure linearity. C_n is the internal standard used.

Table 17. 2,2',4,4'-Tetrachlorobiphenyl (2.9×10^{-3} M) in Methanol. Quenching with 1,3-Cyclohexadiene[a]

(Quencher), 10^{-3}M	$(PCB)_{reacted}$, 10^{-4}M	ϕ_r^o/ϕ_r
0.00	7.10	1.00
3.61	5.30	1.34
4.90	4.80	1.49
6.55	4.30	1.65
7.70	4.00	1.79

[a] C_{20}, 0.005 M internal standard. Correlation 0.9990.

Table 18. 2,2',5,5'-Tetrachororbiphenyl (2.02×10^{-3} M) in Methanol. Quenching with 1,3-Cyclohexadiene[a]

(Quencher), 10^{-2}M	$(PCB)_{reacted}$, 10^{-4}M	ϕ_r^o/ϕ_r
0.00	3.00	1.00
0.34	2.30	1.30
0.70	1.90	1.59
1.01	1.60	1.85
1.70	1.20	2.50

[a] C_{20}, 0.002 M internal standard. Correlation 0.9686.

Table 19. 2,2',3,3'-Tetrachlorobiphenyl (3.26×10^{-3} M) in Methanol. Quenching with 1,3-Cyclohexadiene[a]

(Quencher), 10^{-3}M	$(PCB)_{reacted}$, 10^{-4}M	ϕ_r^o/ϕ_r
0.00	8.20	1.00
2.69	6.90	1.19
5.38	5.50	1.49
8.07	4.70	1.74
13.50	3.50	2.33

[a] C_{20}, 0.002 M internal standard. Correlation 0.9980.

Table 20. 2,2',6,6'-Tetrachlorobiphenyl (2.65×10^{-3} M) in Methanol. Quenching with 1,3-Cyclohexadiene[a]

(Quencher), 10^{-3}M	$(PCB)_{reacted}$, 10^{-4}M	ϕ_r^o/ϕ_r
0.00	5.60	1.00
3.44	4.40	1.27
6.88	3.50	1.61
10.30	2.90	1.91
17.20	2.20	2.56

[a] C_{20}, 0.002 M internal standard. Correlation 0.9995

Table 21. 3,3',4,4'-Tetrachlorobiphenyl (3.28×10^{-3} M) in Methanol. Quenching with 1,3-Cyclohexadiene[a]

(Quencher), 10^{-4}M	$(PCB)_{reacted}, 10^{-4}$	ϕ_r^o / ϕ_r
0.00	7.00	1.00
2.00	6.50	1.07
6.10	5.90	1.18
10.10	5.50	1.28
14.30	5.01	1.40

[a] C_{22}, 0.003 M internal standard. Correlation 0.9992.

Table 22. 3,3',5,5'-Tetrachlorobiphenyl (1.49×10^{-3} M) in Methanol. Quenching with 1,3-Cyclohexadiene[a]

(Quencher), 10^{-4}M	$(PCB)_{reacted}, 10^{-4}$	ϕ_r^o / ϕ_r
0.00	6.20	1.00
0.93	4.40	1.40
1.86	3.70	1.69
2.79	3.50	1.79
3.72	3.20	1.96

[a] C_{22}, 0.002 M internal standard. Correlation 0.9686.

Table 23. 2,2',4,4'-Tetrachlorobiphenyl (6.19×10^{-3} M) in Cyclohexadiene. Quenching with 1,3-Cyclohexadiene[a]

(Quencher), 10^{-3}M	$(PCB)_{reacted}$, 10^{-4}M	ϕ_r^o / ϕ_r
0.00	9.00	1.00
3.84	7.40	1.22
5.76	6.30	1.43
7.68	5.70	1.58
9.60	5.30	1.70

[a] C_{20}, 0.005 M internal standard. Correlation 0.9943.

