Photochemistry of Dibenzo-*p*-Dioxin

by

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ABSTRACT

The photochemistry of dibenzo-*p*-dioxin (DBD; **34**) (a diphenyl diether)--the parent compound of the notorious 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD; commonly known as dioxin)--has been studied in aqueous CH_3CN, dry CH_3CN and selected organic solvents. The aim of this investigation is to achieve a comprehensive understanding of the photochemical behaviour of cyclic diaryl ethers, which may be relevant to the photodecomposition of TCDD and related contaminants.

In non-hydroxylic solvents (CH_3CN, THF or 1,4-dioxane), photolysis of DBD (**34**) gives rise to an observable (by UV-Vis spectrophotometry) intermediate 2,2'-biphenylquinone (**73**), which could be reduced by the organic solvent to 2,2'-biphenol (**69**) as a major product, or isomerizes to 1-hydroxydibenzofuran (**75**) *via* secondary photolysis. In hydroxylic solvents (aqueous CH_3CN, MeOH or 2-propanol), photolysis of DBD (**34**) gives only one major product, *viz.,* **69**; the formation of **75** is suppressed. Although the intermediate quinone **73** could not be observed by UV-Vis in these solvents, the product yield of **69** is increased dramatically in the presence of added $NaBH_4$, along with > 90% material balance, implicating the formation of **73** as the crucial intermediate. Quinone **73** originates from intramolecular rearrangement of singlet biradical **72**, which is formed from DBD (**34**) *via* aryl-oxygen bond homolysis. The intramolecular *ipso* attack of **72** to form spiro ketone **91** (the precursor of **73**) is the key point of this novel mechanism, which distinguishes it from the general accepted, but incorrect mechanism of the formation of **69** from DBD (**34**).

The generality of this mechanism is demonstrated by the photoreaction of 2,3,7,8-tetramethyldibenzo-*p*-dioxin (TMDBD; **76**), in which 4,4',5,5'-tetramethyl-2,2'-biphenylquinone (**79**) is observed in non-hydroxylic solvents; again the product yield of 4,4',5,5'-tetramethyl-2,2'-biphenol (**77**) is greatly enhanced in the presence of added $NaBH_4$. The pathway of this novel intramolecular isomerization of cyclic diaryl ethers reveals some interesting aspects of the photochemical behaviour of diaryl ethers previously unrealized. In addition, as photodecomposition of TCDD may involve aryl-oxygen bond cleavage, an efficient photodegradation method for dioxin related contaminants could be acquired by understanding the behaviour of DBD (**34**).

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TO THE PERSON

WHO MISSES ME THE MOST

Chapter One: Introduction

Life on this planet would be impossible without photochemical reactions. Photosynthesis harvests the sun's energy and creates carbohydrates from atmospheric carbon dioxide and water, as well as liberating oxygen to the atmosphere. The growth of fruits and vegetables involves direct utilization of the sun's energy. In addition, the meat that we eat comes indirectly to us through plant life.

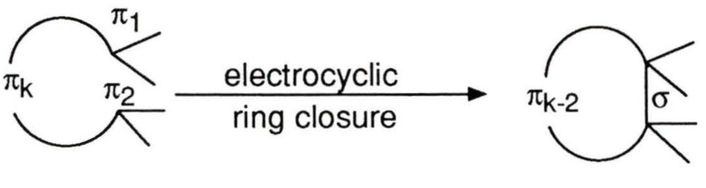
Photochemical reactions in the laboratory have been known for almost as long as chemistry has been studied. Most of the observations were accidental and remained uninterpreted. The first systematic study of the behaviour of organic compounds towards light was undertaken by Ciamician and Silber at the end of the nineteenth century.[1] Employing sunlight, they explored the photoreduction of aldehydes, ketones, quinones, and nitro compounds in alcoholic media, as well as the photoisomerization and dimerization of double bonds. Due to their contributions, organic chemists at last paid serious attention to the possibilities of chemical transformations caused by light. However, prior to about 1960, photochemistry was widely regarded as a branch of physical chemistry. General interest in photochemistry by organic chemists arose in the 1950's. Since then, organic photochemistry has continued to grow rapidly.

The 1960's saw the emergence of mechanistic organic photochemistry. As many new photoreactions have been discovered since then, the understanding of the mechanism of photochemical reactions continues to be a challenge. With the aid of powerful spectroscopic techniques (laser flash spectroscopy, steady-state and time resolved fluorescence spectrophotometry, ESR, *etc.*) as well as classical chemical techniques, photochemists have investigated in detail the mechanisms of various photochemical reactions such as the reactions of carbonyls, enones, alkenes and aromatic compounds.

Photochemical reactions may be broadly classified as unimolecular, in which the electronically excited molecule itself undergoes chemical change, or bimolecular if the electronically excited molecule reacts with another molecule. In the case of unimolecular processes, the excited molecule can react via radicals formed by homolysis, which lead to radical-derived products (eq. 1.1), or react via ions formed by heterolysis, which lead to ion-derived products (eq. 1.2). In addition, the excited molecule can undergo electrocyclic reactions to give ring closure products (eq. 1.3). The reactions which will be discussed in this Thesis are unimolecular photoreactions.

$$R\text{—}X \xrightarrow{h\nu} R\cdot\cdot X \longrightarrow \text{radical-derived products} \qquad (1.1)$$

$$R\text{—}X \xrightarrow{h\nu} R^{+}X^{-} \longrightarrow \text{ion-derived products} \qquad (1.2)$$



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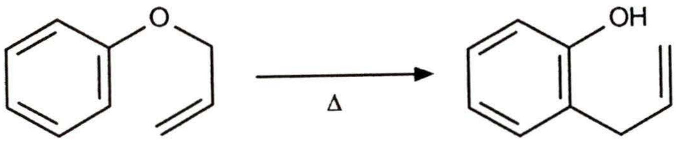
1.1 Photochemistry of Diaryl Ethers

The photochemistry of diaryl ethers[2-6] involves unimolecular reactions. Photoreactions of diaryl ethers can be initiated by homolysis of the aryl-O bond, to give a radical pair, which can escape or recombine to give substituted phenols (Scheme 1.1). When a labile substituent is *ortho* to the aryl-O bond, photoreaction of diaryl ethers may also proceed by electrocyclization to give dibenzofuran (Scheme 1.2). In addition, ring closed diaryl ethers may react via intramolecular rearrangement on photolysis (Scheme 1.3). The mechanistic details of these reaction are described below.

1.1.1 Simple Cleavage and Rearrangement

Pyrolysis of allyl phenyl ether results in the Claisen rearrangement of the allyl group to form *ortho*-allylphenol (eq. 1.4). However, a similar rearrangement has never been observed for diaryl ethers upon heating. The photochemically induced rearrangement of diaryl ether was first reported by Kharasch[7] and coworkers in 1952, who observed that photolysis of diphenyl ether (**1**) gave phenol (simple cleavage product) and the *p*-phenylphenol (rearranged product). These observations started a considerable interest in the subject of photochemically induced rearrangements. In 1965, Bach and Barclay[8] reported that in addition to the *p*-phenylphenol and phenol products,



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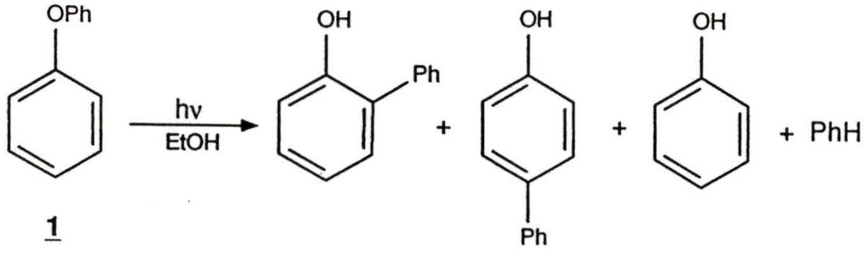
o-phenylphenol was also formed upon photolysis of diphenyl ether (**1**) (eq. 1.5).



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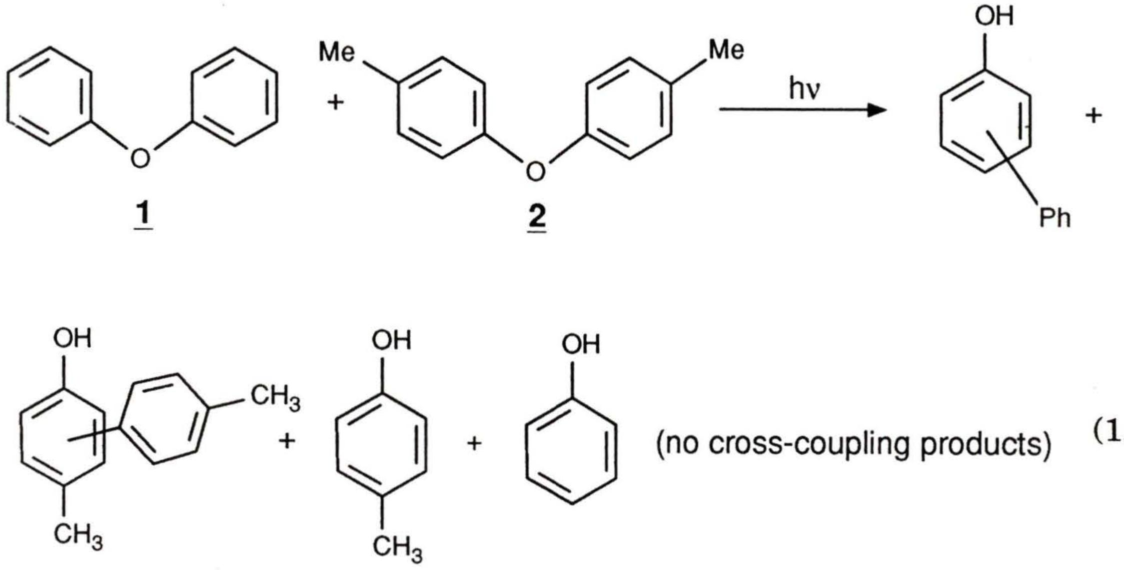

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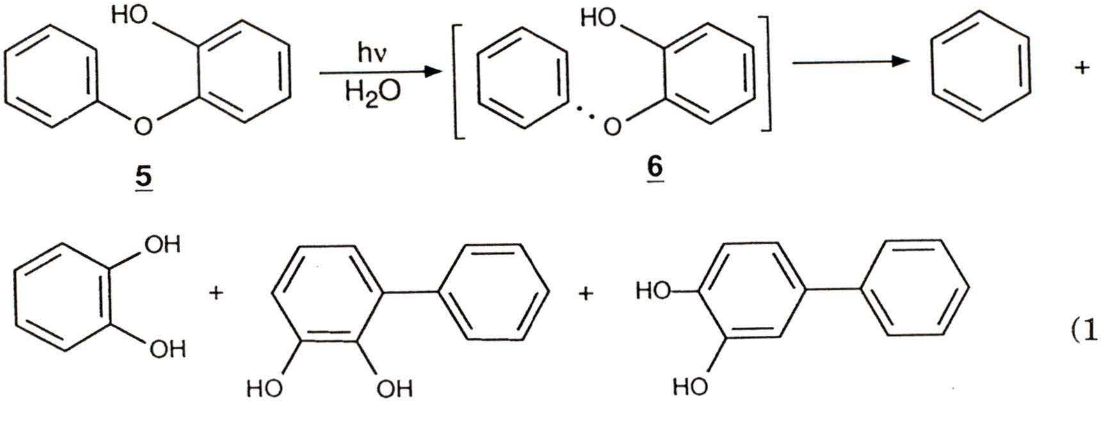
When an equimolar mixture of **1** and bis(*p*-methylphenyl) ether (**2**) was irradiated in an alcoholic solution, no cross-over products were detected (eq. 1.6),[2] indicating that *ortho* and *para* rearrangements occur within a solvent cage. This assumption was further supported by solvent effects on the ratio of rearranged to cleavage products.[3] When **1** was photolyzed in diethyl ether instead of 2-propanol, the ratio of rearranged products to phenol was decreased from 1.65 (2-propanol) to 0.38 (diethyl ether). Since the viscosity of 2-propanol is eight times higher than that of diethyl ether, this result demonstrated that the amount of cleavage products formed was dependent on the ease of escape of the formed radicals from the solvent cage.

Photoconversion of diaryl ethers to rearranged products and phenol proceeds at a significantly higher rate in hydroxylic solvents such as ethanol, t-butanol, 2-propanol and acetic acid than in non-polar aprotic solvents such as benzene, cyclohexane and ether.[2] This may be due to the stabilization of the more polar cyclohexdienone intermediates **3a** and **3b** (Scheme 1.1) by hydrogen bonding, which is not available in non-polar solvents.

The regiochemistry of the homolytic cleavage of the aryl-O bond can be affected by the substituents. That is, it is governed by the stability of the radicals formed. When 2-phenoxyphenol (**5**) or 4-phenoxyphenol (**7**) is photolyzed, cleavage of the aryl-O bond appears to be highly regioselective.[9] The hydroxy group directs the regioselective cleavage of the unsymmetrical aryl-O bonds, by forming the more stabilized *ortho* or *para* hydroxy phenoxy radicals (**6** or **8**) rather than the parent phenoxy radical (eqs. 1.7 and 1.8).



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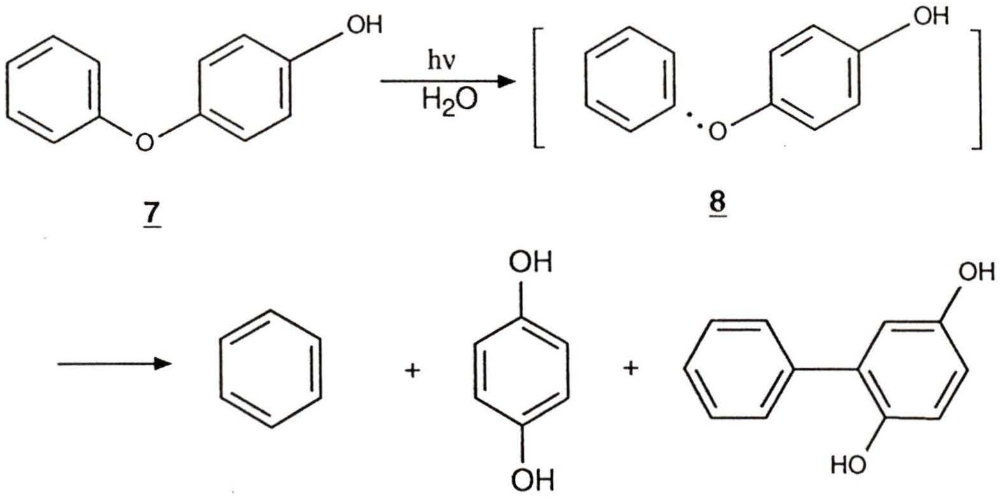
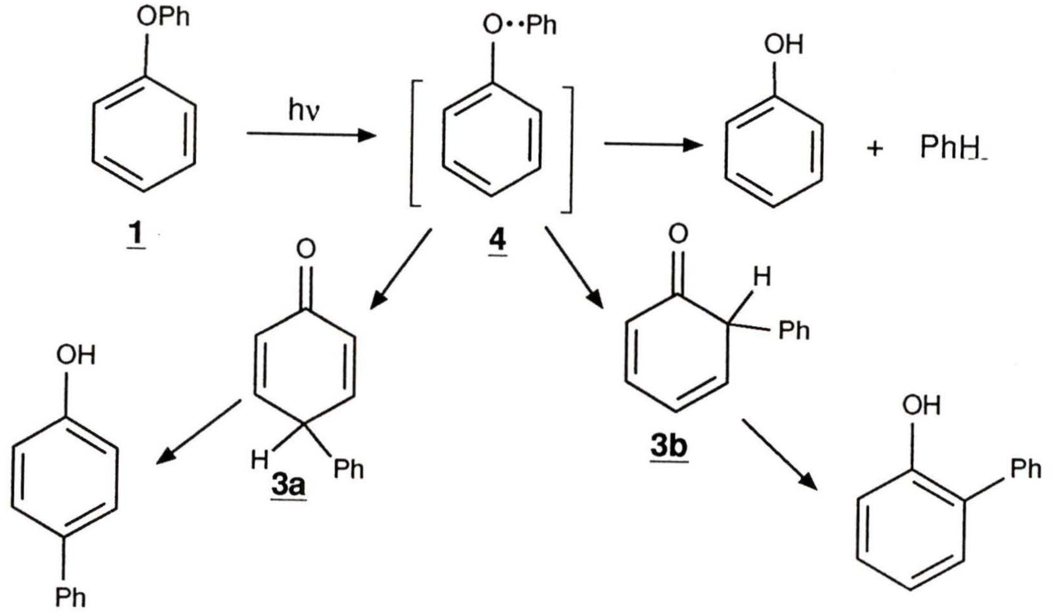


(1.8)

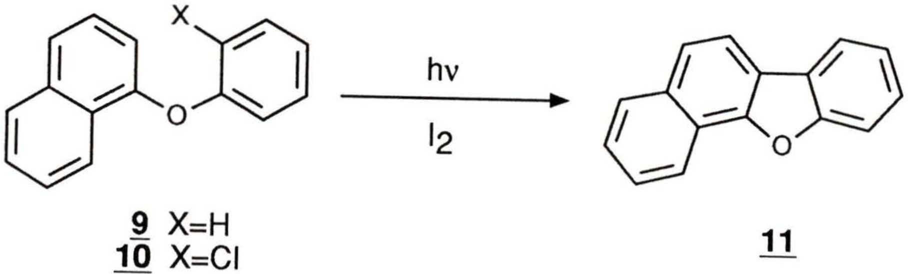
In summary, studies indicate that photoreactions of diaryl ethers can proceed through initial aryl-O bond cleavage within a solvent cage, to give a radical pair, which can recombine to give substituted phenols, or escape from the solvent cage (Scheme 1.1). In the case of unsymmetrical diaryl ethers, the regioselectivity of the rearrangement is governed by the stability of phenoxy radicals formed by homolysis.



Scheme 1.1

1.1.2 Electrocyclic Ring Closure

In 1966, Stegemeger[10] made the claim that dibenzofuran is produced on irradiation of diphenyl ether (**1**) in ethanol and cyclohexane solutions. However, this result could not be confirmed by subsequent studies.[2,3] Henderson and Zweig[11] reported that irradiation of phenyl-1-naphthyl ether (**9**) in benzene solution for 24 hours failed to undergo photoreaction, even in the presence of added iodine and oxygen, which are believed to enhance photocyclization yields, by acting as oxidizing agents for the initially generated electrocyclization product. In contrast, *o*-chlorophenyl-1-naphthyl ether (**10**) gave benzo[b]naphtho[2, 1-d]furan (**11**) in 45% isolated yield on photolysis in the presence of iodine (eq 1.9).



(1.9)

Formation of dibenzofurans by photocyclization of chlorinated diaryl ethers has now been widely reported.[12-14] Dibenzofurans are formed only from *ortho*-chlorinated diphenyl ethers, not from the *meta* or *para* isomers (Table 1.1). Dibenzofurans can be formed not only in non-polar solvents such as hexane or cyclohexane, but also in the hydroxylic solvents such as methanol. The largest yields were observed in acetone[11], which may indicate the involvement of a triplet state in the photocyclization, as acetone can act as a triplet sensitizer for the photoreaction. No rearrangement products were reported in these cases.

Table 1.1 Photolytic Products of Chlorinated Diphenyl Ethers

Substrate (Cl-DPE)[a]	Product (Cl-DPE)	Product (Cl-DBF)[b]
2,4'-Cl_2-DPE[c]	n/a	2-Cl-DBF
2',3,4-Cl_3-DPE[c]	n/a	1,2-Cl_2-DBF 1,3-Cl_2-DBF
2,4,5-Cl_3-DPE[c]	n/a	2,3-Cl_2-DBF
2,2',4,4',5-Cl_5-DPE[c]	n/a	1,2,4,8-Cl_4-DBF 2,3,6,8-Cl_4-DBF Cl_3-DBF
3,3',4,4'-Cl_4-DPE[c]	Cl_3-DPE, Cl_2-DPE	n/a
4-Cl-DPE[d]	diphenyl ether (DPE)	n/a
4,4'-Cl_2-DPE[d]	4-Cl-DPE and DPE	n/a

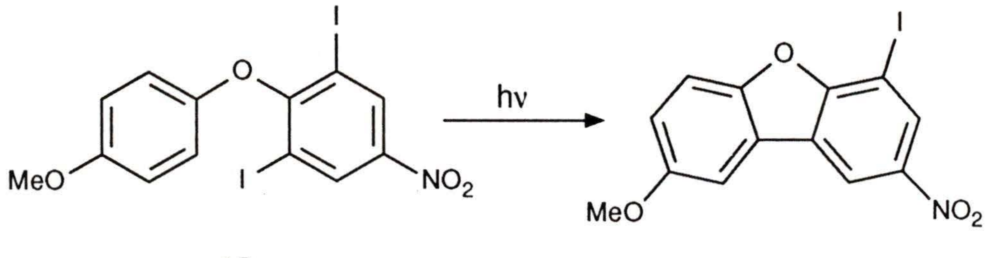
[a] Cl-DPE: chlorinated diphenyl ethers

[b] Cl-DBF: chlorinated dibenzofuran

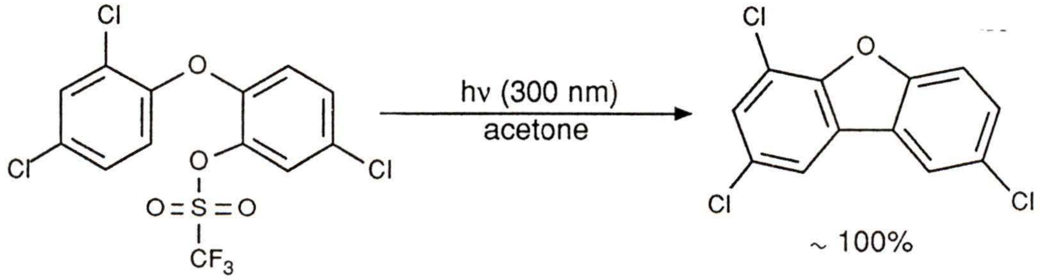
[c] photolyzed in acetone solution[13]

[d] photolyzed in methanol solution[14]

Photocyclization of iodinated diphenyl ethers has also been reported.[14,15] Irradiation of 3,5-diiodo-4-(4'-methoxyphenoxy)nitrobenzene (**12**) in acetone for 48 hours gave 4-iodo-8-methoxy-2-nitrodibenzofuran (**13**) as the major product (eq. 1.10). The functionalized dibenzofuran framework produced in this reaction has considerable potential for the development of novel, rigid thyroid hormone analogues.[15] The photocyclization of *ortho*-chlorinated or iodinated diphenyl ethers suggests that a good leaving group *ortho* to the ether bond is necessary to effect photocyclization. This argument is further supported by the complete conversion of **14** to **15** (eq. 1.11).[16]



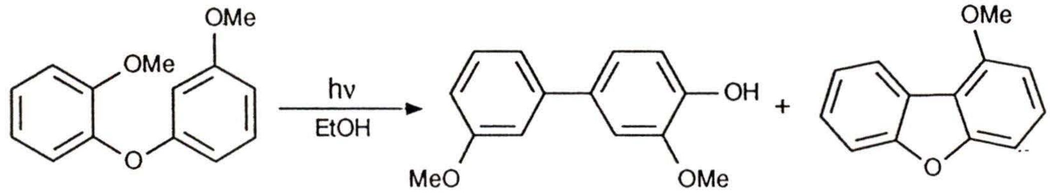
12 **13** (1.10)



14 **15** (1.11)

Changing the *ortho* substituent from a good leaving group such as Cl, I, or trifluoromethylsulfonyl to a poor leaving group such as methoxy resulted in both cyclization and rearrangement products.[4] Irradiation of 2-

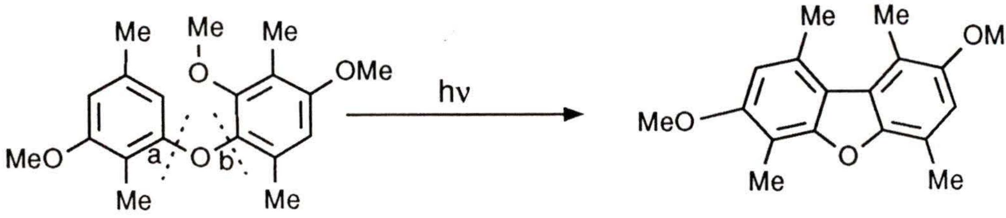
methoxyphenyl-3'-methoxyphenyl ether (**16**) gave predominantly the *para* rearrangement product, 3,3'-dimethoxybiphenyl-4-ol (**17**) with a smaller amount of 1-methoxydibenzofuran (**18**) (eq. 1.12). This indicates that cleavage and rearrangement are more favourable in the absence of a good leaving group *ortho* to the aryl-O bond.



(1.12)

16 17 (major) 18 (minor)

Irradiation of an ethanolic solution of **19** gave **20** exclusively (eq. 1.13).[4] Ether **19** can undergo cleavage *via* two pathways, *viz.* cleavage path **a** or **b**. As the phenoxy radical is more stabilized on the dimethoxy-substituted benzene ring, path **a** is more favourable than path **b**. However, cleavage *via* path **a** cannot proceed *via ortho* or *para* rearrangement. Therefore, photocyclization is the predominant reaction. Similarly, irradiation of **21** and **22** gave the corresponding dibenzofurans as major products (eqs. 1.14 and 1.15).[4]



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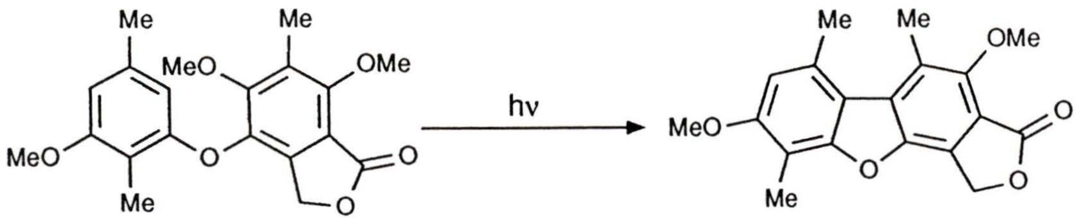
19 20



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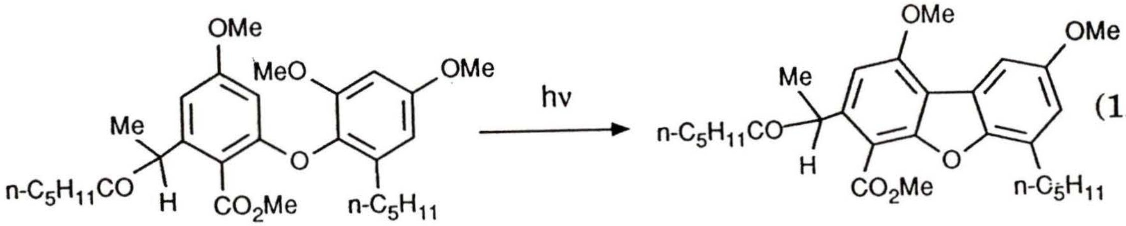

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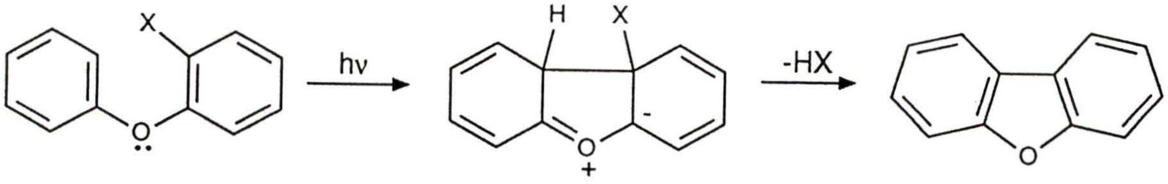
(1.15)

All of the above studies indicate that photocyclization of *ortho*-substituted diaryl ethers is an important reaction pathway, independent of photocleavage of the aryl-O bond. This photocyclization pathway may involve a 6π electrocyclic ring closure leading to a zwitterionic intermediate **23** (Scheme 1.2). Elimination of the *ortho*-substituents gives rise to the dibenzofuran as the final observed product.



23

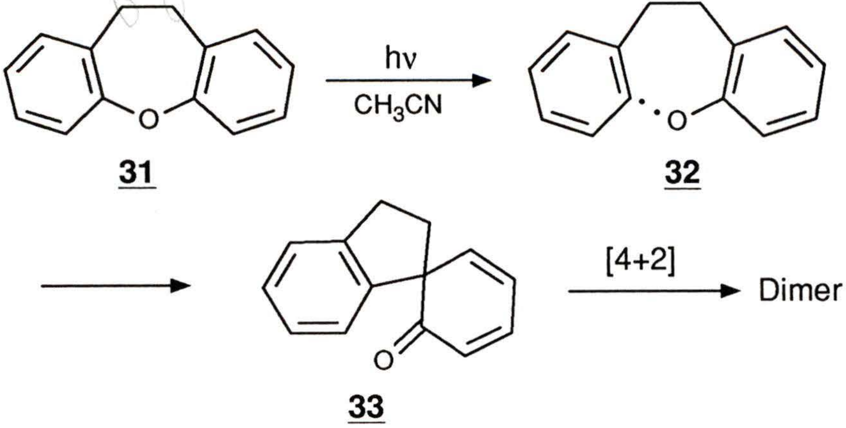
Scheme 1.2

Of the two pathways resulting from the photolysis of diaryl ethers, electrocyclization is dominant if there is a good leaving group *ortho* to the aryl-

O bond. Cleavage and rearrangement will be dominant in the absence of such a labile groups *ortho* to the aryl-O bond.

1.1.3 Intramolecular Rearrangement

If the phenyl groups of diphenyl ether (**1**) are joined by a carbon chain, then intramolecular rearrangements are observed. Xanthene (**24**) (scheme 1.3) is an example which has only one carbon in the joining chain. Photolysis of **24** involves initial aryl-O bond homolysis from the singlet excited state to generate biradical **25**.[17] Biradical **25** may revert back to substrate or rebond at the *ortho* position of the phenoxy moiety to give the spiro ketone **26**. Intermediate **26** may ring open to give the biphenyl-*o*-quinone methide **27**, which can cyclize to pyran **28**, or nucleophilically trapped by water to give alcohol **29**, or by methanol to give ether **30** (Scheme 1.3). Spiro ketone **26** has so far eluded detection, probably due to its high reactivity. However, a similar spiro ketone **33**, which comes from the photolysis of 10,11-dihydrodibenzo[b,f]oxepin (**31**), has been "trapped" as its [4+2] dimer (eq. 1.16).[18]



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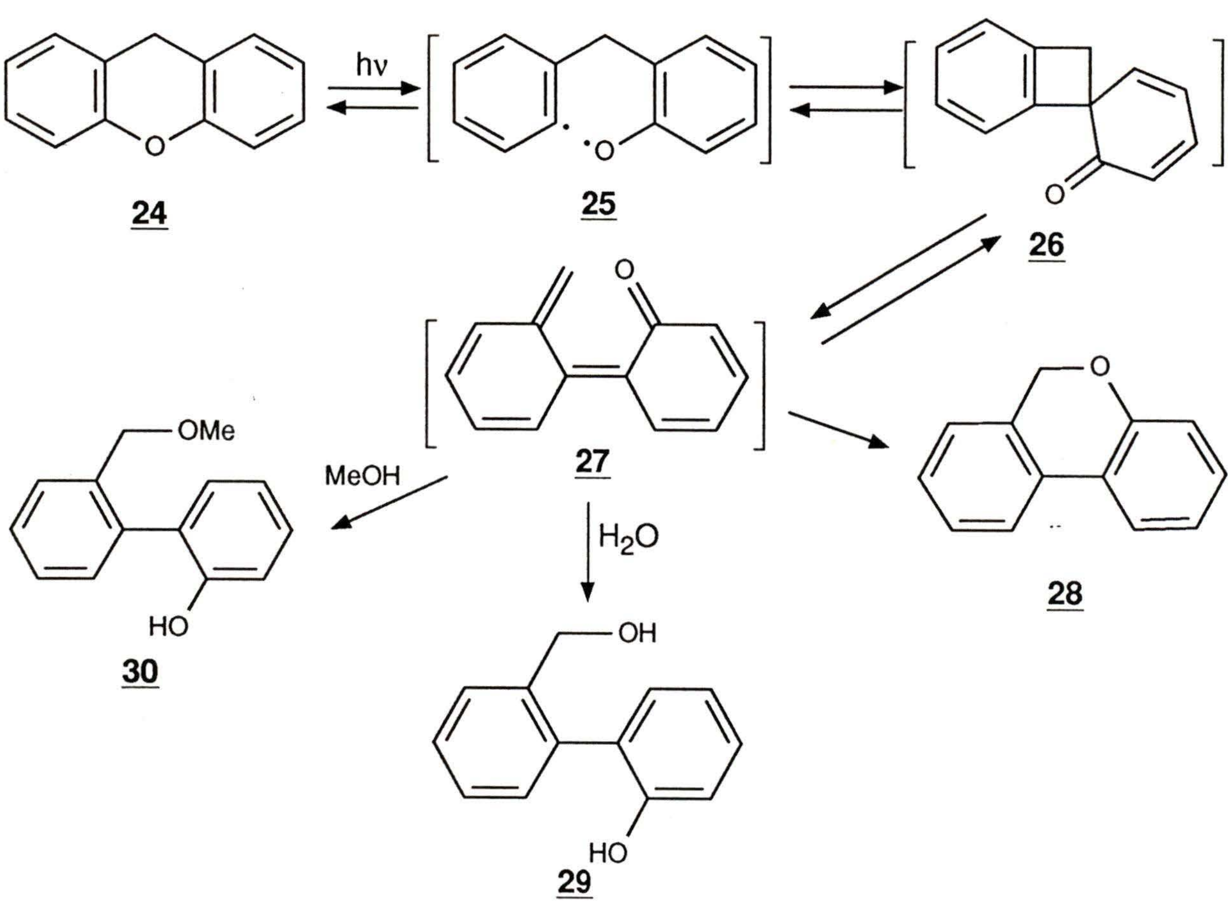


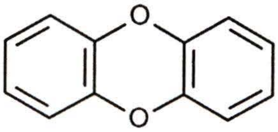
Scheme 1.3

Compound **31** is a ring closed diaryl ether which has two carbons in the joining chain. Upon photolysis[18], **31** was found to react *via* initial aryl-O bond homolysis (as the primary photochemical step), to give radical pair **32**, which recombines to give the intermediate spiro ketone **33** *via* attack on the adjacent phenol ring. Ketone **33** was not isolable. Instead, a [4+2] dimer was found to be the final product (eq. 1.16).[18] The observation of the isolated [4+2] dimer of **33** supports the pathway of intramolecular rearrangement *via* the spiro ketones **26** and **33**.

In summary, *ortho*-substituents are crucial to the outcome of photochemical reactions of diaryl ethers. Electrocyclic ring closure is dominant with a labile group ortho to the aryl-O bond. Otherwise cleavage and rearrangement will be favourable. Intramolecular rearrangements take place if two *ortho* position are connected by a carbon chain.

1.2 Photochemistry of Dibenzo-*p*-dioxins

If the phenyl groups of diphenyl ether (**1**) are joined by an oxygen instead of a carbon atom, then a diphenyl diether is obtained, which is commonly known as dibenzo-*p*-dioxin (DBD; **34**). Dibenzo-*p*-dioxin is the parent compound of the notorious polychlorinated dibenzo-*p*-dioxins (PCDDs). Owing to their much publicized high toxicity, research into the environmental fate of PCDDs, especially 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD; **35**), including its photodecomposition, has attracted considerable interest. The photochemistry of **34** is the topic of investigation of this Thesis (*vide infra*). A brief history of the environmental effects of dioxins is warranted.



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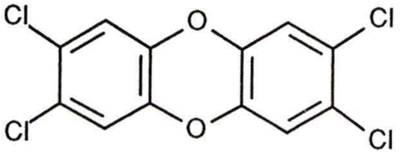

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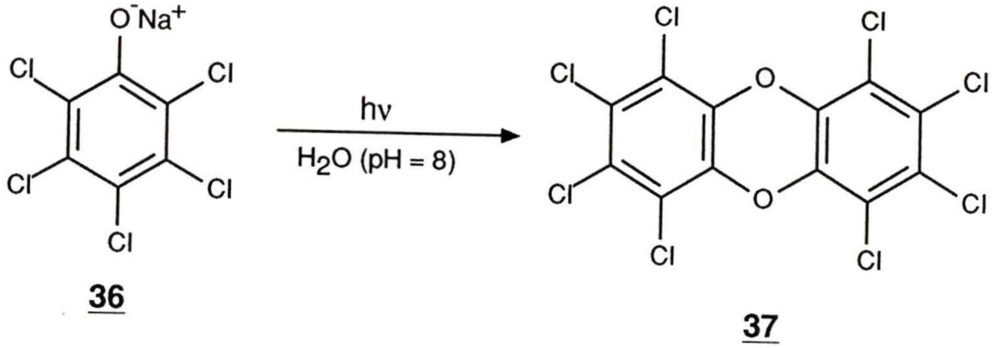
1.2.1 The Formation of Polychlorinated Dibenzo-p-dioxins

In the annals of environmental contamination, TCDD (**35**) has achieved the most notoriety due to its extreme toxicity. As little as 0.6 µg per kg of body weight given orally will kill half of the male guinea pigs tested within about a week. Humans and animals exposed to **35** have shown acute, subchronic and chronic effects. TCDD (**35**) adversely affects the skin, the liver, the nervous system, and the immune system of humans and animals. In addition, TCDD (**35**) is classified as a probable carcinogen in humans on the basis of animal carcinogenicity studies.[19] TCDD (**35**) was first implicated as the culprit responsible for illnesses among chemical industry workers in 1949[20], when an industrial accident at a herbicide plant in Nitro, West Virginia, exposed 250 workers to TCDD (**35**), resulting in severe skin rash called chloracne.[21] TCDD (**35**) was thought to be of only industrial health concern until 1976, when an explosion at a chemical plant in Seveso, Italy, resulted in the release of an estimated 13 kg of **35** into the surrounding environment. Many animals died within a few days, and some humans who were exposed developed chloracne. As a result, hundreds of people were evacuated from the region and years of clean-up ensued.[22] Shortly afterwards in the U.S.A., many Vietnam veterans began wondering if their range of illnesses could have been caused by exposure to the herbicide "agent orange" (contaminated with TCDD (**35**)) which was sprayed between 1962 to 1969 in Vietnam. The most impressive event was the evacuation and purchase by the American government of the entire town of Time Beach, Missouri in 1983, due to high concentrations of TCDD (**35**) in the environment resulting from previous waste disposal activities.[23]

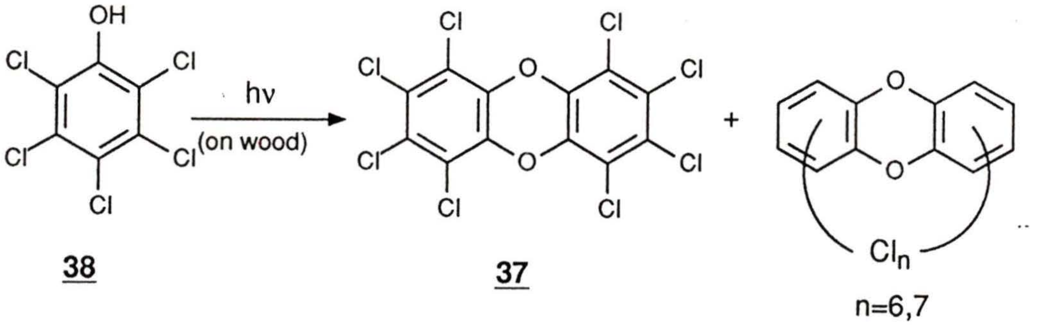
In 1977, Olie *et al.*[24] first reported the presence of PCDDs in the fly ash and flue gas from municipal waste incinerators. Subsequently, more combustion sources of PCDDs were identified. The paper industry was surprised in 1985 when TCDD (**35**) was discovered in the effluent and sludge from pulp and paper mill.[25,26] It was found that chlorine bleaching of the pulp caused the formation TCDD (**35**). Research carried out by Ryan *et al.*[27] indicated that the concentration of PCDDs in human adipose tissue was greater for British Columbia than for other regions in Canada. This may be due to the by-products of the pulp and paper industry, which has been prominent in British Columbia for the last century. As a result, the British Columbian government decided to reduce the chlorine content of waste from its pulp and paper mills to 1.5 kg per ton of pulp manufactured by 1995 and 0 kg per ton of pulp by 2002.[28]

PCDDs can also be formed photochemically. Photolysis of sodium pentachlorophenolate (**36**) with different light sources has been reported by Stehl and his coworkers.[29] A small amount of octachlorodibenzo-*p*-dioxin (**37**) (approximately 0.03%) was formed during the photolysis at pH 8 (eq. 1.17)



(1.17)

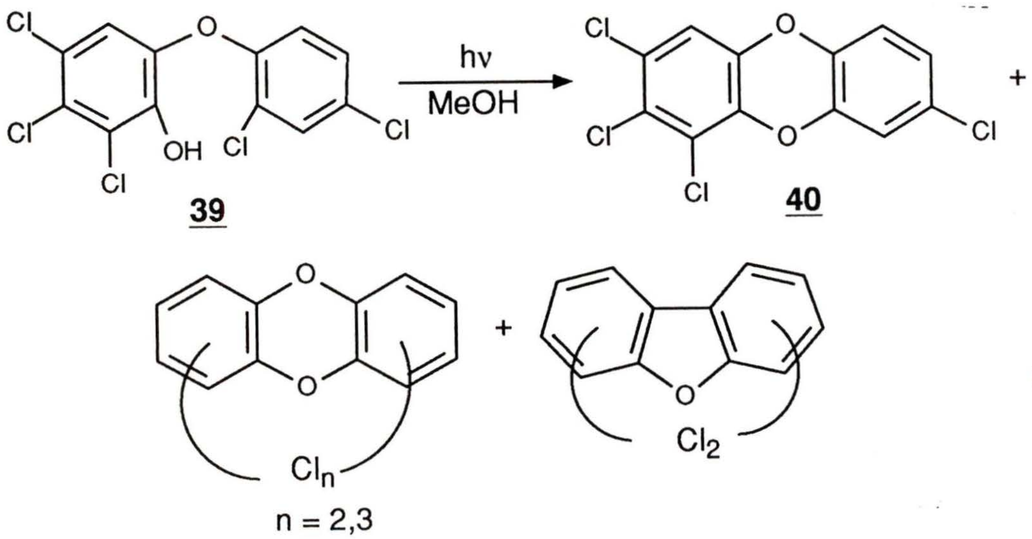
The photolytic formation of **37**, heptachlorodibenzo-*p*-dioxins (Cl_7-DBDs), and hexachlorodibenzo-*p*-dioxins (Cl_6-DBDs) was also reported from pentachlorophenol (**38**) impregnated in a solid (wood) matrix using either artificial sunlamps or natural sunlight (eq. 1.18).[30] All of the Cl_6-DBDs and Cl_7-DBDs were believed to be formed through photochemical degradation of **38**.



38 37

(1.18)

Photochemical formation of PCDDs in organic solvents has also been reported. Photolysis of 4,5,6-trichloro-2-(2',4'-dichlorophenoxy)phenol (**39**) in methanol produced 1,2,3,8-tetrachlorodibenzo-*p*-dioxin (**40**), two isomers of trichlorodibenzo-*p*-dioxin, dichlorodibenzo-*p*-dioxins, and dibenzofuran as major products (eq. 1.19).[31]



39 40

(1.19)

In summary, PCDDs can come from a variety of sources including incinerators, pulp and paper mills, herbicide/pesticide production, and other industrial processes where chlorinated phenols are used. PCDDs can be formed photochemically as well as thermally. Since PCDDs have been identified in soil, water, plants, fish, human adipose tissue, breast milk, and other biological medium[32,33], the destruction and detoxication of such compounds has continued to be a subject of much interest.

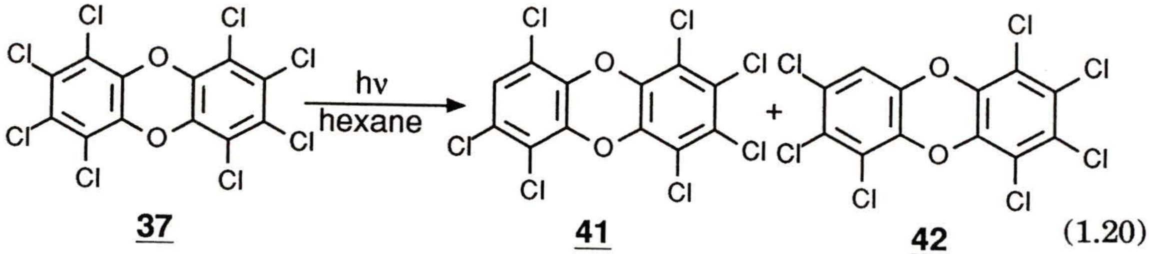
1.2.2 Photochemistry of Polychlorinated Dibenzo-*p*-dioxins

Incineration is a technically approved method for the destruction of PCDDs.[34] However, mere "burning" is not a satisfactory method for disposing of PCDDs, which have a remarkablely high thermodynamic stability. For example, a temperature of at least 1000°C is required to decompose 1,3,7-trichlorodibenzo-*p*-dioxin, to achieve destruction efficiencies of over 99%.[35] If temperatures are not high enough, there is a good possibility of not only failing to destroy all the PCDDs already present, but also actually forming new PCDDs from precursor compounds contained in the wastes. A number of remediation technologies have been proposed, and in some cases have reached the development stage.[36-39] However, few of them have been applied to full-scale usage.

Aside from incineration, the only TCDD (**35**) destruction method to be employed on a large scale (by TCDD standards) is photolysis.[40] In such an operation, 7 kg of TCDD (**35**) was extracted with hexane from 4600 gal of trichlorophenol waste and then degraded to relatively nontoxic compounds by photolysis. Photolytic destruction was carried out batchwise, over a period of several weeks, with a destruction efficiency of 99.94%.

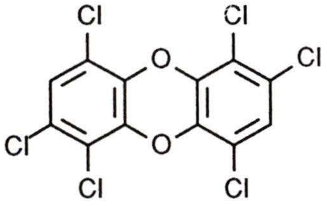
Photolysis of PCDDs has been studied since 1970, although attempts to use ultraviolet light sources such as sunlight were fruitless at first. Pure crystalline TCDD (**35**) was found to be stable to sunlight for at least 14 days, as was TCDD (**35**) suspended in distilled water.[41] However, when Crosby *et al.*[41] irradiated TCDD (**35**) in methanol or ethanol solution, substantial decomposition was observed. They concluded that the minimum necessary conditions for TCDD (**35**) photolysis were ultraviolet light and the presence of an organic hydrogen donor.

Photochemical reaction of PCDDs in organic solvents has been studied extensively since the work of Crosby *et al.*[41] Dobbs and Grant[42] reported the photolysis of octa-, hepta-, and some hexa-chlorodibenzo-p-dioxins in hexane with a concentration of approximately 1 µg/ml. The initial products were mono dechlorinated compounds, *e.g.*, **41** and **42** from **37** (eq. 1.20).

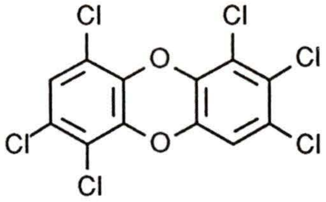


(1.20)

Buser[43] reported the formation of tetrachlorodibenzo-p-dioxins (Cl_4-DBDs) and Cl_5-DBDs from the photolysis of two isomers 1,2,3,6,7,8-Cl_6-DBD (**43**) and 1,2,3,7,8,9-Cl_6-DBD (**44**) (Scheme 1.4). The principal isomers 1,3,6,8-Cl_4-DBD (**51**) (from **43**) and 1,3,7,9-Cl_4-DBD (**53**) (from **44**) were formed *via* dechlorination at the lateral positions (*i.e.*, with chlorine atoms at the 2-, 3-, 7-, and 8- positions). A trace amount of TCDD (**35**) was also observed from the photolysis of both **43** and **44**.



55

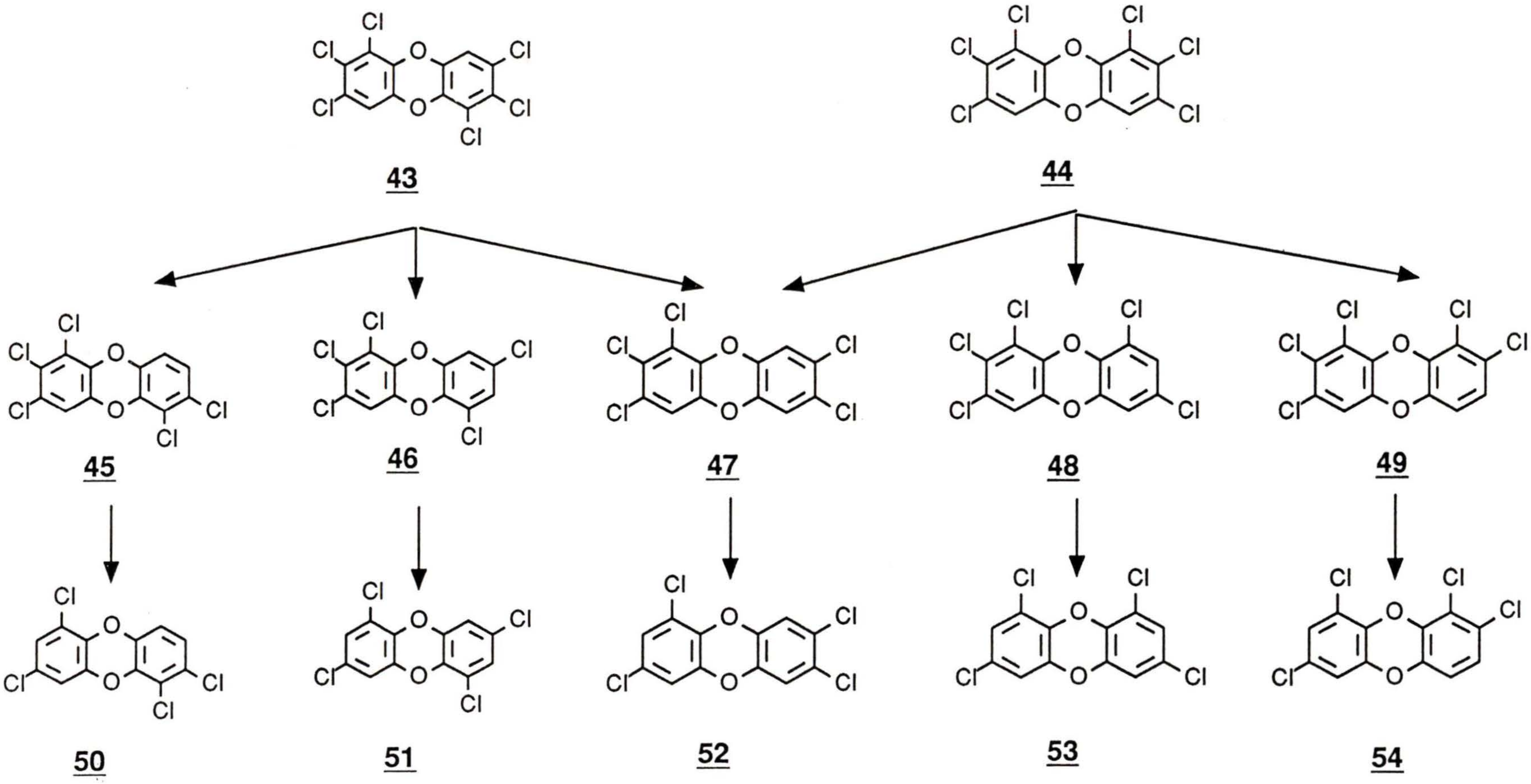


56

The half-lives ($t_{1/2}$'s) of **37**, Cl_7-DBD (**41, 42**) and Cl_6-DBD (**44, 55, 56**) were reported as Table 1.2,[42] which demonstrate that **42** is more susceptible to photodegradation than **41**, and **44** is more susceptible than **55, 56**. The results indicate that PCDDs with lateral chlorine atoms decompose more rapidly than those with peri chlorine atoms (*i.e.*, with chlorine atoms at the 1-, 4-, 6-, and 9- positions).