Table 24. 2,2',6,6'-Tetrachlorobiphenyl (2.25×10^{-3} M) in Cyclohexane. Quenching with 1,3-Cyclohexadiene[a]

(Quencher), 10^{-3}M	$(PCB)_{reacted}$, 10^{-4}M	ϕ_r^o / ϕ_r
0.00	4.00	1.00
1.92	3.10	1.28
5.76	2.50	1.56
7.68	2.50	1.56

[a] C_{22}, 0.003 M internal standard. Correlation 0.9914.

D. Determination of Intersystem Crossing Quantum Yields

Table 25. Triplet Sensitized cis-trans Isomerization of Piperilene[a]

Compound[b]	Sample 1 % trans	Sample 2 % trans	Sample 3 % trans	Average % trans
Benzophenone	0.218	0.217	0.212	0.215
VI	0.211	0.215	0.210	0.212

[a] 0.38 M initial cis-piperilene

[b] 0.20 M.

Table 26. Triplet Sensitized Phosphorescence of Biacetyl[a]

Compound[b]	Average Intensity	Average Intensity	Average Intensity
Benzophenone	47.4	47.0	47.2
I	47.6	46.8	47.2
III	45.9	46.2	46.1
V	47.1	46.7	46.9
VI	46.9	46.9	46.9

[a] 0.04 M Biacetyl in Benzene.

[b] 0.03-0.05 M.

LIST OF REFERENCES

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1. *New Scientist*, **32**, 612 (1966).
2. R. W. Risebrough, P. Rieche, D. B. Peakall, S. G. Herman and M. N. Kirvan, *Nature*, **220**, 1098 (1968).
3. C. G. Gustafson, *Environmental Science and Technology*, **4**, 814 (1970).
4. D. B. Peakall and J. L. Lincer, *BioScience*, **20**, 958 (1970).
5. G. D. Veith and G. Lee, *Water Research*, **4**, 265 (1970).
6. A. Richardson, J. Robinson, A. Crabtree and M. K. Baldwin, *Pesticide Monitoring Journal*, **4**, 169 (1971).
7. R. Edwards, *Chem. and Ind.*, 1340 (1971).
8. L. Acker and E. Schulte, *Naturwiss.*, **57**, 497 (1970).
9. F. J. Biros, A. Walker and A. Medbery, *Bull. Environ. Contam. Toxicol.*, **5**, 317 (1970).
10. O. Hutzinger, S. Safe and V. Zitko. *Analabs Research Notes*, **12**, 1 (1972).
11. M. Kuratsune, T. Yoshimura, J. Matzuzaka and A. Yamaguchi, H.S.M.H.A. *Health Reports*, **86**, 1083 (1971).
12. H. Hubbard, Kirk-Othmer *Encyc. Chem. Teach.*, 2nd Edition, **5**, 289 (1964).
13. W. D. Block and H. H. Cornish, *J. Biol. Chem.*, **234**, 3301 (1959).
14. R. Hoopingarner, A. Samuels and D. Krause, *Environmental Health Perspectives*, **1**, 155 (1972).
15. W. F. Forbes and J. C. Dearden, *Can. J. of Chem.*, **40**, 1977 (1959).
16. a. E. Latowska and T. Latowski, *Rocz. Chem.*, **40**, 1977 (1966)

    b. J. R. Majer and J. P. Simmons, *Advances in Photochemistry*, **2**, 137 (1964).
17. W. A. Henderson and A. Zweigh, *J. Amer. Chem. Soc.*, **89**, 1142 (1967).
18. J. A. Barltrop, N. J. Bunce and A. Thompson, *J. Chem. Soc.*, (c) 1142 (1967).
19. D. G. Crosby and Ming Yu-Li, *J. Agr. Food Chem.*, **14**, 596 (1966).
20. E. Havinga and M. E. Kronenberg, *Pure and Appl. Chem.*, **16**, 137 (1968).