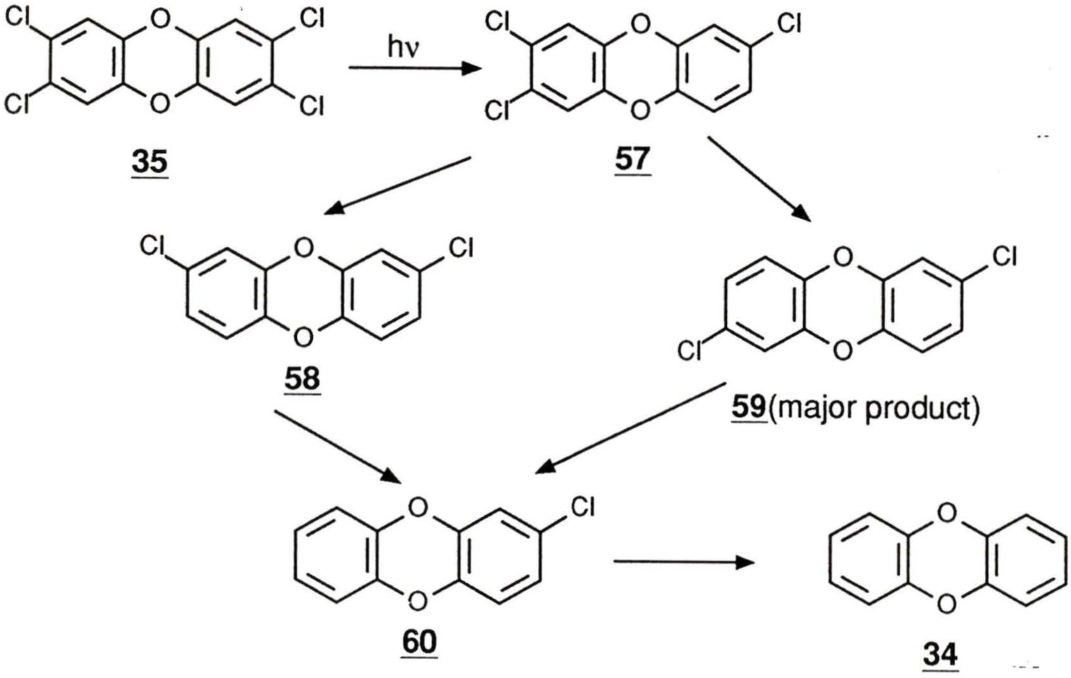
Table 1.2 Degradation Half-Lives of Several PCDDs in Hexane

PCDDs	**37**	**41**	**42**	**44**	**55**	**56**
$t_{1/2}$(h)	16	28	11	5.4	47	17



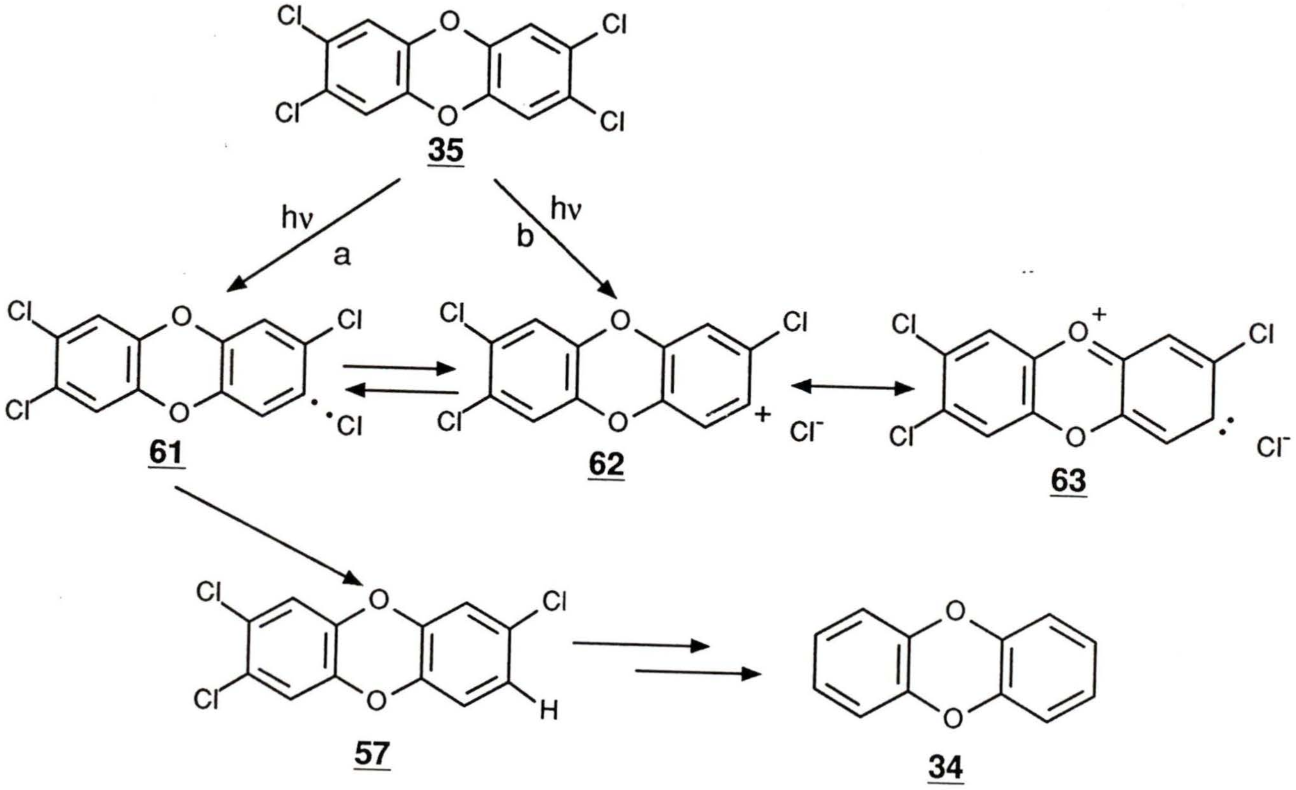
Scheme 1.4

The photodegradation of TCDD (**35**) was suggested to involve a step-by-step dechlorination (eq 1.21).[40,44] As it has four lateral chlorine atoms, TCDD (**35**) is the most susceptible to photodegradation of all the 22 Cl_4-DBD isomers.[45]



(1.21)

Dechlorination of TCDD (**35**) may proceed through initial homolysis of a C-Cl bond, yielding the substituted aryl radical **61** as shown in path *a* (Scheme 1.5). Abstraction of hydrogen from the solvent by **61** gives rise to the corresponding photoreduced product **57.** An alternative is heterolysis of TCDD (**35**) to yield the aryl cation **62**, as shown in pathway *b*. A carbene resonance structure **63** may be written[46] for the cation **62**. Electron transfer may then occur from chloride ion to the cation-carbene **62/63**, to yield **61**, which is again reduced to **57**. PCDD **57** is then further degraded to **34** via analogous mechanistic steps.



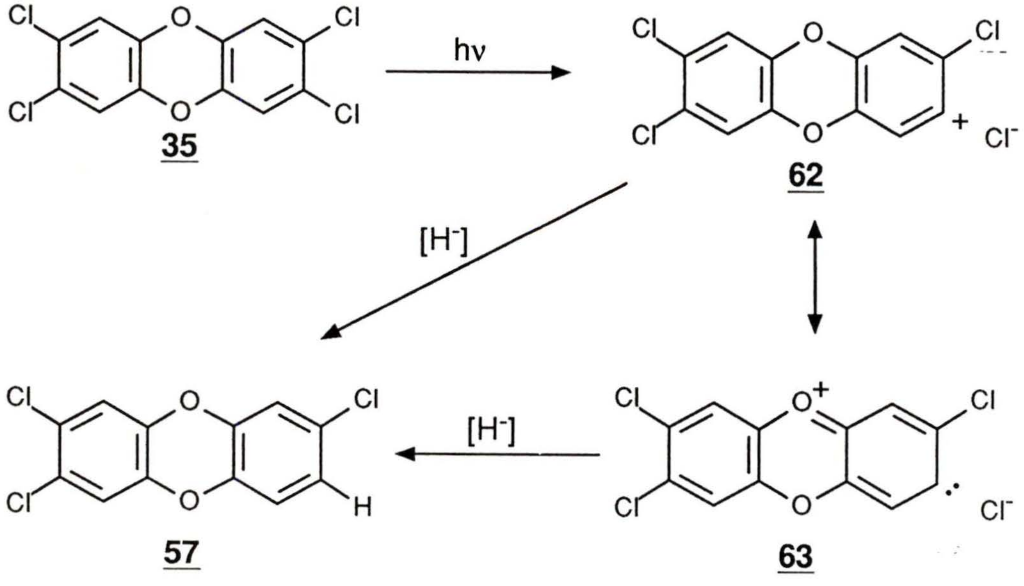
Scheme 1.5

The formation of a cation-carbene **62/63** intermediate is supported by the hydride-enhanced photodegradation of PCDDs, where the photochemical reactions of PCDDs proceed more rapidly in the presence of sodium borohydride (Table 1.3).[47] The enhancement may be attributed to the reduction of **62/63** by hydride ion (eq. 1.22), since it is unlikely that hydride will react with the aryl radical **61**.

Table 1.3 Sodium Borohydride Enhanced Degradation of PCDDs

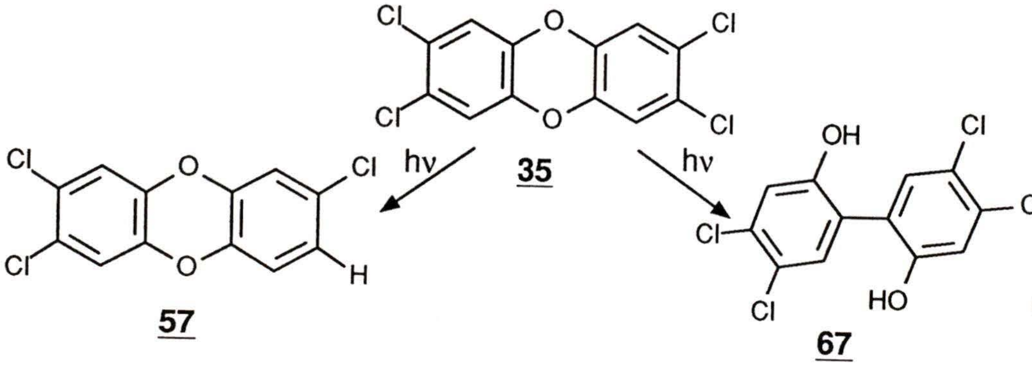
Compound	Enhancement Ratio[a]
1-chlorodibenzo-p-dioxin (**64**)	5.9
2-chlorodibenzo-p-dioxin (**60**)	2.2
2,3-dichlorodibenzo-p-dioxin (**65**)	1.6
2,7-dichlorodibenzo-p-dioxin (**59**)	2.1
1,2,3,4-tetrachlorodibenzo-p-dioxin (**66**)	4.1
octachlorodibenzo-p-dioxin (**37**)	4.2

[a] Relative rate of degradation in the presence and absence of $NaBH_4$ (9:1 CH_3CN-H_2O)



(1.22)

Besides dechlorination, carbon-oxygen bond cleavage has also been noted as a possible pathway. Dulin *et al.*[48] reported that **57** could not be detected as a photoproduct of TCDD (**35**) in 50:50 water-acetonitrile. They suggested that C-O cleavage may be an important photolysis pathway. When TCDD (**35**) was photolyzed in isooctane, both dechlorination, giving rise to **57**, and C-O cleavage, giving rise to 4,4',5,5'-tetrachloro-2,2'-biphenylphenol (**67**), were observed (eq. 1.23),[49] each of which accounted for approximately 10% loss of the starting material TCDD (**35**).



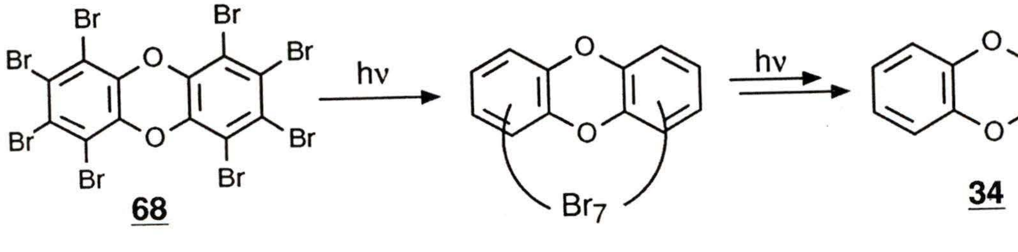
(1.23)

The quantum yields of direct phototransformation of several PCDDs in aqueous acetonitrile has been reported.[48,50,51] The quantum yields were measured by monitoring the disappearance of starting PCDDs (Table 1.4). According to these results, Φ(1,3,6,8-Cl_4-DBD) is greater than Φ(1,2,3,7-Cl_4-DBD), which contradicts the well known statement that substrates with lateral chlorine atoms are photodecomposed more rapidly than those with peri chlorine atoms (*vide supra*). This contradiction indicates that more work is required to understand the process of photolytic dechlorination of PCDDs.

Table 1.4 Quantum Yields for Disappearance of PCDDs in H_2O-CH_3CN

Substrate	Init. Concn. (10^{-6}M)	Quantum Yield (Φ)
1,2,3,7-Cl_4-DBD[51]	6.40	$(5.42 \pm 0.42) \times 10^{-4}$
1,3,6,8-Cl_4-DBD (**51**)[51]	10.55	$(2.17 \pm 0.14) \times 10^{-3}$
2,3,7,8-Cl_4-DBD (**35**)[48]	0.361	2.2×10^{-3}
1,2,3,4,7-Cl_5-DBD[50]	2.81	$(9.78 \pm 2.38) \times 10^{-5}$
1,2,3,4,7,8-Cl_6-DBD[50]	3.33	$(1.10 \pm 0.02) \times 10^{-4}$
1,2,3,4,6,7,8-Cl_7-DBD (**42**)[51]	2.78	$(1.53 \pm 0.17) \times 10^{-5}$
Cl_8-DBD (**39**)[51]	0.31	$(2.26 \pm 0.33) \times 10^{-5}$

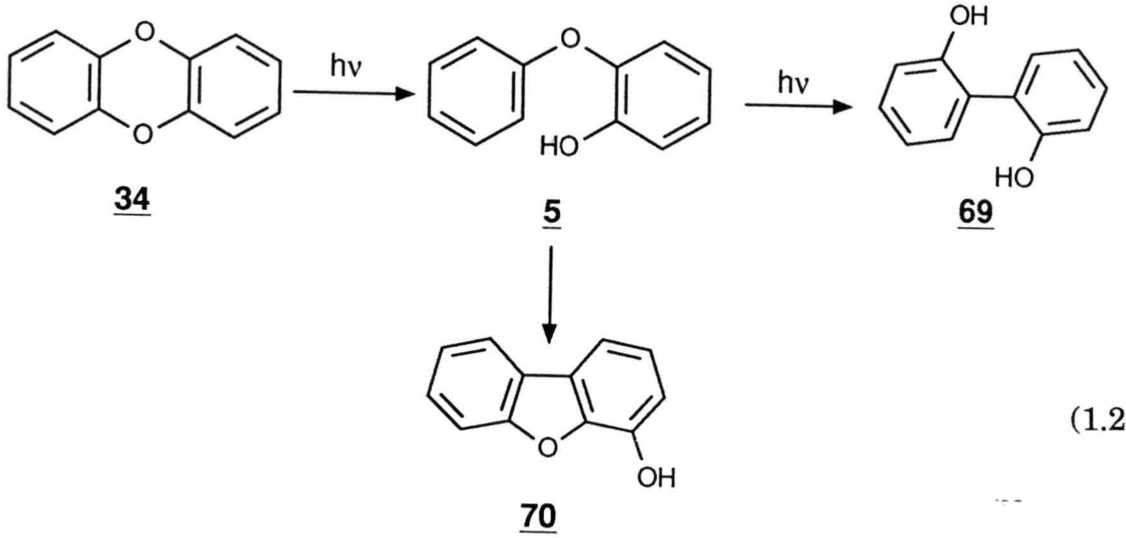
Photodegradation of polybrominated dibenzo-*p*-dioxins (PBDDs) has been reported recently.[52,53] The reactions were carried out in hydroxylic solvents and non-hydroxylic solvents. Photodecomposition of PBDDs in n-hexane is approximately six times faster than in methanol, with debromination as the major pathway (eq. 1.24). Compared to PCDDs, the bromine compounds react an order of magnitude faster.



(1.24)

1.2.3 Photochemistry of Dibenzo-*p*-Dioxin

Although the photochemistry of PCDDs has been extensively studied, the photobehaviour of dibenzo-*p*-dioxin (**34**), the parent molecule of PCDDs, is seldom studied.[54,55] Plimmer *et al.*[54] first reported that irradiation of DBD (**34**) in methanol gave 2-phenoxyphenol (**5**) *via* aryl-oxygen bond homolytic cleavage, which underwent further aryl-O bond cleavage yielding 2,2'-biphenol (**69**) as the major product along with trace 4-hydroxydibenzofuran (**70**) in the photoproduct mixture (eq. 1.25).

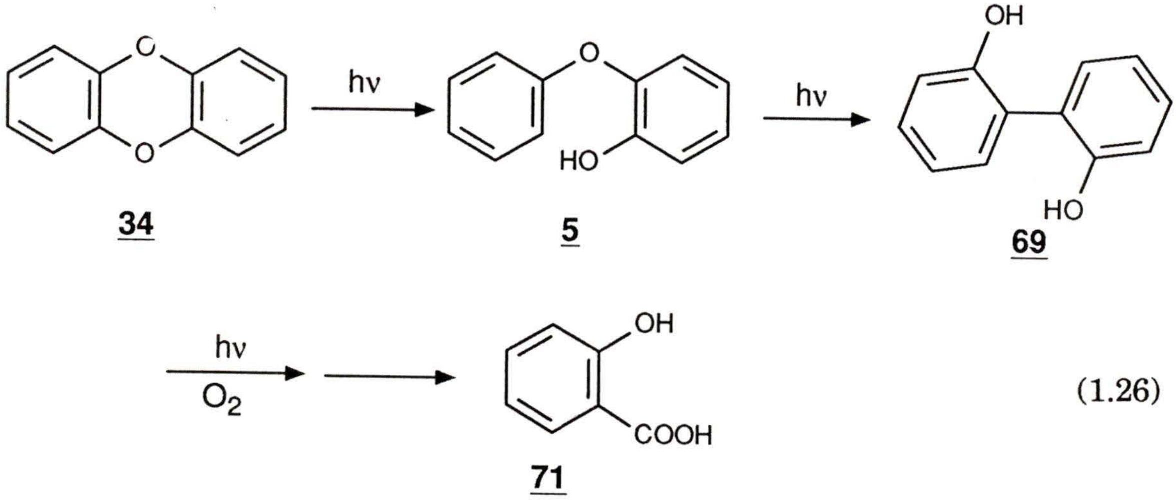


(1.25)

Massé and Pelletier[55] have studied the photochemical behaviour of DBD (**34**) in acetonitrile, hexane and methanol. The proposed mechanism was not significantly different from the one already proposed by Plimmer *et al.*[54] However, further photolysis of product **69**, in the presence of oxygen, resulted in *o*-hydroxybenzoic acid as the final major product (eq. 1.26).

The generally accepted[40,44,54,55] mechanism, in which **69** is formed *via* the secondary photoreaction of **5**, contradicts the known photochemistry of **5** (eq.

1.7), where **69** was not observed as a product! We set out to re-investigate the mechanism of the photodecomposition of DBD (**34**) and report in this Thesis several novel findings, including the observation of a reaction intermediate and the enhancement of decomposition due to added $NaBH_4$.



(1.26)

1.3 Proposed Research

The photochemistry of DBD (**34**) is of interest not only because it is a special diphenyl ether (a diphenyl diether), but also since it is involved in the photodegradation of PCDDs, especially TCDD (**35**), which is an important method for detoxication of PCDDs in the environment. Photodegradation of PCDDs involves dechlorination and aryl-O bond cleavage. Therefore, understanding the mechanism of the photochemical reaction of DBD (**34**) is essential for a complete understanding of photodegradation of PCDDs.

As the generally accepted mechanism is debatable (*vide supra*), a series of experiments will be carried out to unravel the mechanism involved in the photodegradation of dibenzo-*p*-dioxin (**34**). Therefore, a mechanistic study of the photoreactions of DBD (**34**) and one of its derivative 2,3,7,8-tetramethyldibenzo-*p*-dioxin (**76**) will be carried out in hydroxylic solvents such as aqueous CH_3CN, CH_3OH and 2-propanol, as well as non-hydroxylic solvents such as CH_3CN, THF and 1,4-dioxane.

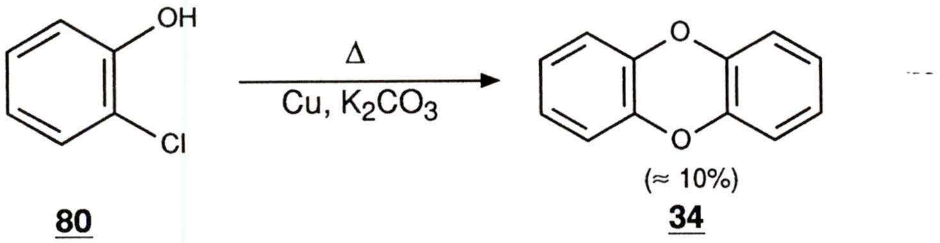
Chapter Two: Results and Discussion

2.1 Synthesis

Several compounds were prepared and utilized as starting materials for the photoreactions. These compounds were synthesized based on the Cu-catalyzed condensation[56] of phenol and chlorobenzene.

2.1.1 Dibenzo-*p*-dioxin (34)

Dibenzo-*p*-dioxin (DBD; **34**) was synthesized according to the method outlined in eq. 2.1. Substrate *o*-chlorophenol (**80**) was purchased from Aldrich and used as received after a purity check by gas chromatography (GC), which showed it was of > 98% purity. Condensation of neat **80** in the presence of Cu/K_2CO_3[56] afforded crude **34**, which was purified by extraction and recrystallization, giving rise to white needles (> 99% purity by GC).

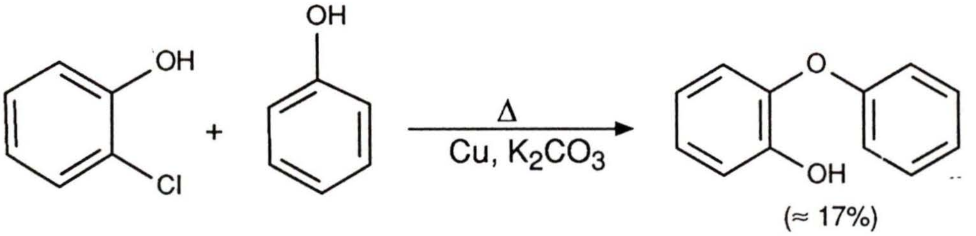


(2.1)

The purified product was identified by its melting point (m.p.), ^{1}H NMR (360 MHz) and mass spectrum (MS). The measured m.p. of the product agreed with the literature value[57] while its ^{1}H NMR spectrum was consistent with the structure of **34**. In addition, the expected molecular weight of **34** (m/e = 184) was observed in the MS (CI).

2.1.2 2-Phenoxyphenol (5)

2-Phenoxyphenol (**5**) was prepared by the condensation of **80** and phenol (eq. 2.2).[56] Purification of the crude product was accomplished by extraction, column chromatography and recrystallization, yielding white needles (> 99% purity by GC).

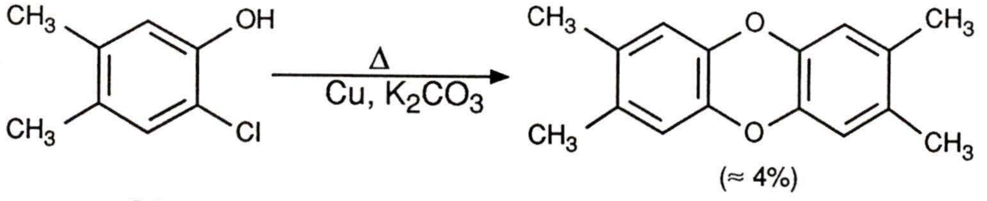


80 **5** (2.2)

The purified product was characterized by its ^{1}H NMR (360 MHz), m.p., and MS. The measured m.p. of the product agreed with the literature value[58] and its ^{1}H NMR spectrum was consistent with the structure of **5**. In addition, the expected molecular weight of **5** (m/e = 186) was observed in the MS (CI).

2.1.3 2,3,7,8-Tetramethyldibenzo-*p*-dioxin (76)

Compound **76** was synthesized using the method described above (eq. 2.1). Substrate 2-chloro-4,5-dimethylphenol (**81**) was purchased from Aldrich and used as received after a purity check by GC (> 98% purity). Condensation of **81**[56] afforded crude **76** (eq. 2.3), which was purified by extraction and recrystallization, affording white needles (> 99% purity by GC). The m.p. of purified **76** agreed with the literature value,[59] while its ^{1}H NMR (250 MHz) spectrum was consistent with the structure of **76**. Further confirmation of the product's identity was obtained by analysis of its MS (CI), which gave the expected molecular weight of **76** (m/e = 240).



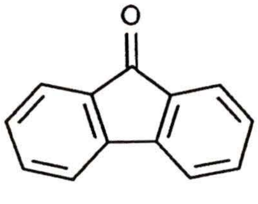
81 **76** (2.3)

2.2 Product Studies

The photoproducts of DBD (**34**) and TMDBD (**76**) in hydroxylic and non-hydroxylic solvents are determined in this section. Possible pathways for photoreaction are proposed based on the products observed.

2.2.1 Irradiation of DBD in Aqueous CH_3CN Solution

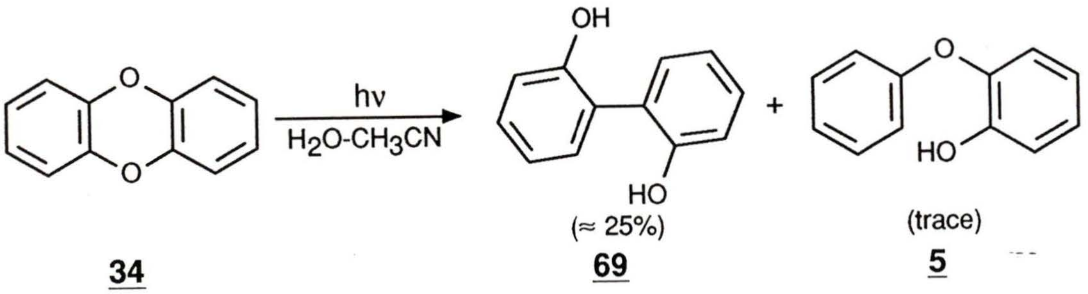
Irradiation of an argon purged 1:1 H_2O-CH_3CN solution of DBD (**34**) (1.3 x 10^{-3} **M**) in a Rayonet RPR 100 photochemical reactor (300 nm lamps) at ≈ 18°C for 20 min gave only one major product (eq. 2.4). This product was isolated by preparative TLC (silica gel, 18:1 CH_2Cl_2-ethyl acetate) and characterized as 2, 2'-biphenol (**69**), by comparing its GC/MS and ^1H NMR spectra with a sample of authentic compound, which is commercially available. The product yield of **69** (≈ 25%) was measured by GC using 9-fluorenone (**88**) as an internal standard (mass balance ≈ 60%; uncharacterizable material was



88

observed in the reaction vessel after photolysis). In addition to **69**, 2-phenoxyphenol (**5**) was also observed as a minor product (yield < 1% at all conversion of **34**). A control experiment performed in the absence of light did not result in any observable reaction and unreacted DBD (**34**) could be recovered completely.

A mechanism of photoreaction of DBD (**34**) has been proposed,[54,55] which stated that this reaction is initiated by homolysis of the aryl-oxygen bond, giving rise to biradical **72**. Biradical **72** then abstracts a hydrogen atom from the organic solvent, to yield in 2-phenoxyphenyl (**5**) (eq. 2.5), which then undergoes secondary photoreaction to afford **69** *via* a second aryl-oxygen bond homolysis, the mechanistic details of which has not been proposed (eq. 1.25).



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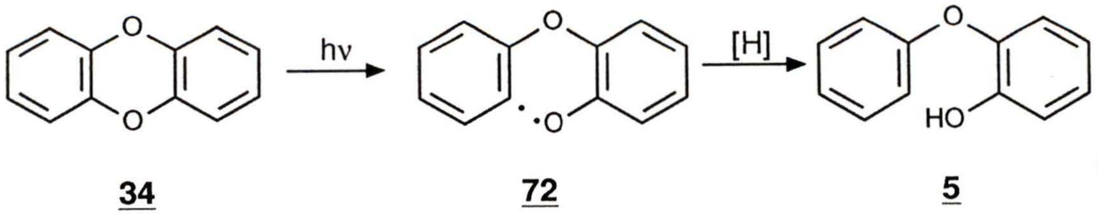
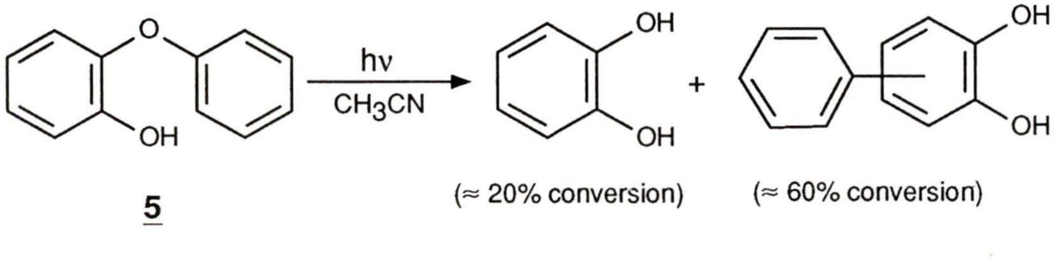


(2.5)

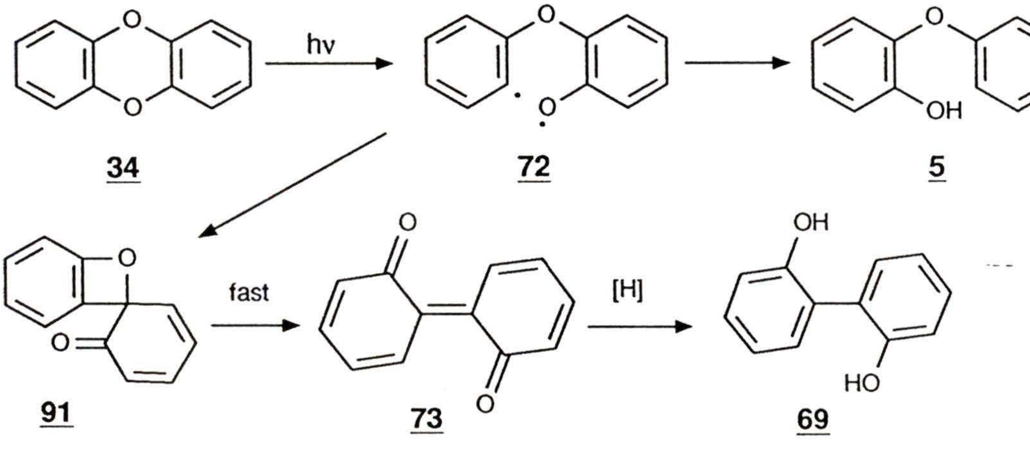
The present results support the assumption of the first aryl-oxygen bond homolysis step. However, it is unlikely that **69** arises from photolysis of **5** since no change in the yield of **5** *vs* photolysis time (conversion of **34**) was observed. If **5** were the primary photoproduct, and **69** were a secondary product of **5**, the yield of **5** would be expected to maximize after some initial photolysis time, with the yield of **69** growing steadily as more of **5** is converted. Additional support that **5** could not be a precursor to **69** comes from the work of Joschek *et al.*[9], who reported that photolysis of **5** in aqueous solution resulted in the formation of coupling and escape products expected from regioselective aryl-oxygen bond homolysis (eq. 1.7); and **69** was not observed. To further verify this important finding, **5** was photolyzed under identical conditions as that for DBD (**34**) (*vide infra*).

Irradiation of an argon purged 1:1 H_2O-CH_3CN solution of **5** ($\approx 1.3 \times 10^{-3}$ **M**) in a Rayonet RPR 100 photochemical reactor (300 nm lamps) at ≈ 18°C for 20 min gave several products (eq. 2.6). The major products were identified as catechol (≈ 20%) (by comparing the GC/MS with a sample of authentic compound), and two dihydroxybiphenyls (≈ 60%) (by GC/MS). However, **69** could not be detected in this product mixture. This result is consistent with those reported by Joschek *et al.*[9], and clearly shows that **69** is not formed *via* the secondary photolysis of **5** (eq. 1.25).[54,55]



(2.6)

The formation of **69** (a biphenyl) from DBD (**34**) involves isomerization of the initial ring system. In section 1.1.3, a related intramolecular photoisomerization was reported for xanthene (**24**) and **31**. Based on these results, an alternative mechanism is proposed to account for the formation of **69** from DBD (**34**). This working mechanism involves initial aryl-oxygen bond homolysis, to give a biradical **72**, consistent with the known photoreaction pathway of many diaryl ethers. Intramolecular *ipso* attack of **72** gives spiro ketone **91**, which further isomerizes to give 2,2'-biphenylquinone (**73**). Reduction of **73** by hydrogen donor (CH_3CN) gives **69** as the major product (eq. 2.7). Direct reduction of **72** gives **5**, which is a minor pathway since **5** was observed only in trace yields.



(2.7)

If **73** is indeed formed during the reaction, it may be reduced more efficiently to **69** by adding more powerful reducing agents. Therefore, the photoreaction should be enhanced in the presence of such an added reducing agent, assuming that **73** can give rise to polymeric material in competing side reactions, which is indicated by a low (≈ 60%) mass balance and formation of some uncharacterizable material in the reaction vessel. Intermediate **91** is also reducible, but, several reduction products would be expected from such a reaction. However, since only **69** (and **5**) were observed, it is possible to rule out **91** as being the crucial reducible intermediate in the mechanism. In addition, it is also reasonable to assume that **91** will be quickly converted to **73** (or reverts to **72**). The photoreaction of DBD (**34**) was carried out in the presence of $NaBH_4$. Irradiation of an argon purged 1:1 H_2O-CH_3CN solution of DBD (**34**) (2.7×10^{-3} **M**) in the presence of $NaBH_4$ (0 to 2.7×10^{-2} **M**) gave only one major product, *viz.*, **69**; The yield of **69** jumps dramatically, even in the presence of a very small amount of $NaBH_4$ (four times enhancement at $[NaBH_4]/[DBD] = 1$), while further increasing the concentration of $NaBH_4$ did not have any significant effect on the product yield (Figure 2.1). The reaction

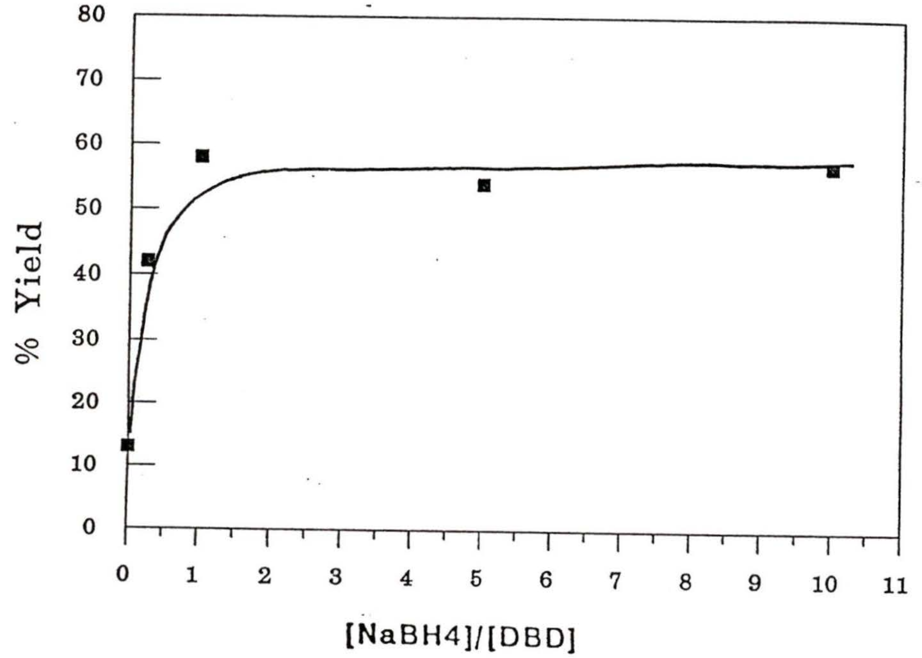
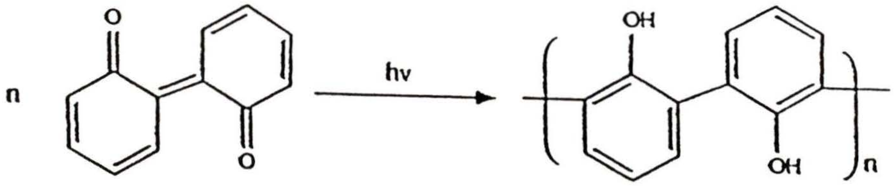


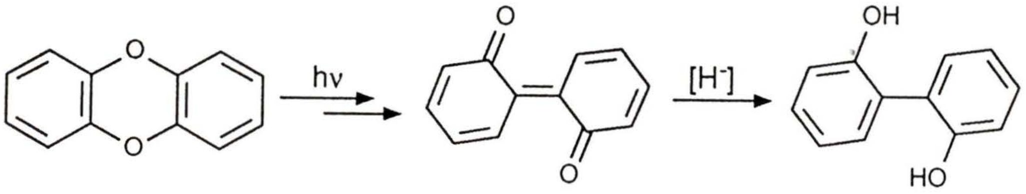
Figure 2.1 Yield of **69** on photolysis of **34** in the presence of added $NaBH_4$

mass balance was measured by GC using 9-fluorenone (**88**) as the internal standard. The mass balance in the presence of $NaBH_4$ (> 90%) is much better than that in its absence (≈ 60%), also indicating that $NaBH_4$ can help the conversion of the intermediate to product **69**. Thus, in the absence of $NaBH_4$, intermediate **73** may undergo some polymerization (eq. 2.8) and the formed polymer will not be detected by GC. Both enhancements of the product yield and reaction mass balance are consistent with the formation of quinone **73** as a critical intermediate in the reaction mechanism (eq. 2.9).



73

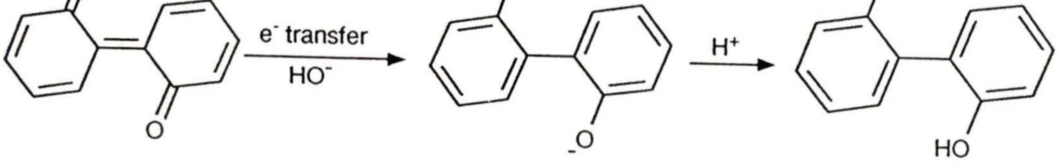
(2.8)



34 73 69

(2.9)

In addition to being a hydride source, $NaBH_4$ can also act as a base, to raise the concentration of hydroxide ion in aqueous solution, which may reduce quinone **73** to phenolate **74** *via* two sequential electron transfer steps (eq. 2.10).



73 74 69

(2.10)

To rule out the possibility that hydroxide may be the "reducing agent" on addition of $NaBH_4$, photolysis of DBD (**34**) was carried out in aqueous CH_3CN solutions of different acidities. Irradiation of an argon purged 1:1 H_2O-CH_3CN solution of DBD (**34**) (1.3×10^{-3} **M**) at different pH (3.10-12.73) gave only one major product **69**. The product yield of **69** did not change as the pH value changed (Table 2.1). This result indicates that the reduction is not due to electron transfer from hydroxide ion, but *via* hydride attack from $NaBH_4$ (eq. 2.9).

Table 2.1 The Effect of pH on the Product Yield of **69**

pH value of H_2O portion	3.10	7.50	10.22	12.73
Product yield of **69** (%)	67 ± 3	63 ± 3	64 ± 2	65 ± 2

The above results are consistent with formation of a hydride-reducible intermediate, giving rise to the observed product **69**. The fact that the yield of **69** is enhanced several fold concurrent with enhancement in the mass balance of the photoreaction is consistent with hydride attack of intermediate quinone **73**. Although it is not possible to completely rule out hydride attack of **91**, the observation of a single major photoproduct in **69** argues against such a possibility since several products would be anticipated from such a reaction. On the other hand, it can be readily shown that hydride attack of **73** (at any position) leads only to **69** (*vide infra*).

To gage the lifetime of photogenerated **73** and to rule out the possibility that added $NaBH_4$ may be altering the mechanism of the reaction itself, the effect of adding $NaBH_4$ *after* photolysis was examined. An argon purged 1:1 H_2O-CH_3CN solution of DBD (**34**) (1.3×10^{-3} **M**) was irradiated for 20 min. After photolysis, the reaction mixture was divided into two portions, to one of which was added excess $NaBH_4$ ($[NaBH_4]/[DBD] = 5$) immediately and then acidified to pH = 1 after 20 min (before workup); another portion acted as a control and was worked up without adding $NaBH_4$ but otherwise treated in exactly the same manner. The time intervals from the end of the photolysis to the workup were kept the same for both portions. In both portions, **69** was observed as the only major product. However, the yield of **69** was increased substantially (*e.g.*, from 7% to 11%) in the presence of $NaBH_4$ added after photolysis (Table 2.2). This result indicates that the reducible intermediate has a significant lifetime, which is consistent with **73** as the crucial intermediate rather than **91**.

Table 2.2 The Effect of $NaBH_4$ added after Photolysis on the Product Yield

Irradiation Time	20 min
Increase[a] of Yield of **69** by Added $NaBH_4$	(9 ± 2)%

[a] Enhancement was calculated by comparing the yield of **69** in the presence and absence of $NaBH_4$.

As indicated earlier, hydride attack at any of the positions of **73** will give **69**. To investigate the actual location of hydride attack, the photoreaction of **34** was carried out in the presence of $NaBD_4$. Irradiation of an argon purged 1:1 H_2O-CH_3CN solution of DBD (**34**) (2.7×10^{-3} **M**) in the presence of $NaBD_4$ (1.3×10^{-2} **M**) for 20 min gave only one major product, which was isolated by preparative TLC and identified as **69**. No trace of deuterated **69** (**69**-*d*) could be detected in the GC/MS spectrum. This result shows that hydride must attack the carbonyl carbon (C-2 in Fig. 2.2) or C-7, to reduce quinone **73** to product **69** (eq. 2.11). Otherwise, deuterated **69** (**69**-*d*) would be formed if hydride attacked **73** at any of the other carbons (eq. 2.12), since the relative rate of loss of H or D from the addition intermediate would be governed by a primary isotope effect ($k_H/k_D \leq 6$). That is, the major product should be **69**-*d*.

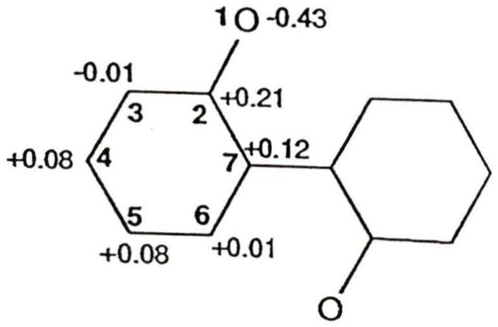
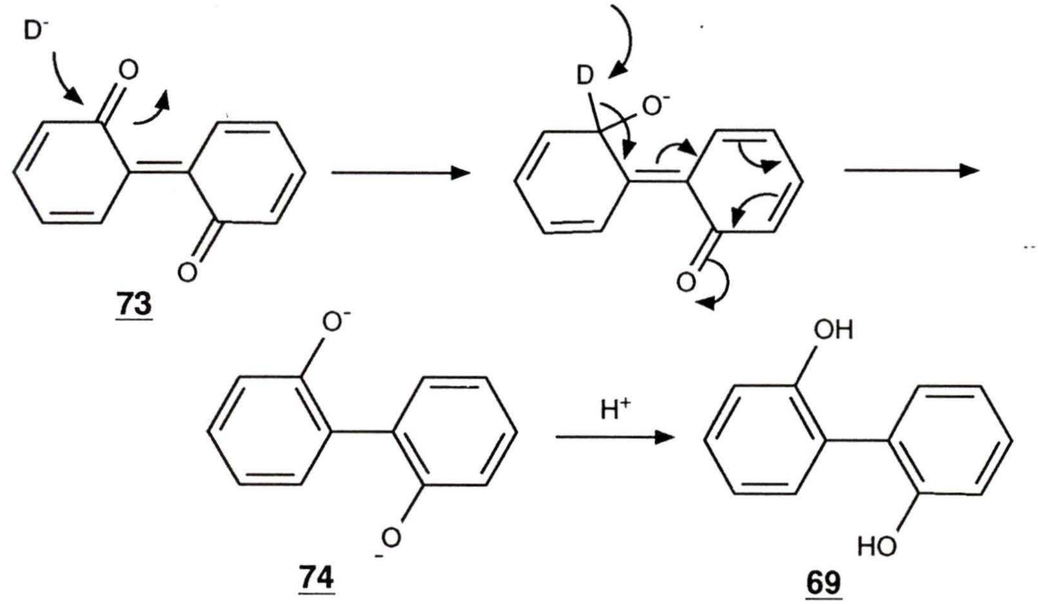
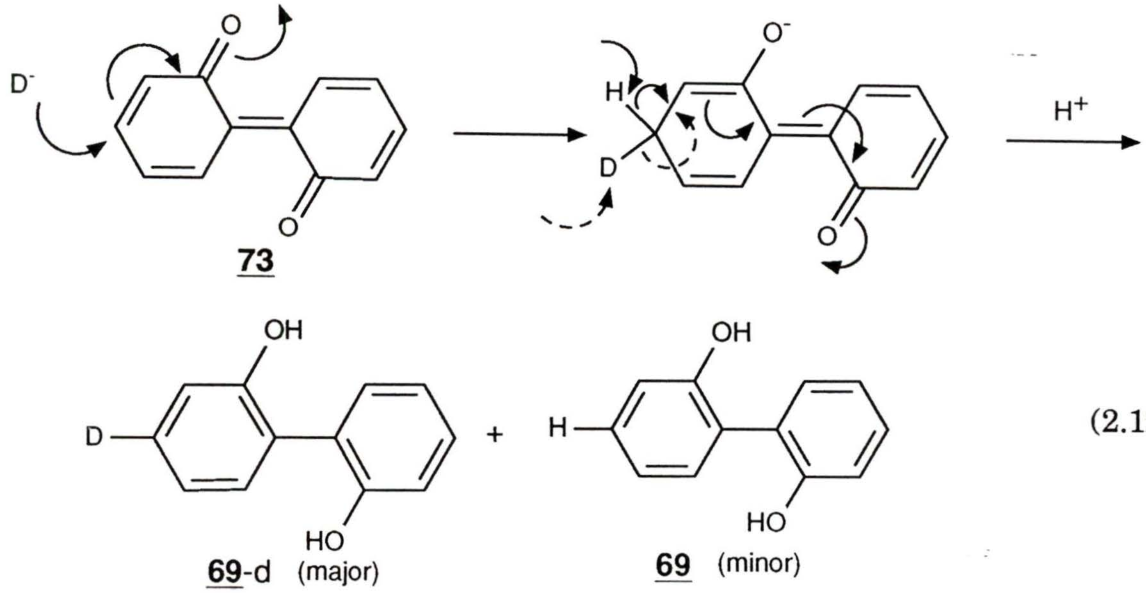


Figure 2.2 Charge density of **73** as calculated by HMO theory

The charge density distribution of quinone **73** (Fig. 2.2) was calculated using Hückel Molecular Orbital (HMO) theory, to rationalize the site of observed attack by hydride. This calculated charge distribution shows that carbons 2 and 7 have the lowest electron density. Thus, hydride should attack quinone **73** predominantly at carbons 2 and 7 (eq. 2.11), instead of the other carbons (eq. 2.12). This agreement between the experimental results and HMO calculation is further evidence that the proposed pathway involving quinone **73** is the crucial reaction intermediate in the photoreaction of DBD (**34**).