21. N. Kharasch and R. K. Sharma, *Ang. Chem. Int. Ed.*,**1**, 36 (1968)

22. R. B. Ingalls, W. Wolfe and N. Kharasch, Abstracts of the 146th Meeting of the American Chemical Society, 1964, p. 6D.

23. S. Safe and O. Hutzinger, *Nature*,**232**, 641 (1971).

24. L. O. Ruzo, M. J. Zabik and R. D. Schuetz, *J. Environ. Contam. Toxicol.*,**8**, 217 (1972).

25. O. Hutzinger, S. Safe and V. Zitko, *Environmental Health Perspectives*,**1**, 15 (1972).

26. K. Anderson, A. Norstrom, C. Rappe, B. Rasmuson and H. Swahlin, Abstracts of the 166th Meeting of the American Chemical Society, Chicago, Ill. August 1973.

27. N. Kharasch, *Chem. Comm.*,492 (1967).

28. T. Sato, S. Shimada and K. Hata, *Bull. Chem. Soc. Jap.*,**42**, 766 (1969).

29. C. Adams and L. Yuan, *Chem. Rev.*,**12**, 261 (1933).

30. L. W. Pickett, G. Walter and H. France, *J. Amer. Chem. Soc.*,**58**, 2296 (1936).

31. R. J. LeFevre and H. Vine, *J. Chem. Soc.*,967 (1938).

32. L. W. Pickett, *J. Amer. Chem. Soc.*,**58**, 2299 (1936).

33. G. N. Lewis and N. Kasha, *J. Amer. Chem. Soc.*,**66**, 2100 (1944).

34. G. H. Beaven and D. M. Hall, *J. Chem. Soc.*,4637 (1956).

35. C. A. Coulson and J. Jacobs, *ibid* 2805 (1969).

36. L. S. Bartell, *J. Amer. Chem. Soc.*,**83**, 3567 (1961).

37. K. T. Leffek, *Can. J. of Chem.*,**45**, 2115 (1967).

38. P. J. Wagner, *J. Amer. Chem. Soc.*,**89**, 2820 (1967).

39. P. Pringheim, *Fluorescence and Phosphorescence*, Interscience Publishers, Inc. N. Y. 1949, p. 299.

40. O. Bastiansen, *Acta Chem. Scand.*,**3**, 408 (1949).

41. H. Suzuki, *Bull. Chem. Soc. Jap.*,**32**, 1340 (1959).

42. J. Trotter, *Acta Crystallogr.*,**14**, 1135 (1961).

43. N. Hirota, *J. Chem. Phys.*,**44**, 2199 (1966).

44. F. Wilkinson and T. Dubosis, *J. Chem. Phys.* **39**, 377 (1963).

45. P. J. Wagner and J. Scheeve, unpublished results.

46. S. McGlynn, J. Daigre and F. J. Smith, *J. Chem. Phys.*, **39**, 375 (1963).

47. T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965).

48. G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **38**, 1187 (1963).

49. M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 3255 (1965).

50. M. A. El-Sayed, *J. Chem. Phys.*, **41**, 2462 (1964).

51. P. J. Wagner in *Creation and Detection of the Excited State*, Vol. I, part A, A. A. Lamola, Ed., Marcel Dekker, Inc. N. Y., 1971, p. 175.

52. P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **99**, 2232 (1968).

53. P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

54. P. J. Wagner, A. E. Kampainen and T. Jellinek, *J. Amer. Chem. Soc.*, **94**, 7512 (1972).

55. R. E. Barker, *Photochem. and Photobiol.*, **7**, 275 (1968).

56. Research News, *Science*, **180**, 578 (1973).

57. *Org. Syn.*, Coll. Vol. II, 351.

58. N. Kornblum, *J. Amer. Chem. Soc.*, **74**, 5782 (1957).

59. M. Tsutsui, *ibid.* **79**, 3062 (1957).

60. F. G. Moses, R. Liu and O. Monroe, *Mol. Photochem.* **1**, 245 (1969).

61 A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).