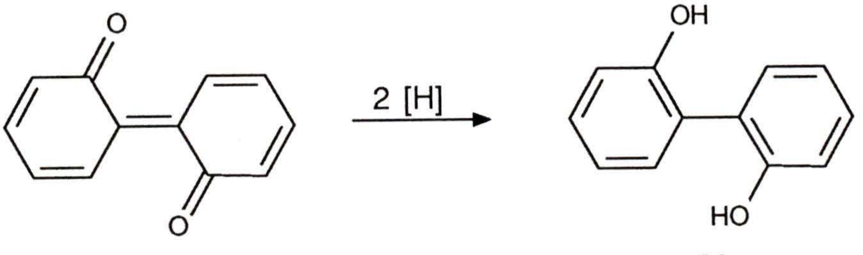


(2.11)



(2.12)

The results so far support the working mechanism that 2,2'-biphenylquinone (**73**) is formed as the crucial intermediate during photoreaction of DBD (**34**), which can be reduced to **69** by added $NaBH_4$ (eq. 2.9). In the absence of $NaBH_4$, quinone **73** is reduced to **69**, probably by abstracting hydrogen from the organic co-solvent (CH_3CN) (eq. 2.13). This reduction pathway of quinone **73** will be investigated in section 2.3.3.



73

69

(2.13)

2.2.2 Irradiation of DBD in Dry CH_3CN and Other Organic Solvents

Irradiation of an argon purged CH_3CN (dry) solution of DBD (**34**) (1.3×10^{-3} **M**) gave two major products (Figure 2.3), one of which was isolated from preparative TLC and identified as **69**. Another major product was also isolated by preparative TLC (silica gel, 6:4 CH_2Cl_2-hexane). The molecular weight of this product (m/e = 184) was observed in the MS (CI), suggesting the product to be a mono-hydroxydibenzofuran, since it is the only reasonable isomer of DBD (**34**). However, the position of the hydroxyl group in the product could not be ascertained based only on its molecular weight. Therefore, a ^1H NMR (360 MHz) spectrum of the photoproduct (Figure 2.4) was recorded, which showed three hydrogen atoms appearing as "triplets" (coupling to two different

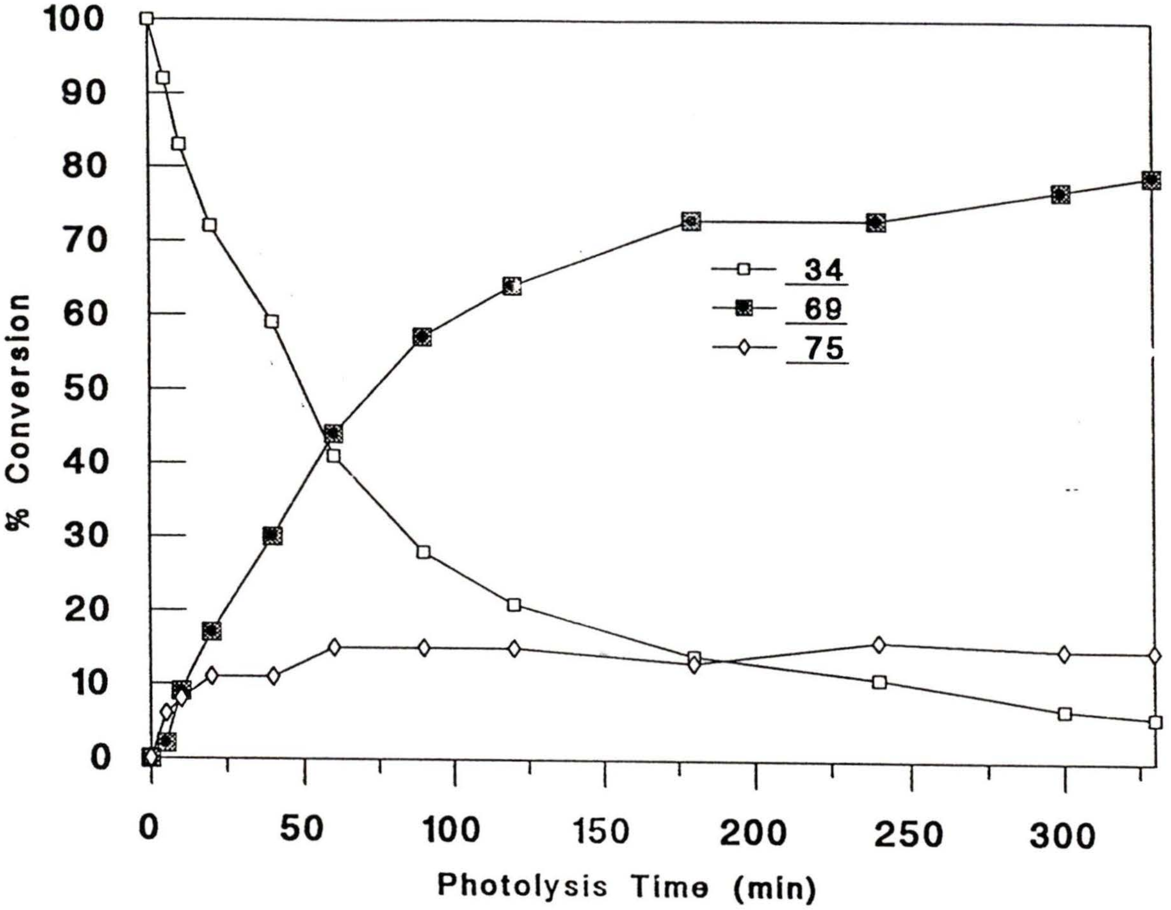
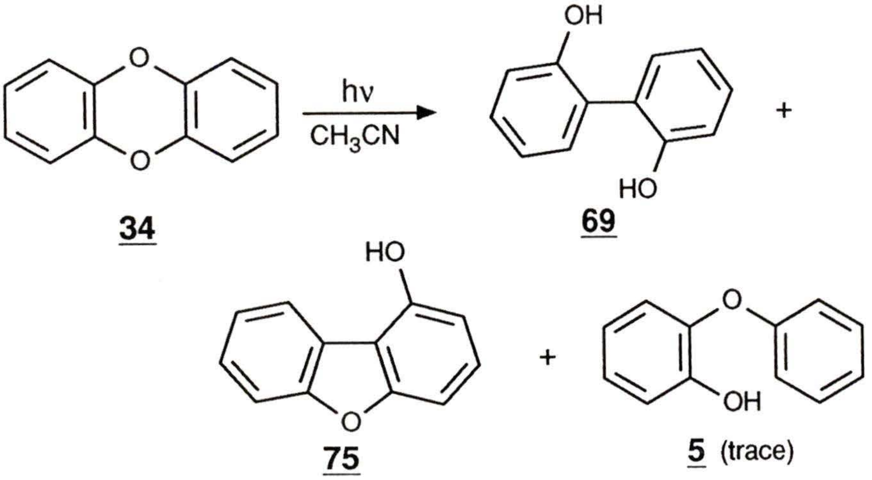


Figure. 2.3 Conversion of DBD (**34**) *vs* photolysis time in dry CH_3CN

adjacent protons). There are four possible mono-hydroxydibenzofuran isomers, but only 1-hydroxydibenzofuran (**75**) or 4-hydroxydibenzofuran (**70**) will exhibit the above ^1H NMR coupling pattern. Isomer **70** has been reported[54,55] to be one of the photoproducts in the photoreaction of DBD (**34**) (eq. 1.25). It was synthesized based on the method developed by Kemp and Galakatos.[60] However, the ^1H NMR spectrum of synthesized **70** is distinctly different from the one recorded for the isolated photoproduct. Therefore, the photoproduct is most likely **75**. Proof came by comparing the ^{1}H NMR (360 MHz) spectrum of the isolated product (Figure 2.4) with that of independently synthesized **75**[61] (Figure 2.4); these two spectra coincide with each other. In addition to the two major products, 2-phenoxyphenol (**5**) was also observed as a minor product (yield < 1% at all conversion of DBD (**34**)) (eq. 2.14).



(2.14)

It is unlikely that **75** is a secondary photoproduct of **69**, since the yield of both **75** and **69** are increased *vs* photolysis time (Figure 2.3). To further confirm this, irradiation of a dry CH_3CN solution of **69** (1.3×10^{-3} **M**) was performed, affording completely recovered **69**. Therefore, **75** is not a secondary photoproduct of **69**.

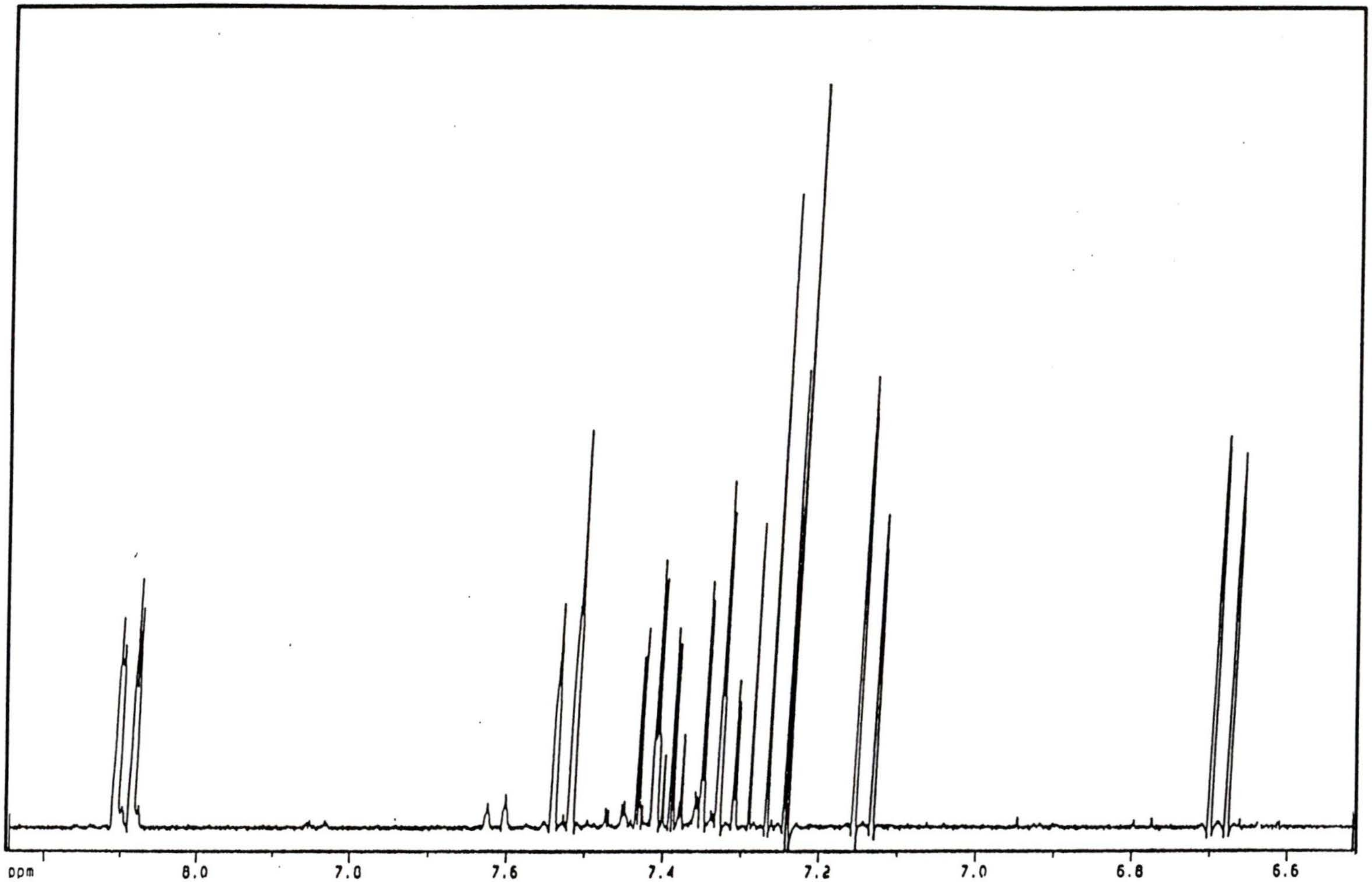


Figure 2.4 The ^{1}H NMR (360 MHz) Spectrum of 1-Hydroxydibenzofuran (**75**)

Two major products (**69** and **75**) are formed (eq. 2.14) when DBD (**34**) is irradiated in dry CH_3CN, while only one major product (**69**) is formed when DBD (**34**) is photolyzed in aqueous CH_3CN. Therefore, the formation of **75** is obviously affected by H_2O present in the reaction mixture. Irradiation of an argon purged CH_3CN solution of DBD (**34**) (1.3 x 10^{-3} **M**) with a variety of concentrations of H_2O for 20 min gave two major products which were identified as **69** and **75**. The product yield of **75** was decreased as the concentration of H_2O in the solution was increased; at the same time, the product yield of **69** was increased. However, the total conversion of DBD (**34**)

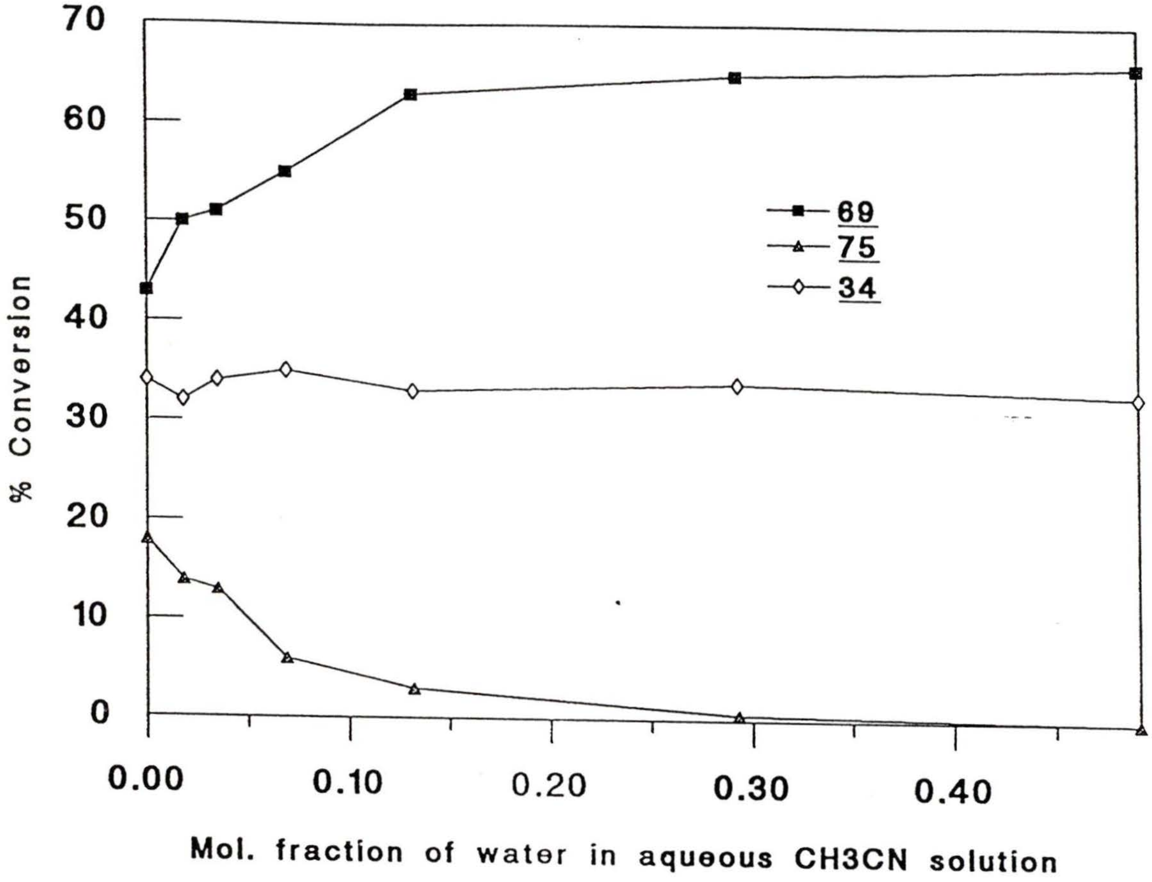
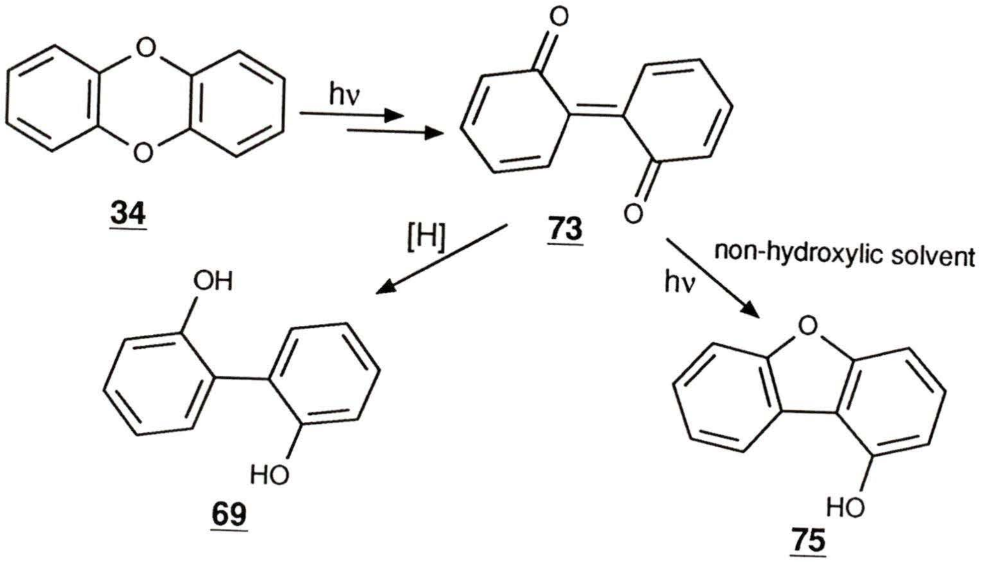


Figure 2.5 The effect of added water on the photoreaction of **34** in CH_3CN

kept constant (Figure 2.5). These results indicate that both of **69** and **75** originate from the same intermediate **73**. That is, in addition to be reduced to **69** by organic solvents (*vide infra*), quinone **73** can also undergo ring closure in the absence of hydroxylic solvent, to afford **75** as one major product (eq. 2.15). The total product yield of the reaction will therefore be governed by the amount of **73** formed during photolysis.



(2.15)

Aqueous CH_3CN is a hydroxylic solvent due to the presence of H_2O, while dry CH_3CN is a non-hydroxylic solvent. The above effect of H_2O promoted us to investigate the effect of other hydroxylic solvents as well as non-hydroxylic solvents on the reaction. Irradiation (300 nm) of an argon purged DBD (**34**) (1.3 x 10^{-3} **M**) in a hydroxylic solvent (MeOH or 2-propanol) for 20 min gave only one major product, which was identified as **69** (Table 2.3). However, irradiation of DBD (**34**) (1.3 x 10^{-3} **M**) in a non-hydroxylic solvent (THF or 1,4-dioxane) gave two major products, *viz.*, **69** and **75** (Table 2.3).

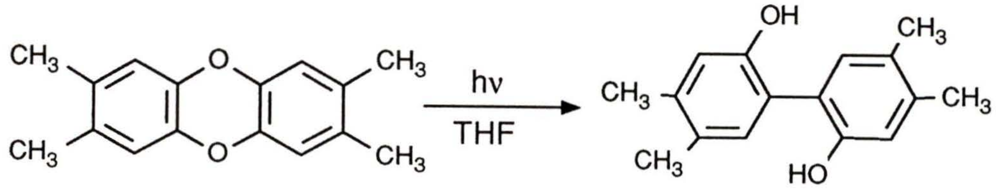
These results clearly indicate that the formation of **75** is blocked by hydroxylic solvents, and the possible reason will be discussed in section 2.3.1.

Table 2.3 The Effect of Solvents on the Photoproducts of DBD (**34**)

Compound	THF	1,4-dioxin	CH_3CN	2-propanol	MeOH
34	(38 ± 2)%	(32 ± 2)%	(37 ± 2)%	(29 ± 2)%	(27 ± 2)%
69	(39 ± 2)%	(49 ± 2)%	(43 ± 2)%	(70 ± 2)%	(71 ± 2)%
75	(22 ± 2)%	(18 ± 2)%	(19 ± 2)%	0	0

2.2.3 Irradiation of 2,3,7,8-Tetramethyldibenzo-*p*-dioxin (76)

To investigated the generality of the above reaction mechanism, the photochemical behaviour of 2,3,7,8-tetramethyldibenzo-*p*-dioxin (**76**; TMDBD), a derivative of DBD (**34**), was also studied. Due to solubilities problems, only THF was used in the photolysis. Direct irradiation of an argon purged THF solution of TMDBD (**76**) (≈ 10^{-3} **M**) in a Rayonet RPR 100 photochemical reactor (300 nm lamps) at ≈ 18°C for 20 min resulted in one major product (conversion ≈ 20% by GC) (eq. 2.16), which was isolated by preparative TLC (silica gel, 18:1 CH_2Cl_2-ethyl acetate). The molecular weight of the product (m/e = 242) was

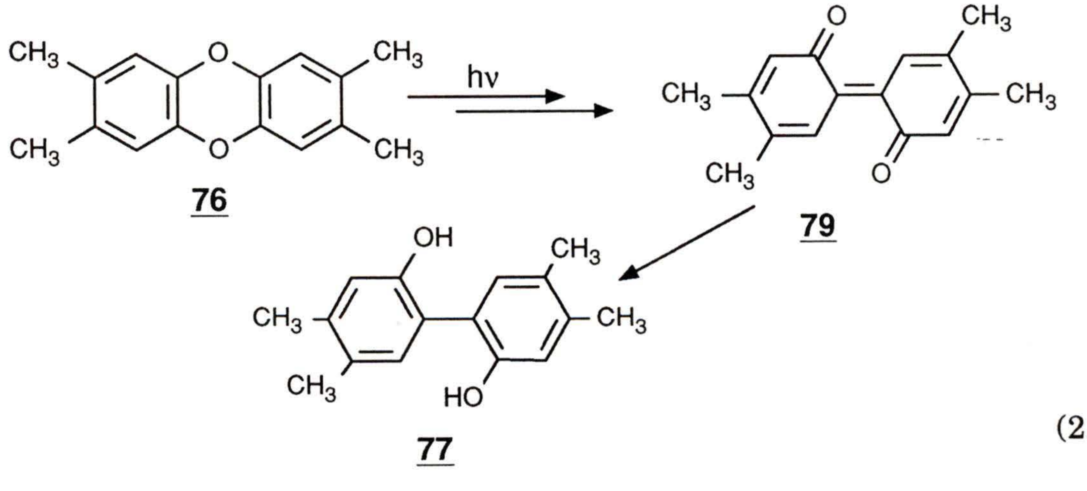


(2.16)

76

77 (≈ 20%)

observed in the GC/MS (CI), suggesting it to be 4,4',5,5'-tetramethyl-2,2'-biphenol (**77**). Further confirmation of the product was obtained by comparing its ^1H NMR (250 MHz) spectrum with the reported spectrum,[62] which is identical with that of the photoproduct. Irradiation of 1:15 H_2O-THF solution of TMDBD (**76**) (≈ 10^{-3} **M**) in the presence of $NaBH_4$ ($[NaBH_4]/[TMDBD] = 5$) also gave only one major product **77**, but the product yield of **77** was greatly increased (conversion ≈ 70% by GC). These results suggest that the proposed mechanism for the photoreaction of **34** is operative for **76**. That is, irradiation of **76** generates a quinone intermediate (4,4',5,5'-tetramethyl-2,2'-biphenylquinone (**79**)), which can be reduced to product **77** by hydrogen donors (eq. 2.17). However, it is not clear why the corresponding 1-hydroxy-2,3,8,9-tetramethyldibenzofuran (**78**) is not formed.



(2.17)

The results so far support the proposed working mechanism (*vide supra*) that photolysis of DBD (**34**) generates quinone **73** as an intermediate. Quinone

73 can be reduced to **69**, as well as undergo ring closure (in the absence of hydroxylic solvent) to afford **75** as a major product (eq. 2.15). This mechanism also appears to apply for the reaction of one of its derivatives.

2.3 Characterization of Reactive Intermediate

Product studies have indicated that photoreaction of DBD (**34**) could be proceeding through a quinone intermediate **73**. However, the existence of quinone **73** has not yet been directly verified. In this section, observation of quinone intermediates by UV-Vis will provide proof of the proposed reaction pathway. In addition, the reactivity of quinone **73** will be studied by measuring its rate of decay.

2.3.1 Observation of Quinone Intermediates

In section 2.2.1, the photoreaction of DBD (**34**) in aqueous CH_3CN was found to be enhanced in the presence of $NaBH_4$ added after photolysis. This result prompted us to make an attempt to detect the transient absorption spectrum of a possible reactive intermediate, which leads to the final product **69** *via* a reduction pathway. DBD (**34**) has two strong observation bands at 200-800 region, λ_{max} 228 nm ($\varepsilon \approx 30{,}000\ M^{-1}\ cm^{-1}$) and 288 nm ($\varepsilon \approx 3{,}400\ M^{-1}\ cm^{-1}$) (Figure 2.6). When a dry CH_3CN solution of DBD (**34**) ($\approx 4 \times 10^{-4}$ **M**) in a quartz cuvette was photolyzed at ambient temperature for 30 s, a characteristic pink colour transient was generated and its colour disappeared after several minutes. Recording a UV-Vis spectrum of the transient immediately after photolysis yielded two distinct absorption bands λ_{max} 345 and 532 nm (Figure

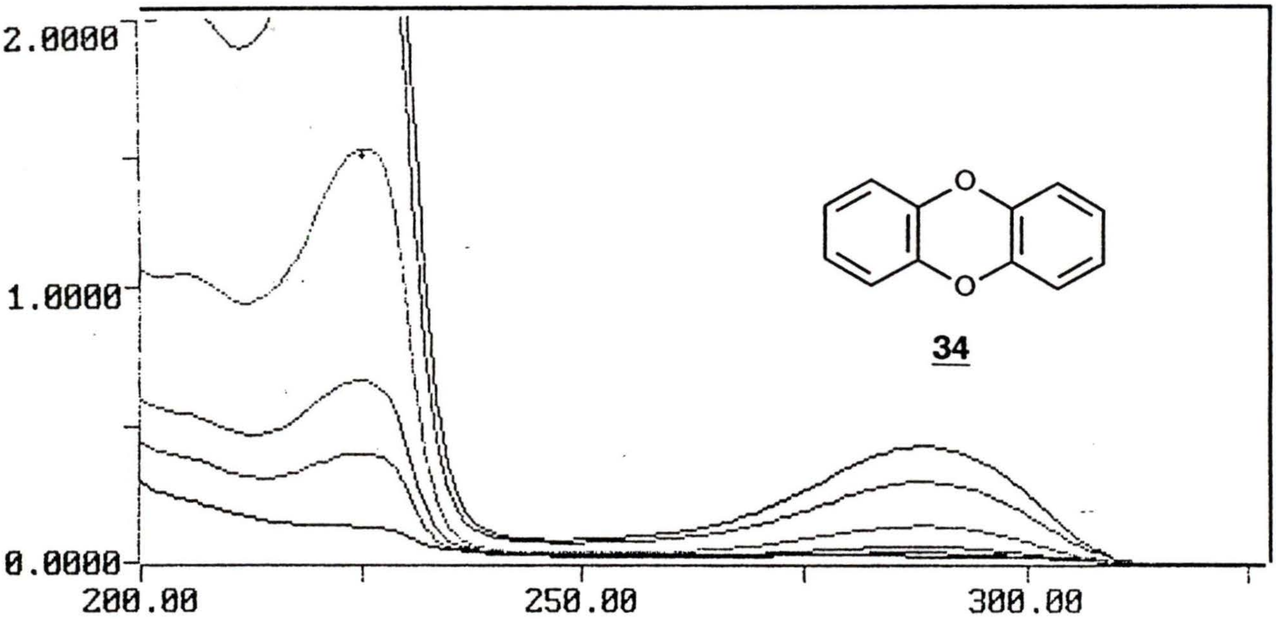


Figure 2.6 Absorption spectrum of DBD (**34**) in CH_3CN

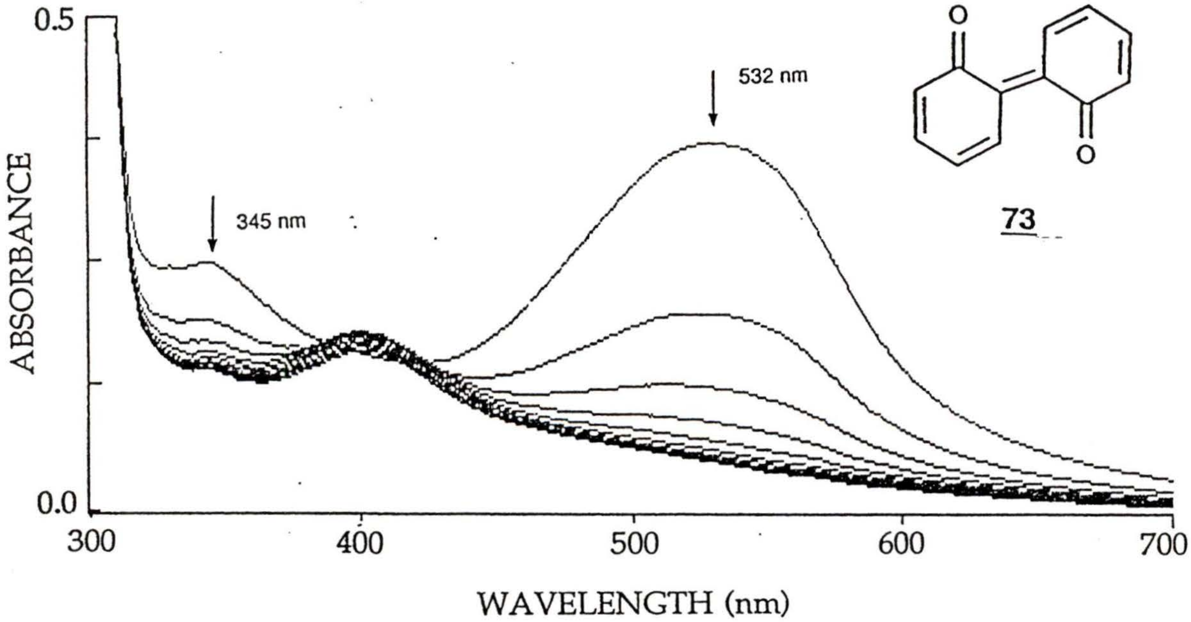
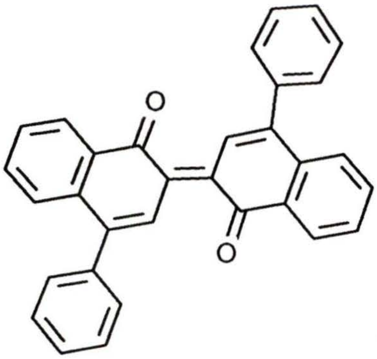


Figure 2.7 Transient decay of photogenerated **73** in CH_3CN.

Decay traces of λ_{max} 345 and 532 nm taken at 60 s intervals

2.7). These absorption bands disappeared in several minutes, concurrent with the increase of the absorption at 240-290 region, probably due to the formation of product **69**, which has an absorption band λ_{max} 282 nm ($\varepsilon \approx 11{,}000$ M^{-1} cm^{-1}). Therefore, the transient is assigned as a reactive intermediate which is the precursor of **69**. A reasonable intermediate in this reaction is 2,2'-biphenylquinone (**73**) which can be reduced to **69**. Irradiation of a dry CH_3CN solution of TMDBD (**76**) ($\approx 4 \times 10^{-4}$ **M**) in a quartz cuvette at ambient temperature for 30 s also resulted in a characteristic pink colour transient which disappeared after several minutes; a UV-Vis spectrum recorded immediately after photolysis afforded two distinct absorption bands, λ_{max} 353 and 566 nm. Similarly, this species is assigned to be 4,4',5,5'-tetramethyl-2,2'-biphenylquinone (**79**). Further confirmation of these assignments comes from the reported spectra of stable substituted 2,2'-biphenylquinones such as **82**[63], **83**[64], **84**[65], **85**[66] and **86**[67], all of which have two distinct absorption bands λ_{max} in the 340-380 nm and 530-600 nm regions. Among these substituted 2,2'-biphenylquinones, **85**[66](λ_{max} 353 and 547 nm) and **86**[67] (λ_{max} 375 and 550 nm) have been isolated.



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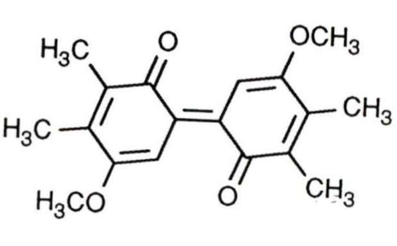

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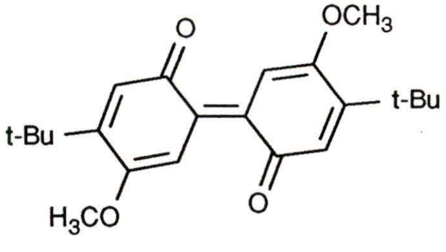

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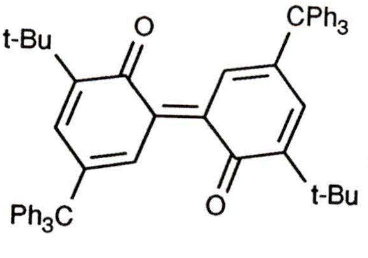

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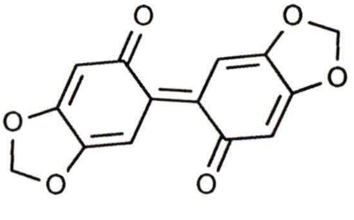


86

Irradiation of DBD (**34**) (≈ 4 x 10^{-4} **M**, 3 mL) in other non-hydroxylic solvents (THF or 1,4-dioxane) also gave a pink transient, which had two absorption bands λ_{max} 345 and 532 nm, and disappeared in several minutes. However, irradiation of DBD (**34**) (≈ 4 x 10^{-4} **M**, 3 mL) in hydroxylic solvents (aqueous CH_3CN, MeOH and 2-propanol) did not give the pink transient observed in non-hydroxylic solvents. Since the photoreaction is still observed in hydroxylic solvents, the implication is that the transient (**73**) is much shorter lived (more reactive to reduction) in these solvents, or that it is hydrated (in H_2O) or exists as the acetal (in alcohol), both of which will remove the carbonyl from the chromophore. The fact that **75** was not observed in hydroxylic solvents is probably intimately connected to the lack of a long-lived **73** in the same solvent. This connection is further explored below.

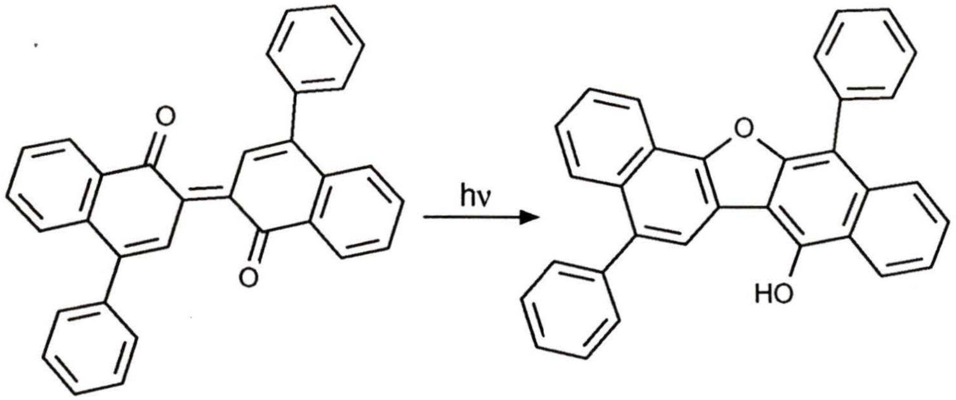
2.3.2 The Formation of 1-Hydroxydibenzofuran (75)

As mentioned above, **75** is formed only in non-hydroxylic solvents (eq. 2.15). However, the mechanism to form **75** from **73** has not been addressed so far. In principle, formation of **75** could be achieved thermochemically or photochemically. To investigate whether **75** is a secondary photoproduct of **73** or not, photolysis was carried out with 300 and 350 nm lamps (in same experiment) to investigate a possible wavelength effect on yield of **75**. Irradiation of an argon purged dry CH_3CN solution of DBD (**34**) (1.3×10^{-3} **M**) (sixteen 300 nm lamps or eight 300 nm lamps/eight 350 nm lamps) at ≈ 18°C for 20 min gave two major products which were identified as **69** and **75**. The ratio of the product yields (**75/69**) was recorded in each case, showing that the ratio **75/69** was increased substantially in the presence of 350 nm lamps, comparing to the run with sixteen 300 nm lamps (Table 2.4). The result that formation of **75** is enhanced in the presence of the 350 nm lamps strongly suggests that **73** isomerizes photochemically to **75** .

Table 2.4 The Effect of Wavelength on the Ratio of Product Yields (**75/69**)

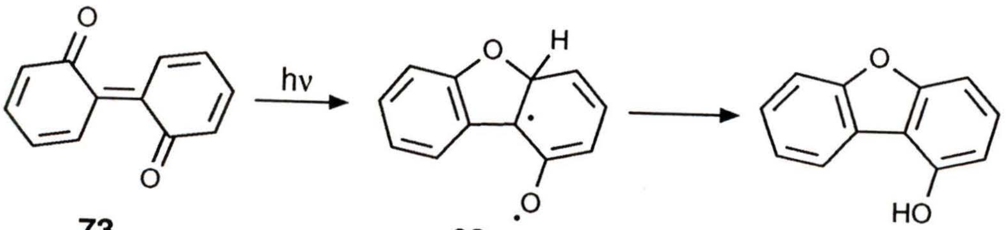
Arrangement of Lamps	Ratio of the yield of **75** over **69**
300 nm/350 nm lamps (8:8)	0.80 ± 0.05
300 nm lamps (16)	0.57 ± 0.05

Support of this finding comes from the photoreaction of quinone **82** (a derivative of **73**), which was reported[63] to give the corresponding substituted dibenzofuran **85** as the predominant photoproduct (eq. 2.18).



82 87 (2.18)

A possible mechanism for the photo isomerization of **73** to **75** is shown in eq. 2.19. The primary step involves attack of triplet carbonyl n, π^* onto the alkene moiety of the second ring, giving rise to a biradical **92**, which subsequently isomerizes to **75** *via* a hydrogen shift. Alternatively, it is possible to visualize the ring closure as a radical coupling step of the triplet n, π^* of quinone **73** where the radical in the π^* orbital is extensively delocated to the other ring.

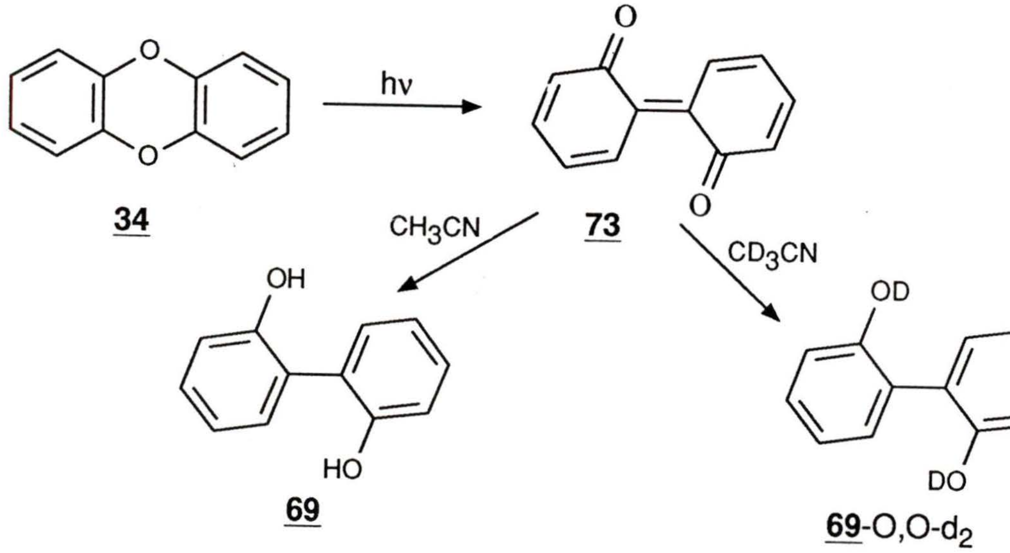


73 92 75 (2.19)

2.3.3 Solvent Isotope Effect

Organic solvents have been proposed as a hydrogen donor, to reduce **73** to **69** (eq. 2.13), based on the product studies. To further confirm it, solvent isotope effects on the decay of **73** as well as on the product yield of **69** were investigated. Irradiation (300 nm lamps) of an argon purged dry CH_3CN or CD_3CN solution of DBD (**34**) ($\approx 6 \times 10^{-4}$ **M**) in a 3.0 mL quartz cuvette at ambient temperature for 30 s generated a pink species. The decay of **73** (at 532 nm) was monitored and found to be the first order. Decay rate constants were tabulated and the solvent kinetic isotope effect was calculated, by comparing the decay rate constant of **73** in dry CH_3CN (k_H) to the decay rate constant in dry CD_3CN (k_D). The observed isotope effect ($k_H/k_D = 1.16 \pm 0.06$) shows that the decay of the intermediate **73** is faster in CH_3CN than in CD_3CN, supporting the proposal that hydrogen abstraction from the solvent by **73** is responsible at least in part for its decay.

The solvent isotope effect on the product yield of **69** was also investigated. Irradiation (300 nm lamps) of argon purged dry CH_3CN and CD_3CN solutions of DBD (**34**) with identical concentration ($\approx 10^{-3}$ **M**) in a 3.0 mL quartz cuvette was performed, using a merry-go-round apparatus cooled by air. In CH_3CN solution, **69** was identified as the major product, while dideuterated **69** (**69**-*O,O*-d_2) was identified as the major product in CD_3CN (eq. 2.20) by FT-IR (Nujol mull), based on that the O-D bond stretch of **69**-*O,O*-d_2 (2360 ± 10 cm^{-1}). The product yields of **69** and **69**-*O,O*-d_2 in a parallel reaction were measured by GC, giving rise to the product isotope effect $P_H/P_D = 1.34 \pm 0.09$, where P_H stands for the product yield of **69** in dry CH_3CN and P_D stands for the product yield of **69**-*O,O*-d_2 in dry CD_3CN. The solvent isotope effect on the product yield is higher than that observed for the decay of **73**, probably due to the fact that the decay of **73** need not involve abstraction of H (D) from CH_3CN (CD_3CN).



(2.20)

2.4 Triplet Sensitization

The aryl-O bond cleavage of DBD (**34**) could originate from S_1 or T_1. To determine the reactivity of S_1 and T_1, triplet sensitization of DBD (**34**) was carried out.

Triplet sensitization is a photochemical process used to selectively place a molecule in its T_1 state, by energy transfer. In order for energy transfer to occur, the sensitizer (donor) utilized must have a T_1(D) energy higher than the T_1(A) energy of the molecule to be sensitized (acceptor) (Fig. 2.8). Acetone was chosen as the triplet sensitizer for DBD (**34**) since is has a triplet energy (E_T) of 79-81 kcal mol^{-1}[68], while the E_T of DBD (**34**) is less than 74 kcal mol^{-1}, as estimated from its phosphorescence spectrum.[69]

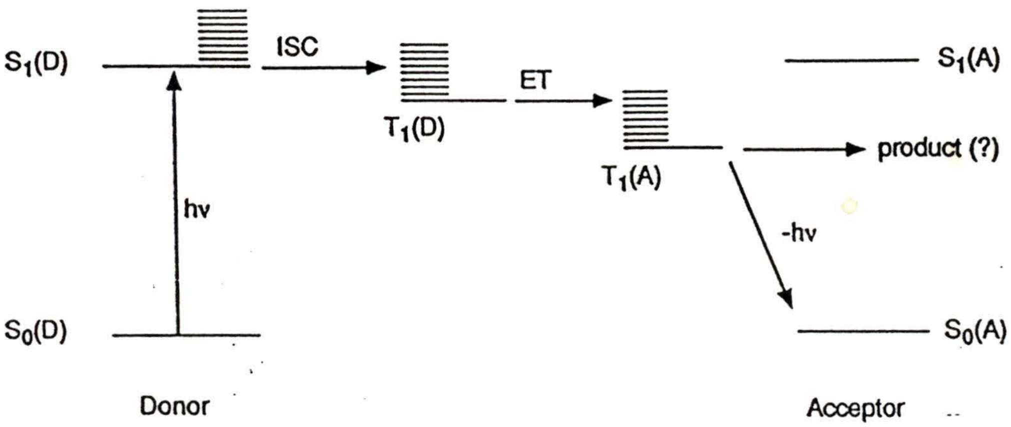


Figure 2.8 Triplet-triplet Excitation Transfer

Irradiation of an argon purged acetone solution of DBD (**34**) (1.3 x 10^{-3} **M**; 300 nm lamps) for 20 min gave completely recovered starting material; and no **69** or **75** could be observed. A control photoreaction, using CH_3CN instead of acetone as solvent, gave **69** and **75** as major photoproducts (eq. 2.14). Assuming that triplet energy transfer does occur from acetone to DBD (**34**), this result indicates singlet-state reactivity in this system.

Photoreaction of DBD (**34**) was also carried out in the presence of oxygen, which is a good triplet quencher. Irradiation of an oxygen purged CH_3CN solution of DBD (**34**) (1.3 x 10^{-3} **M**; 300 nm lamps) for 20 min gave two major products, *viz.*, **69** and **75**, with the same product yields as in the absence of oxygen. The fact that oxygen (a good triplet quencher) does not affect the product yield also supports S_1 reactivity of DBD (**34**).

Singlet-state reactivity is reasonable since the T_1 ($E_T < 74$ kcal mol^{-1}) of

DBD (**34**) would not have sufficient energy to induce the homolysis of the aryl-oxygen bond, which is believed to be the primary photochemical step. However, the S_1 energy (E_S) of DBD (**34**), estimated to be 84 kcal mol^{-1} based on its fluorescence emission band at 340 nm, is high enough to break a typical aryl-oxygen bond, whose dissociation energy was estimated by Joschek and Miller[9] to be in the range 70-80 kcal mol^{-1}.

2.5 Product Quantum Yield

Photochemical efficiencies are quantified by the measurement of product quantum yield (Φ_p), which is a measure of the number of moles of photoproducts produced per mole (or einstein) of radiation absorbed (eq. 2.21).

$$\Phi_P = \frac{Moles\text{-}of\text{-}Product}{Einsteins\text{-}of\text{-}Light\text{-}Absorbed} \tag{2.21}$$

Measurement of quantum yields for the appearance of photoproduct **69** was performed on an optical bench utilizing a mercury arc lamp in conjunction with a monochromator to obtain an excitation wavelength of 280 nm. Samples were irradiated in 3 mL quartz cuvettes at ambient temperature while purged with argon. The einsteins were measured with a potassium ferrioxalate ($K_3[Fe(C_2O_4)_3]\bullet 3H_2O$) chemical actinometer.[68,70] The product yields and reaction mass balances were measured by GC, using 9-fluorenone (**88**) as internal standard. The results of quantum yields and reaction mass balances (Table 2.5) indicate that the formation of **69** can be enhanced in the presence of water, while in the presence of $NaBH_4$, both the product yield of **69** and the reaction mass balance were enhanced dramatically, the later having already been demonstrated in section 2.2.1.

Table 2.5. Product Quantum Yields of **69** and Reaction Mass Balances

Condition	Dry CH_3CN	1:1 CH_3CN/H_2O	1:1 CH_3CN/H_2O ($NaBH_4$)[a]
Mass Balance[b]	55% ± 5%	62% ± 2%	94% ± 7%
Quantum Yield[c]	0.013 ± 0.001	0.016 ± 0.001	0.063 ± 0.008

[a] $[NaBH_4]/[DBD] = 5$.

[b] Mass balance of the reaction of DBD (**34**) using **88** as an internal standard.

[c] Quantum yields for the appearance of **69**.

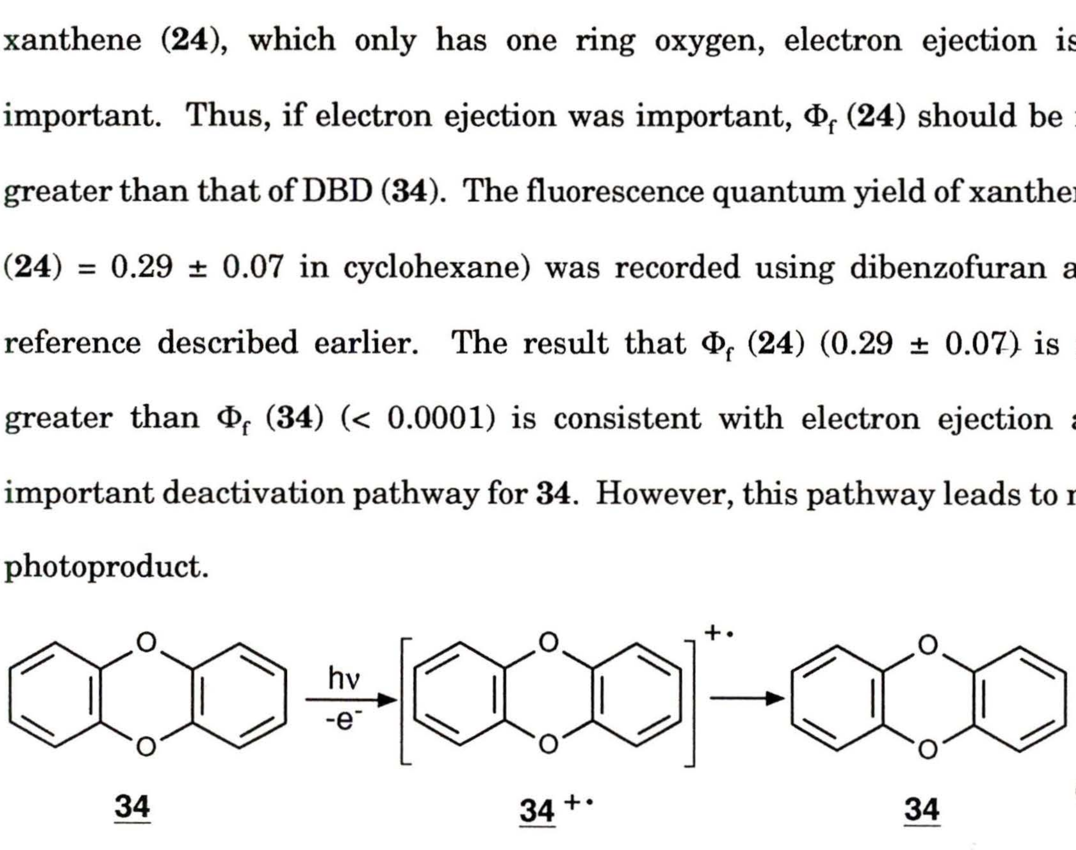
2.6 Fluorescence Studies

Results presented indicate that homolysis of the aryl-O bond of DBD (**34**) involves the singlet excited state (S_1). In general, deactivation of S_1 can occur by fluorescence (emission of light from the excited species), intersystem crossing (change in spin multiplicity by crossing from S_1 to T_1 state), internal conversion and photochemical reaction.

A fluorescence quantum yield (Φ_f) is a measure of that portion of the excited species which is deactivated by fluorescence. The fluorescence quantum yield of a compound can be obtained by comparing its fluorescence intensity with that of a standard which has a known fluorescence quantum yield. DBD (**34**) has a fluorescence emission at $\lambda_{max} = 340$ nm, but its fluorescence quantum yield was too low to be measured precisely ($\Phi_f < 0.001$).

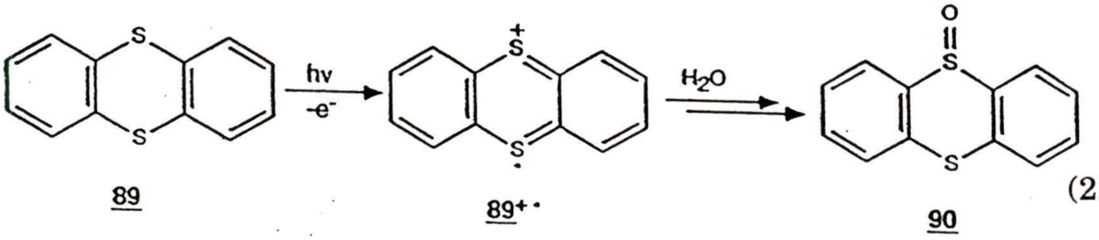
Of all the pathways to deactivate S_1 of DBD (**34**), the contribution of fluorescence is very small (less than 0.1%). Also internal conversion is generally not important because of the large energy gap between S_1 and S_0. Although the product quantum yield is not large, even in the presence of $NaBH_4$ ($\Phi_p = 0.063 \pm 0.008$), the quantum yield of aryl-oxygen bond homolysis may be substantial, resulting in a very short lived S_1.

Electron ejection from the S_1 (eq. 2.22), which competes with fluorescence and homolysis of aryl-O Bond, may be another significant pathway to deactivate DBD (**34**). There are two electron rich oxygens in the ring system of DBD (**34**), so the electron ejection pathway may be very favourable. As for xanthene (**24**), which only has one ring oxygen, electron ejection is less important. Thus, if electron ejection was important, Φ_f (**24**) should be much greater than that of DBD (**34**). The fluorescence quantum yield of xanthene (Φ_f (**24**) = 0.29 ± 0.07 in cyclohexane) was recorded using dibenzofuran as the reference described earlier. The result that Φ_f (**24**) (0.29 ± 0.07) is much greater than Φ_f (**34**) (< 0.0001) is consistent with electron ejection as an important deactivation pathway for **34**. However, this pathway leads to no net photoproduct.



(2.22)

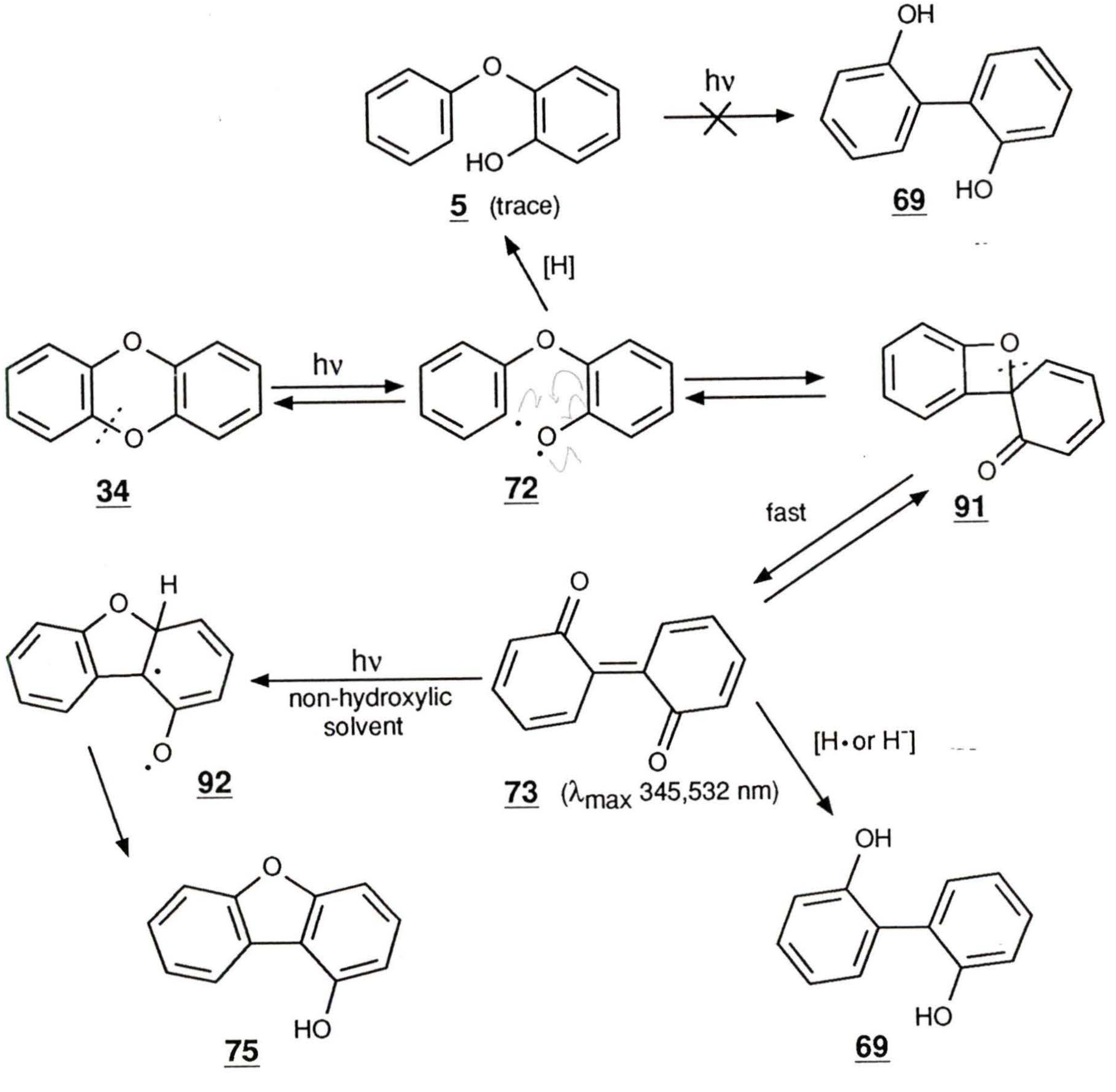
If the two oxygens are replaced by two sulfurs, thianthrene (**89**) is obtained. Photolysis of **89** has been shown[71] to give a radical cation from electron ejection *via* S_1. Irradiation of **89** did not cause aryl-S bond cleavage, instead, the formed radical cation proceeded to give sulfoxide (**90**) (eq. 2.23).



(2.23)

2.7 Mechanism

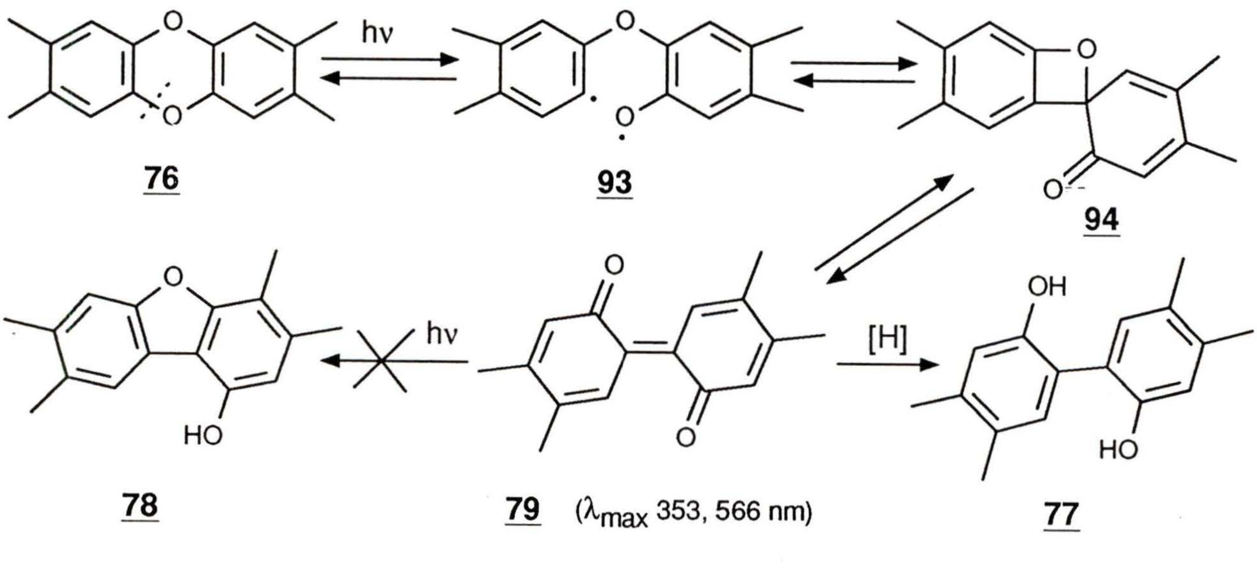
The results suggest that the mechanism for photoreaction of DBD (**34**) involves initial aryl-oxygen bond homolysis in S_1, to generate the singlet biradical **72** (scheme 2.1). The quantum yield of this process is unknown but it is probably substantially higher than the measured Φ for the formation of **69**, since the biradical can recombine to give back starting material. Recombination of the phenyl radical *via ipso* attack on the adjacent phenyl ring gives the intermediate ketone **91**. Reduction of **72** by solvent (to give **5**) is a very minor pathway. Subsequent homolysis of the aryl-oxygen bond of **91** gives the observable 2,2'-biphenylquinone (**73**). In the presence of $NaBH_4$, **73** is efficiently reduced to **69** in high yield (hence mass balance > 90%). In its absence, **73** is reduced by solvent to give **69**, but in lower yield and lower mass balance. Since the mass balance is much lower in this case, a significant fraction of **73** goes to product which were not characterizable and believed to be polymeric in nature. A significant decrease in yield of **69** was observed when CD_3CN was used as the organic solvent, indicating that solvent acts as the hydrogen donor to **73** in the absence of $NaBH_4$. In non-hydroxylic solvents



Scheme 2.1

such as CH_3CN, THF and 1,4-dioxane, **73** can also undergo ring closure *via* secondary photolysis, giving rise to biradical **92**, which gives **75** by hydrogen migration. The isomerization from **91** to **73** is probably very fast. Therefore the relative product yields of **75** and **69** depend on competition reaction between reduction and isomerization pathway of **73**.

Photoreaction of TMDBD undergoes a similar pathway (Scheme 2.2), involving initial aryl-oxygen bond homolysis to generate biradical **93**, which undergoes intramolecular radical attack to give spiro ketone **94**. Subsequent homolysis of the aryl-oxygen bond of **94** gives the observable biphenylquinone **79** (λ_{max} 353 and 566 nm). Quinone **79** can be further reduced to phenol **77**, but ring closure to afford **78** was not observed in the solvent (THF) used.



Scheme 2.2

2.8 Summary

The photochemistry of dibenzo-*p*-dioxin (DBD; **34**) has been studied in non-hydroxylic solvents such as CH_3CN, THF and 1,4-dioxane, as well as in hydroxylic solvents such as aqueous CH_3CN, MeOH and 2-propanol. The major product was 2,2'-biphenol (**69**) in both hydroxylic and non-hydroxylic solvents; 1-hydroxydibenzofuran (**75**) was observed as an additional major product in non-hydroxylic solvents. Quinone **73** was observed as an intermediate of the photoreaction, which could be reduced to **69** or react *via* ring closure, to give **75** in non-hydroxylic solvents. A mechanism (Scheme 2.1) of photoreaction is proposed to describe the overall photochemical behaviour. This mechanism also applies for the most part to the photobehaviour of 2,3,7,8-tetramethyldibenzo-*p*-dioxin (TMDBD; **76**), a derivative of DBD (**34**). As the photodecomposition of TCDD (**35**) must eventually involve aryl-oxygen bond cleavage, understanding of the photochemistry of DBD (**34**) is essential in future studies of TCDD (**35**) photodegradation.

Chapter Three: Experimental

3.1 Instrumentation

Gas chromatography (GC) was carried out on a Varian 3700 gas chromatograph with a Hewlett-Packard 3390A integrator using a DB-5 capillary column. Analytical thin layer chromatography (TLC) was performed on plastic precoated silica gel plates (Macherey-Nagel, Sil/UV-Vis$_{254}$), using solvent systems as indicated in each experiment. Preparative TLC was performed on Analtech GF 1000 micrometer silica gel plates. Mass spectra were taken on Finnigan 3300 or Kratos Concept H instruments. ^{1}H NMR spectra were recorded on either a Perkin-Elmer R32 (90 MHz), Bruker WM 250 (250 MHz) or Bruker AM 360 (360 MHz) instruments using $CDCl_3$ or acetone-d_6 as solvent. Tetramethylsilane (TMS) was used as an internal standard in the 90 MHz instrument. Chemical shifts are reported in ppm down field from TMS and splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and b, broad. UV-Vis spectra were obtained on a Varian Cary 5 UV-Vis-NIR or a Perkin-Elmer Lambda 4B UV-Vis spectrophotometer. Melting points were obtained on a Koefler hot stage microscope and were uncorrected. IR spectra were recorded on a Bruker IFS 25 FT-IR spectrophotometer, and Nujol mull NaCl plates were employed to prepare the samples. Fluorescence studies were performed on a Perkin-Elmer MPF-66 fluorescence spectrophotometer. Preparative photolyses were performed in a Rayonet RPR 100 photochemical reactor with 100 mL or 200 mL quartz tubes unless stated otherwise. Quantum Yields were measured on an optical bench utilizing an Oriel 200 W Hg arc lamp and an Applied Physics monochromator set at 280 nm with 7 nm slits. Small scale photolysis analytical experiments were performed in suprasil quartz cuvettes.

3.2 Synthesis

Several substrates such as DBD (**34**), **5**, **75** have been prepared for use in photoreactions; and several compounds such as **70**, **75**, and **77** have been synthesized in order to confirm the identity of products formed in the photoreactions. All the reagents utilized for the syntheses were purchased from Aldrich and were used as received after a purity check by GC, showing > 98% purity. The products were identified by m.p., GC/MS and ^{1}H NMR.

Dibenzo-*p*-dioxin (34). The synthesis was based on the procedure of Tomita.[56] *o*-Chlorophenol (102.5 g, 0.79 mole), anhydrous K_2CO_3 (55 g, 0.4 mole) and copper powder (6 g) were heated under N_2 in an oil-bath at 170-180°C for 6 h. The tarry mixture was then further refluxed under N_2 with 100 ml 5 M KOH solution for 2 h, allowed to cool down, dissolved in CH_2Cl_2 and vacuum filtered. The collected solid was then extracted with CH_2Cl_2 and washed with 2 M KOH (3 x 100 ml). The dark CH_2Cl_2 solution was filtered through a sintered glass funnel filled with ≈ 3 cm of silica gel and covered ≈ 0.5 cm of sand, resulting in a yellow effluent. The crude product was obtained by evaporating CH_2Cl_2 from the effluent. Recrystallization from EtOH/H_2O

afforded pure **34** as white needles (7.3 g, 10%): m.p. 120-122°C (lit.[57] m.p. 119°C); MS, m/z = 185 (M^+ + 1); ^{1}H NMR (360 MHz, acetone-d_6) δ 6.91 (4 H, m, H-1,4,6,9), 6.94 (4H, m, H-2,3,7,8).

2-Phenoxyphenol (5). To 5 g of *o*-chlorophenol (0.039 mol) was added 5.4 g of K_2CO_3 (0.039 mol), 0.6 g copper powder (0.0094 mol), and 15 g phenol (0.16 mol). The mixture was heated for 12 h at 170-180°C, and refluxed with 50 ml 5 M KOH for 5 h. The product mixture was then acidified and extracted with CH_2Cl_2. The combined organic phases were extracted with 5% NaOH solution, acidified with conc. HCl, and extracted with CH_2Cl_2, giving rise to the crude product. Further purification were carried out by recrystallization (75% EtOH/ 25% H_2O) and column chromatography (CH_2Cl_2), affording pure **5** as white needles (1.2 g, 17%): m.p. 104-106°C (lit.[58] m.p. 104.7 -104.9°C); MS, m/z = 187 (M^+ + 1); ^{1}H NMR (360 MHz, acetone-d_6) δ 6.89 (4 H, m), 7.05 (3 H, m), 7.30 (2 H, m), 8.27 (1 H, s, Ar-OH, exchangeable with D_2O).

4-Hydroxydibenzofuran (70). The procedure of Kemp and Galakatos was used.[60] To dibenzofuran (11.9 g, 0.071 mole) in dry diethyl ether (130 ml) was added dropwise at room temperature under N_2 *n*-BuLi (0.082 mole) in *n*-hexane (34.1 ml), and the mixture was refluxed for 15 h. The resulting yellow suspension 4-lithiodibenzofuran was then allowed to cool to room temperature and was used immediately in the next step. *n*-Butylmagnesium bromide (0.115 mole) was prepared at the same time. To a 1-liter, three-necked dry flask equipped with a magnetic stirrer was added dry Et_2O (120 ml). The vessel was cooled to -78°C and the solvent was saturated with dry O_2. To the cooled solvent mixture was added dropwise and simultaneously the solution of 4-lithiodibenzofuran in Et_2O, and fresh *n*-butylmagnesium bromide (0.115 mole) in Et_2O. The mixture was then allowed to warm up slowly to room temperature and was stirred for 15 h with a slow flow of oxygen. The resulting yellow suspension was then cooled to 0°C and cautiously acidified with 6 **M** HCl until both phases became clear. The aqueous phase was extracted with diethyl ether and the combined organic layers were washed with 1 **M** HCl and extracted with 1 **M** NaOH. The combined alkaline phases were acidified to pH 1 with conc. HCl and extracted with Et_2O. The organic layers were combined, washed with brine, dried with $MgSO_4$ and evaporated to yield a tan solid residue. Recrystallization from hexane afforded pure **70** as white needles (2.6 g, 20%): m.p. 96-98°C (lit.[60] m.p. 97-99°C); MS m/z = 185 (M^+ + 1); ^1H NMR (360 MHz, $CDCl_3$) δ 5.59 (1 H, bs, Ar-OH, exchangeable with D_2O), 7.01 (1 H, dd, J = 8, 1 Hz, H-3), 7.21 (1 H, m, H-2), 7.36 (1 H, m, H-8), 7.45 (1 H, m, H-7), 7.50 (1 H, dd, J = 8, 1 Hz, H-1, or H-6), 7.58 (1 H, dd,J = 8, 1 Hz, H-6 or H-1), 8.92 (1 H, dm, J = 8 Hz, H-9).

1-Hydroxydibenzofuran (75). The procedure of Tashiro *et al.* was employed[61] To 2,4-di-*t*-butylphenol (20.6 g, 0.1 mole) in DMF (100 ml) was added dropwise NBS (21 g, 0.1 mole) in DMF (100 ml), and the mixture was stirred at room temperature for 24 h. The product mixture was then poured into water and extracted with CH_2Cl_2 (3 x 100 ml). The combined organic layers were washed with water, and dried with $MgSO_4$. Evaporation of CH_2Cl_2 afforded 20 g (70% product yield) 2-bromo-4,6-di-*t*-butylphenol (99% pure by GC).

A two-neck 1000 ml reaction flask was charged with a solution of 2-bromo-4,6-di-*t*-butylphenol (5.7 g, 20 mmol) in benzene (330 ml), and a solution of potassium hexacyanoferrate (33 g, 100 mmol) and potassium hydroxide (33 g, 590 mmol) in distilled water (500 ml). After the mixture was stirred at room temperature under N_2 for 20 min, the aqueous layer was removed and the organic layer was washed with distilled water (5 x 150 ml) and dried with $MgSO_4$, whereby the colour was changed to red brown. Fine powdered aluminium chloride (9.3 g, 70 mmol) was then added to the mixture, which was stirred for 3 h at room temperature. This mixture was poured into ice/water (500 ml) and extracted with benzene (2 x 100 ml). The combined organic layers were further extracted with 10% aqueous sodium hydroxide (3 x 100 ml) and the aqueous-alkaline extract was acidified with 10% hydrochloric acid. Extraction of the acidic solution with CH_2Cl_2, followed by evaporation of the solvent, gave rise to the crude product, which was purified by percolation column chromatography (silica gel, 1:1 hexane/CH_2Cl_2). Further recrystallization from hexane afforded pure **75** as white needles (0.20 g, 11 %):

m.p. 139-140°C (lit.[58] m.p. 140-140.5°C); MS m/z = 185 (M^+ + 1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 5.72 (1 H, bs, Ar-OH, exchangeable with D_2O), 6.69 (1 H, dd, J = 8, 1 Hz, H-2), 7.14 (1 H, dd, J = 8, 1 Hz, H-4), 7.27 (1 H, m, H-3), 7.33 (1 H, m, H-8), 7.41 (1 H, m, H-7), 7.53 (1 H, dd, J = 8, 1 Hz, H-6), 8.10 (1 H, dm, J = 8 Hz, H-9).

2,3,7,8-Tetramethyldibenzo-*p*-dioxin (76). The adapted procedure for the synthesis of DBD (**34**) was used. 2-Chloro-4,5-dimethylphenol (20 g, 0.13 mole), anhydrous K_2CO_3 (9 g, 0.065 mole) and copper powder (1 g) were heated under N_2 in an oil-bath at 190-200°C for 10 h. The tarry mixture was then refluxed under N_2 with 100 ml 5 **M** K_2CO_3 solution for 2 h. The product mixture was extracted with CH_2Cl_2, and the organic portion was washed with 2 **M** KOH (3 x 100 ml). Evaporation of CH_2Cl_2 from the solution gave a crude product, which was recrystallized from CH_3CN, resulting in pure **76** as white needles (0.48 g, 3%): m.p. 167-169°C (lit.[59] m.p. 167°C); MS m/z = 241 (M^+ + 1); ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.11 (12 H, s, CH_3), 6.59 (4 H, s, Ar-H).

4,4',5,5'-tetramethyl-2,2'-biphenol (77). To TMDBD **76** (150 mg) in 195 ml THF was added $NaBH_4$ (10 mg) in 5 ml H_2O. Irradiation of the solution in a Rayonet RPR 100 photochemical reactor (300 nm lamps) at ≈ 18°C for 1 h gave a product mixture consisting of **76** and **77**. Separation of this mixture by preparative TLC (19:1 CH_2Cl_2-ethyl acetate) afforded 25 mg pure product **77** (Rf ≈ 0.38) (16%): m.p. 150-151°C (lit.[62] m.p. 151-152°C); MS m/z 243 (M^+ + 1);

^{1}H NMR (250 MHz, acetone-d_6) δ 2.19 (6 H, s, $c_{5,5'}$-CH_3), 2.20 (6 H, s, $c_{4,4'}$-CH_3), 5.6 (1 H, s, Ar-OH, exchangeable with D_2O), 6.76 (2 H, $c_{3,3'}$-H), 7.01 (2 H, $c_{6,6'}$-H).

3.3 Product Studies

In general, direct photolysis was performed by dissolving samples (20 - 100 mg) in aqueous CH_3CN, dry CH_3CN or other organic solvents. The resulting mixture was poured into a 100 mL quartz tube, cooled with a cold finger (≈ 18°C) and purged with argon for 10 min. Both purging and cooling were continued during photolysis in a Rayonet RPR 100 photochemical reactor (300 nm lamps). The length of photolysis varied from 5-30 min depending on the efficiency of the photochemical reaction.

The solvents CH_3CN, MeOH, 2-propanol and 1,4-dioxane were purchased from Aldrich and used as received after purity checks; CH_2Cl_2 and THF were also purchased from Aldrich but were distilled before use. Spectrophotometric grade (glass-distilled) acetone was used as the solvent of GC and GC/MS analyses. Reagents such as $MgSO_4$, $NaBH_4$ and $NaBD_4$ were used without further purification.

Workup of photoreactions performed in a wholly organic solvent was accomplished by simple evaporation of the solvent. Photoreactions performed in aqueous solution were worked up by adding a saturated aqueous solution of

NaCl and extracting 3 x 100 mL portions of CH_2Cl_2. The organic extracts were then combined and dried over $MgSO_4$. Filtration of the $MgSO_4$ and evaporation of CH_2Cl_2 provided the crude photoproducts which were separated on preparative TLC as required and characterized by ^{1}H NMR, GC and GC/MS. The major parameter for the Varian 3700 GC was set as (or stated otherwise): initial column temp., 60°C, initial colure hold time, 3 min; temp. increase rate, 10°C/min; final column temp., 240°C, final column hold time, 10 min; injector temp., 220°C.

Photolysis of DBD (34) in aqueous CH_3CN. A solution of DBD (**34**) (20 mg, 80 mL 1:1 H_2O-CH_3CN) was irradiated at 300 nm for 20 min. After photolysis, 100 mL saturated NaCl aqueous solution was added, and the solution was extracted with 3 x 100 mL CH_2Cl_2. Uncharacterizable precipitate was observed during extraction. The combined extracts were dried over $MgSO_4$ and evaporated to give a crude product mixture (brown in colour), which was detected by GC/MS. Two strong peaks were observed: retention time, 4.00 ± 0.02 min ($\approx$ 60%; m/e = 184, unreacted **34**); and 4.81 ± 0.02 min ($\approx$ 40%; m/e = 186, product **69**). In addition, a very minor peak was observed at retention time 3.74 ± 0.02 min (< 1% at all conversion) (identified as **5**). Material balance ($\approx$ 60%) of this reaction was measured by GC, using 9-fluorenone (**88**) as the internal standard. The major product was separated on preparative TLC (silica gel, 19:1 CH_2Cl_2-ethyl acetate; Rf, 0.28 (**69**), 0.77 (**34**)); and was identified to be **69** by comparison with a sample of authentic compound, is commercial available: ^{1}H NMR δ 6.97 (4 H, m, H-3,4,5,6), 7.25 (4 H, m, H-3',4',5',6'), 8.39 (s, Ar-OH, exchangeable with D_2O); MS (CI) *m/z* 187 (M^+ + 1).

Photolyses of DBD (**34**) in aqueous CH_3CN solutions with various pH were carried out using the same procedure described above, except that the concentration of hydrogen ion was adjusted with NaOH or HCl solution, as required.

Dark reaction of DBD (34) in aqueous CH_3CN. A solution of DBD (**34**) (20 mg, 80 mL 1:1 H_2O-CH_3CN) was poured into a 100 mL quartz tube, cooled with a cold finger (≈ 18°C) and purged with argon for 30 min. After workup, only unreacted starting material DBD (**34**) was found. Dark reactions were also carried out as controls for all the photoreactions discussed in this Thesis, and all the starting materials were recovered.

Photolysis of 2-phenoxyphenol (5) in CH_3CN. A solution of **5** (20 mg, 80 ml CH_3CN) was irradiated at 254 nm for 20 min. Direct evaporation of the solvent gave the product mixture, which was characterized by GC/MS (initial column temp., 60°C, initial colure hold time, 3 min; temp. increase rate, 10°C/min; final column temp., 240°C, final column hold time, 10 min; injector temp., 220°C). Four major peaks were observed: retention time, 7.93 ± 0.02 min (≈ 20%; *m/e* = 110; identified as catechol), 12.59 ± 0.02 min (≈ 20%; *m/e* = 186; unreacted **5**), 14.73 ± 0.02 min (≈ 35%; *m/e* = 186) and 18.67 ± 0.02 min

(≈ 15%; *m/e* = 186). Compound **69** was not detected in this reaction.

Photolysis of DBD (34) in the presence of $NaBH_4$. To a solution of DBD (**34**) (30 g, 60 mL 1:1 H_2O-CH_3CN) was added $NaBH_4$ (0-62 mg). The mixture was irradiated at 254 nm for 20 min. After photolysis, the product mixture was adjusted to pH 1 with HCl, and then was worked up to give the crude product mixture (colorless), no precipitate was observed in the presence of $NaBH_4$. The product was identified as **69** by GC/MS (retention time, 4.00 ± 0.02 min (40-90%; *m/e* = 184, unreacted **34**); 4.81 ± 0.02 min (10-60%; *m/e* = 186, product **69**)). The mass balance (≈ 95%) of the reaction was measured by GC, using fluorenone (**88**) as the internal standard.

Photolysis of DBD (**34**) in the presence of $NaBD_4$ was carried out using the same procedure as that of $NaBH_4$.

Photoreaction of DBD (34) with $NaBH_4$ added after photolysis. Solutions of DBD (**34**) (40 mg, 160 mL 1:1 H_2O-CH_3CN) were irradiated at 300 nm for 20 min and the reaction mixture was divided into two portions. To one portion was added ≈ 30 mg $NaBH_4$ immediately and the mixture was acidified to pH 1 before workup; another portion functioned as a control and was worked up without adding $NaBH_4$. The time between the end of photolysis to the workup was kept constant for both portions. This crude product mixture was identified by GC (retention time: 4.00 ± 0.02 min, unreacted **34**; 4.81 ± 0.02 min, product **69**), giving rise to a typical product yield of **69** in the control

(47%) and in the reaction with $NaBH_4$ added after photolysis (52%).

Photolysis of DBD (34) in hydroxylic organic solvent. A solution of DBD (**34**) (20 mg, 80 ml MeOH or 2-propanol) was irradiated (300 nm) at 18°C for 20 min. After photolysis, the solvent was evaporated directly to give a product mixture, which was identified by GC, showing 69 as the only major product. The typical component of the product mixture is shown in Table 2.3.

Photolysis of DBD (34) in non-hydroxylic solvent. A solution of DBD (**34**) (20 mg, 80 ml CH_3CN, THF, or 1,4-dioxane) was irradiated at 300 nm for 20 min. After photolysis, the solvent was evaporated directly to give a product mixture, which was identified as two major products **69** (≈ 40%) and **75** (≈ 20%). Product **69** was identified as described earlier. Product **75** was separated on preparative TLC (6:4 CH_2Cl_2-hexane) and was identified by m.p., ^1H NMR and GC/MS: m.p. 139-140°C (lit.[61] m.p. 140-140.5°C); MS m/z = 185 ($M^+ + 1$); ^1H NMR (360 MHz, $CDCl_3$) δ 5.72 (1 H, bs, Ar-OH), 6.69 (1 H, dd, J = 8, 1 Hz, H-2), 7.14 (1 H, dd, J = 8, 1 Hz, H-4), 7.27 (1 H, m, H-3), 7.33 (1 H, m, H-8), 7.41 (1 H, m, H-7), 7.53 (1 H, dd, J = 8, 1 Hz, H-6), 8.10 (1 H, dm, J = 8 Hz, H-9).

Photoproduct yields as a function of photolysis time for DBD (**34**) in dry CH_3CN were obtained by monitoring the product distribution in a series of time intervals. In detail, a solution of DBD (**34**) (30 mg, 60 ml CH_3CN) was irradiated at 300 nm for 330 min, and the samples were collected frequently during photolysis, which were detected by GC to obtain the p distributions at different stages of reaction.

Photolysis of 76 in THF. A solution of **76** (20 mg, 80 ml THF) was irradiated at 300 nm for 20 min. After photolysis, the solvent was evaporated directly to give a product mixture, which was separated on preparative TLC (silica gel, 19:1 CH_2Cl_2-ethyl acetate) to give only one product **77** (Rf ≈ 0.38): m.p. 150-151°C (lit.[62] m.p. 151 - 152°C); MS *m/z* 243 (M^+ + 1); ^1H NMR (250 MHz, acetone-d_6) δ 2.19 (6 H, s, $c_{4,4'}$-CH_3), 2.20 (6 H, s, $c_{5,5'}$-CH_3), 5.6 (s, Ar-OH), 6.76 (2 H, $c_{3,3'}$-H), 7.01 (2 H, $c_{6,6'}$-H).

3.4 Characterization of Reactive Intermediates

3.4.1 UV-Vis Studies

Observation of 2,2'-biphenylquinone (73). A dry CH_3CN solution of DBD (**34**) (4 x 10^{-4} **M**) in a suprasil quartz cuvette was irradiated (300 nm lamps) at ambient temperature for 30 s, resulting in a pink colour. A UV-Vis spectrum was taken immediately after photolysis, giving two absorption bands (λ_{max} 345 and 532 nm) which were assigned as **73** by comparing the absorption bands of 2,2'-biphenylquinone derivatives.[63-67] The decay of the bands was monitored, with a half-life ≈ 1 min (good first order decay).

Observation of 4,5,4',5'-tetramethyl-2,2'-biphenylquinone (79). A dry CH_3CN solution of TMDBD (≈ 4 x 10^{-4} **M**) in a suprasil quartz cuvette was irradiated (300 nm lamps) at ambient temperature for 30 s, again resulting in a pink colour. A UV-Vis spectrum was taken immediately, giving rise to two absorptions (λ_{max} 353 and 566 nm) which were assigned to **79**. Its decay rate was similar to that observed for **73**.

3.4.2 Effect of Photolysis Wavelength

Irradiation of an argon purged dry CH_3CN solution of DBD (**34**) (1.3 x 10^{-3} **M**) in a Rayonet RPR 100 photochemical reactor (sixteen 300 nm lamps, or eight 300 nm lamps/eight 350 nm lamps) at 18°C for 20 min gave two major products, which were identified as **69** and **75**. However, the ratio of product yields (**69/75**) was increased significantly in the presence of eight 350 nm lamps comparing to those with sixteen 300 nm lamps (Table 3.3).

Table 3.1 The Effect of Wavelength on the Product Ratio (**75/69**)

Trial	1	2	3	4	5	Average[c]
Ratio I[a]	0.75	0.82	0.83	0.84	0.83	0.80 ± 0.05
Ratio II[b]	0.60	0.54	0.63	0.53	0.57	0.57 ± 0.05

[a] Ratio of **75** over **69** in the presence of eight 300 nm and eight 350 nm lamps.

[b] Ratio of **75** over **69** in the presence of sixteen 300 nm lamps.

[c] Average with 95% confident limit

3.4.3 Isotope Effect

Solvent isotope effect on the decay rate of 73. Irradiation (300 nm lamps) of an argon purged dry CH_3CN or CD_3CN solution of DBD (**34**) (≈ 6×10^{-4} **M**) in a quartz cuvette at ambient temperature for 30 s generated the intermediate **73**, which was measured by absorption at 532 nm immediately. The decay of **73** was monitored against time to give the rate constants of the decay both in CH_3CN and in CD_3CN. The isotope effect was therefore estimated to be $k_H/k_D = 1.16 \pm 0.06$, by comparing the decay rate constants **73** in dry CH_3CN (k_H) and the decay rate constant of **73** in dry CD_3CN (k_D) (Table 3.2).

Table 3.2 Solvent Isotope Effect on the Decay Rate of **73**

Trial	1	2	3	4
k_H[a] (10^{-3} s^{-1})	7.26	7.18	7.19	7.01
k_D[a] (10^{-3} s^{-1})	6.36	6.38	5.87	6.16
k_H/k_D	1.14	1.13	1.22	1.14

[a] With a system error of ± 2%.

Solvent isotope effect on the product yield of 69. An argon purged solution of DBD (**34**) (≈ 10^{-3} mol dm^{-3}) in dry CH_3CN or CD_3CN was photolyzed

(300 nm lamps) at ambient temperature for 20 min. The product yield of **69** was then measured by GC to evaluate the isotope effect. The isotope effect was estimated to be P_H/P_D = 1.34 ± 0.09 with a 95% confident limit (Table 3.2).

Table 3.3 The Isotope Effect on the Product Yield of **69**

Trial	1	2	3	4	5
Yield[a] of **69** in CH_3CN	23.7	21.8	23.4	23.9	22.6
Yield[a] of **69** in CD_3CN	18.6	14.9	17.8	17.7	17.1
P_H/P_D[b]	1.26	1.46	1.31	1.35	1.32

[a] With a system error of ± 5%.

[b] P_H/P_D was estimated to be 1.34 ± 0.09 with 95% confident limit.

Characterization of dideuterated 69 (69-*O,O-d*$_2$). Irradiation (300 nm lamps) of a CD_3CN (3 mL) solution of DBD (**34**) (4 mg) under argon at ambient temperature for 40 min gave a brown solution. Evaporation of CD_3CN directly afforded the crude product, which was immediately characterized by FT-IR (Nujol mull). An absorption band at 2360 ± 10 cm^{-1} was observed, which is assigned to **69**-*O,O-d*$_2$. Dissolving 20 mg authentic **69** in 3 mL CH_3OD and evaporating the solvent after 30 min afforded the product, which was taken of

FT-IR (Nujol mull), giving rise to the authentic FT-IR spectrum of **69**-*O,O*-d_2 (a strong absorption band at 2370 ± 10 cm^{-1}).

3.5 Triplet Sensitization

Acetone was selected as the triplet sensitizer. A solution of DBD (**34**) (20 mg) in acetone (80 ml) was poured into a 100 ml pyrex tube and cooled to ≈ 18°C by a cold finger. Argon was then used to purge the system for 10 min before photolysis. Purging and cooling were both continued during the photolysis in a Rayonet RPR 100 photochemical reactor with 300 nm lamps. Irradiation of the solution for 20 min gave a product mixture, which was worked up by evaporating the acetone. The product was identified as the unreacted DBD (**34**) (100%). Compound **69** was not detected.

Irradiation of an argon purged CH_3CN solution of DBD (**34**) (20 mg DBD (**34**), 80 ml CH_3CN) in a Rayonet RPR 100 photochemical reactor (300 nm lamps) at ≈ 18°C for 20 min gave a product mixture which was worked up by evaporating the solvent CH_3CN directly. The product mixture was characterized as unreacted DBD (**34**) (70%), **69** (20%) and **75** (10%) by GC.

Irradiation of an oxygen purged CH_3CN solution of DBD (**34**) (20 mg **34**, 80 ml CH_3CN) in a Rayonet RPR 100 photochemical reactor (300 nm lamps) was also carried out at ≈ 18°C for 20 min. The product mixture obtained was worked up by evaporating the CH_3CN and characterized as unreacted DBD

(34) (70%), **69** (20%) and **75** (10%) by GC.

3.6 Product Quantum Yields

Product quantum yields were obtained on an optical bench using an Oriel 200 W Hg arc lamp and an applied physics monochromator set for 280 nm with slits of 7 nm. Samples were prepared by taking 0.75 mL of a 2.72 x 10^{-3} **M** stock solution and diluting it to 3.00 mL with the appropriate solvent mixture in suprasil quartz cuvettes. The UV absorption of each sample was obtained at 280 nm to determine what percent of light would be absorbed by the sample on the optical bench. The samples were then purged with argon for 10 min prior to the photolysis. Purging was continued during the photolysis to stir the solutions. No cold finger was utilized since the intensity of the light source was not sufficient to heat up the samples appreciably. Photolysis times varied between 20-60 min depending on the conversion expected for the photoproducts. The yields of these photoproducts were kept low ($\leq$ 20%) to avoid secondary photoproducts.

Samples photolyzed in CH_3CN were simply worked up by evaporation of the solvent. Samples photolyzed in the presence of H_2O were placed in a 10 ml test tube and NaCl added to saturate the aqueous layer. Extractions with 3 portions of CH_2Cl_2 (3 mL each) were then performed utilizing a pasteur pipette to mix the layers. The organic extracts were collected and dried over $MgSO_4$

. Filtration and evaporation of the organic solvents provided the photoproducts required for analysis. These photoproducts were then dissolved in acetone (spec. grade) and quantified by GC using 9-fluorenone (**88**) as an internal standard to calculate the moles of **69** formed and the mass balance of the photoreactions. Three GC injections were performed to achieve an average for the percent conversion to **69** resulted from the reaction.

The light intensity in einsteins/min/3 mL were measured before each photolysis with a chemical actinometer.[70] If the photolysis took longer than an hour, the light intensity was measured before and after the photolysis and an average was taken. The chemical actinometer utilized was potassium ferrioxalate ($K_3Fe(C_2O_4)_3$).[68,70] A solution of 0.0060 **M** potassium ferrioxalate in 0.050 **M** H_2SO_4 (250 mL) was prepared in the dark along with a 0.2% by weight solution of 1,10-phenanthroline (**95**) in distilled H_2O (to be used later). The actinometer solution (3.00 mL) in a suprasil quartz cuvette was then photolyzed on the optical bench in the dark for 5 min with argon purging to mimic the conditions used for photolysis of the samples. Along side the photolyzed potassium ferrioxalate solution was placed another 3.00 mL sample of potassium ferrioxalate, also in a suprasil quartz cuvette, to act as a control.

Irradiation of actinometer solution leads to reduction of the Fe^{3+} (eq. 3.1).[68] The quantity of Fe^{2+} produced was measured by reacting it with 1,10-phenanthroline (**95**) to produce a complex, which has an absorption at λ_{max} 510 nm. The quantity of Fe^{2+} can therefore be determined from the strength of this absorption.

$$2Fe^{3+} + C_2O_4^{2-} \dashrightarrow 2Fe^{2+} + 2CO_2 \tag{3.1}$$

The Fe^{2+} 1,10-phenanthroline complex was prepared by mixing 2.00 mL of **95** stock solution in a 10 mL volumetric flask with a buffer ($NaOAc\bullet3H_2O$), 0.50 mL. A portion of the photolyzed potassium ferrioxalate (1.00 mL) was then added to the volumetric and distilled H_2O added to make the solution up to the mark. The volumetric flask was wrapped with Aluminium foil, shaken vigorously and then stored for 30 min in the dark to allow forming the complex. The above procedure was performed under a red light source and was repeated for the blank. A portion of the complex samples were then transferred to UV cuvettes and the absorption at 510 nm measured. The difference in absorptions (ΔA) of the photolyzed potassium ferrioxalate and the blank potassium ferrioxalate was determined and substituted in the following equation (eq. 3.2) for light intensity (I)[68] in einsteins/min (absorbed by the 3 mL cuvette solution).

$$I = \frac{\Delta A V_2 V_3 x 10^{-3}}{\epsilon \phi_\lambda t V_1} \tag{3.2}$$

Where:

V_1 is the volume of irradiated actinometer withdrawn (1.00 mL).

V_2 is the volume of actinometer irradiated (3.00 mL).

V_3 is the volume of volumetric flask (10.00 mL).

ε is the extinction coefficient for the Fe^{2+}-**95** complex at 510 nm (1.11×10^4 L mol^{-1} cm^{-1}).

Φ_λ is the known quantum yield for Fe^{2+} formation at the wavelength used for photolysis (280 nm, 1.25).

t is the time of photolysis (5 min.).

The measured light intensity was then corrected to take into account only that percentage of the light absorbed by the samples. This corrected value along with the moles of photoproduct obtained in the photolysis of DBD (**34**) were then substituted in eq. 2.21 to find the quantum yield (Φ_p), which is the quantum yield of the formation of **69** from the photoreaction of DBD (**34**).

The mass balances of the photoreactions were also estimated by comparing the amount of the starting material DBD (**34**) with the amount of products recovered from the product mixture (eq. 3.3). The amount of the products was detected from GC, using 9-fluorenone (**88**) as the internal standard.

$$Mass\text{-}Balance = \frac{Moles\text{-}of\text{-}Compounds\text{-}Recovered}{Moles\text{-}of\text{-}Compounds\text{-}Utilized} \qquad (3.3)$$

Quantum yields (Φ_p) of DBD (34) in dry CH_3CN. A sample of **34** (2.03 x

10^{-6} mole) in CH_3CN (3.00 mL) was prepared by transferring 0.75 mL of the DBD (**34**) stock solution (2.72 x 10^{-3} **M** in CH_3CN) to a cuvette and diluting it to 3.00 mL with CH_3CN. This solution was photolyzed under argon on the optical bench for 59 min. The product mixture was worked up by evaporating the solvent directly and the product yields were measured by GC, using 9-fluorenone (**88**) as the internal standard to give the product yield of **69**. The light intensity absorbed by DBD (**34**) was obtained by the method described above. An average value of Φ_p (0.013 ± 0.001) was estimated from three trials (Table 3.4). The mass balance was estimated to be 55% ± 5% (include approximately 15% contribution from product **75**, which was not detected in this experiment), based on the method described above.

Table 3.4 Data from the photolysis of **34** in CH_3CN for Φ_p calculation

Sample Number	1	2	3
Conv. of **34** to **69** (10^{-7} mole)	1.80	2.00	2.00
Intensity Absorbed(10^{-5} mole)	1.50	1.50	1.50
Φ_p (Formation of **69**)	0.012	0.013	0.013
Mass Balance[a]	46%	48%	50%

[a] The contribution of **75** to the mass balance was not included

Quantum yields (Φ_p) of DBD (34) in 1:1 CH_3CN-H_2O. A sample of DBD

(**34**) (2.03×10^{-6} mole) in 1:1 CH_3CN-H_2O (3.00 mL) was prepared by transferring 0.75 mL of the DBD (**34**) stock solution (2.72×10^{-3} **M** in CH_3CN) to a cuvette and diluting it to 3.00 mL with 0.75 mL CH_3CN and 1.50 mL distilled H_2O. This solution was photolyzed under argon on the optical bench for 40 min. The product mixture was placed in a 10 ml test tube and NaCl was added to saturate the aqueous layer. Extraction with 3 portions of CH_2Cl_2 (3 mL each), followed by evaporation of the organic solvent provided the photoproducts, which were then quantified by GC, using 9-fluorenone as the internal standard to give the product yield of **69**. The light absorbed by **69** was obtained by the method described earlier. An average value of Φ_p (0.016 ± 0.001) was estimated from six trials (Table 3.5). The mass balance was estimated to be 62% ± 2%, based on the method described above.

Table 3.5 Data from the photolysis of **34** in 1:1 CH_3CN-H_2O for Φ_p calculation

Sample Number	1	2	3	4	5	6
Yield of **69** (10^{-7} mol)	1.43	1.56	1.56	1.64	1.52	1.59
Light (10^{-5} mol)	1.02	1.02	1.02	1.02	1.02	1.02
Φ_p (Formation of **69**)	0.014	0.016	0.016	0.016	0.015	0.016
Mass Balance	61%	63%	63%	60%	66%	61%

Quantum yields (Φ_p) of DBD (34) in the presence of $NaBH_4$. A sample of DBD

(**34**) (2.03×10^{-6} mole) in 1:1 CH_3CN-H_2O (3.00 mL) was prepared by transferring 0.75 mL of the DBD (**34**) stock solution (2.72×10^{-3} **M** in CH_3CN) to a cuvette and diluting it to 3.00 mL with 0.75 mL CH_3CN and 1.50 mL aqueous $NaBH_4$ (1.02×10^{-5} mole). This solution was photolyzed under argon on the optical bench for 20 min. The product mixture was placed in a 10 ml test tube and NaCl was added to saturate the aqueous layer. Extractions with 3 portions of CH_2Cl_2 (3 mL each), followed by evaporation of the organic solvents afforded the photoproducts, which were then quantified by GC, using 9-fluorenone as the internal standard to give the product yield of **69**. The light absorbed by **69** was obtained by the method described above. A average of the Φ_p (0.064 ± 0.008) was estimated from six trials (Table 3.6). The mass balance was estimated to be 94% ± 3%, based on the method described above.

Table 3.6 Data from the photolysis of **34** in 1:1 CH_3CN-H_2O in the presence of $NaBH_4$ for Φ_p calculation

Sample Number	1	2	3	4
Conv. of **34** to **69** (10^{-7} mole)	3.60	3.00	3.20	3.0
Intensity Absorbed(10^{-6} mole)	5.10	5.10	5.10	5.1
Φ_p (Formation of **69**)	0.070	0.059	0.063	0.059
Mass Balance	91%	95%	95%	95%

3.7 Fluorescence Studies

A fluorescence quantum yield (Φ_f) is a measure of the fraction of an excited species which is deactivated by fluorescence. In general, Φ_f is determined by using a reference with a know Φ_f^r. The fluorescence quantum yield of DBD (**34**) is too small ($\Phi_f < 0.001$) to be measured precisely using this method. However, the fluorescence quantum yield of xanthene (**24**) was detected by using dibenzofuran as a reference. This particular standard was chosen since the region of its emission overlaps the region of emission of xanthene.

Dilute solutions of each were prepared in cyclohexane (dibenzofuran) or CH_3CN (for **24**) to prevent self quenching which can occur at high concentrations. Samples of each were then placed in four sided suprasil quartz cuvettes and a UV spectrum recorded for each on a Varian Cary 5 UV-Vis-NIR spectrophotometer to obtain a crossing point in the two spectra. The absorption of the sample and standard must be same to insure that each absorbs the same number of photons. Dilutions of dibenzofuran and **24** were then performed to match the crossing point at 265 nm.

The samples from UV study were then purged with argon and placed in the fluorometer. Excitation of each compound was done at the wavelength of the matching point (265 nm) and the resulting fluorescence was recorded. The areas in each fluorescence spectrum were then measured and substituted in the following equation (eq. 3.4) to determine Φ_f^s for xanthene.

$$\Phi_f^s=\Phi_f^r\frac{A^s}{A^r}\left(\frac{\eta^s}{\eta^r}\right)^2 \qquad (3.4)$$

Where:

A^s is the area under the sample fluorescence curve.

A^r is the area under the reference fluorescence curve.

Φ_f^s is the fluorescence quantum yield for the sample.

Φ_f^r is the fluorescence quantum yield for the reference (0.44 in cyclohexane).

η^s is the refractive index of the solvent used with the sample (CH_3CN: 1.3442).

η^r is the refractive index of the solvent used with the reference (cyclohexane: 1.4266).

Using all the areas obtained, three trials were carried out to obtained the corresponding Φ_f^s (Table 3.7).

Table 3.7 The fluorescence quantum yield[a] of xanthene (**24**) in CH_3CN

Trial	1	2	3	Average
A^s/A^r	0.72	0.81	0.70	na
Φ_f^s (**24**)	0.28	0.32	0.27	0.29 ± 0.07

[a] Dibenzofuran (Φ_f^r = 0.44 in cyclohexane) as a reference.

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