The Photochemistry of Aryl Halides and Related Compounds

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1 Introduction

There have been several earlier reviews on the photochemistry of alkyl and aryl halides (Sammes, 1973; Sharma and Kharasch, 1968; Kharasch, 1969; Grimshaw and de Silva, 1981). Due to the widespread use of substituted aryl halides as pesticides, electrical insulators, moth proofing agents, etc. and the environmental problems which the use of these compounds pose, it seems worthwhile reconsidering the photochemistry of these compounds. Furthermore, the photoinduced decomposition of aryl halides is used extensively in synthesis, and much of this latter work has been recently reviewed (Grimshaw and de Silva, 1981).

It is well established that on photolysis, many aryl halides undergo homolysis (1) to generate aryl radicals and halogen atoms. The question as to

$$\mathbf{Ar} - \mathbf{Hal} \xrightarrow{h_{\mathbf{V}}} \mathbf{Ar} \cdot + \mathbf{Hal} \cdot \tag{1}$$

whether the excited singlet or triplet state or indeed both excited states are responsible for reaction, is of considerable importance. Thus, if reaction occurs from the excited singlet state, the homolytic process may well be in competition with an electrocyclic reaction. Compound [2] illustrates the point. In principle this compound may photoisomerize to give [1] which



Products

may then undergo further photoreactions. The photoisomerization is in competition with the electrocyclic reaction to give [3] and the homolytic reactions which produces [4]. This example also illustrates the way in which conformational factors affect the outcome of these reactions. That haloaromatic compounds can undergo electrocyclic reactions to the exclusion of homolysis is shown by the elegant work of Begley and Grimshaw (1977).



They showed that [5] photocyclizes to give [6] as the only product. Electrochemical reduction of aryl halides results in the generation of aryl radicals; the formation of [7] must involve such species. The absence of [7] from the products of the photochemical reaction indicates that in this case the electrocyclic reaction takes precedence over the homolytic reaction. In a related piece of work (Grimshaw and Haslett, 1980) it was found that irradiation of [8] in cyclohexane solution produces [9] and [10]. Electrochemical reduction of [8] does not produce [9] but gives a range of other products which are related to [10].



The ability of an electrocyclic reaction to compete with a homolytic reaction will depend upon the relative energies of activation for the two processes and the energy available for reaction. Steric factors should be important in electrocyclic reactions since there is likely to be more steric overcrowding in the transition state. The homolytic reaction may well result in the relief of steric overcrowding in the rate-determining step, e.g. the homolysis of 2-halobiphenyls. The competition between electrocyclic and homolytic processes should also depend upon the nature of the halogen since homolysis becomes progressively easier as the substituent is changed $F \rightarrow Cl \rightarrow Br \rightarrow I$. Thus in the case of [11] irradiation leads to products which were shown, unequivocally, to be derived *via* radical intermediates (Hey *et al.*, 1971, 1972). The formation of cyclized products in this reaction is attributed to the fact that the favoured conformation of the amide is that depicted in [11a] rather than [11b].

The precise mechanism for photoinduced homolysis of aryl—halogen compounds will be dependent upon both the nature of the halogen substituent and the aryl group. However, two facts should be borne in mind. The first of these is the strength of the carbon—halogen bond which is to be homolyzed; some typical values (Egger and Cocks, 1973) are shown in Table 1. The second point is that halogen substituents increase intersystem crossing from both the excited singlet to the triplet state and from the triplet state to the singlet ground state. One may well anticipate that the triplet state of haloaromatics will be efficiently populated and therefore be a likely candidate for



TABLE 1

Bond dissociation energies for some carbon-halogen bonds^a

	<i>D</i> (C-X) ^{<i>b</i>}		<i>D</i> (C-X) ^{<i>b</i>}
Cl	94.5	Br	79.2
I	64.4	F	123.9
CH ₃ CH ₂ —Cl CH ₃ CH ₂ —I	80.8 53.2	CH ₃ CH ₂ —Br	67.6

^aEgger and Cocks, 1973 ^b In kcal mol⁻¹

the state responsible for homolysis. However, the triplet states of many systems, e.g. biphenyl, naphthyl and anthracenyl have energies below the energy required to homolyze the aryl—chlorine bond. It is therefore convenient to discuss the mechanisms of this reaction by compound type.

2 Chloroaromatics

CHLOROBENZENES

Measurement of the fluorescence lifetimes of the dichlorobenzenes in the vapour phase (Shimoda *et al.*, 1979) showed that the chlorine substituents induce fast non-radiative decay of the excited singlet state and that since the aryl—chlorine bond is of lower energy than the first excited singlet state this decay must involve bond homolysis as well as intersystem crossing. The fluorescence lifetimes depend upon the pattern of substitution: 1,2-dichlorobenzene 290 ns, 1,3-dichlorobenzene 280 ns, and 1,4-dichlorobenzene 170 ns. Chlorobenzene has a low fluorescence quantum yield and a high quantum yield for the production of radicals.

The mechanism of bond homolysis for chloro-, bromo- and iodobenzene in the vapour phase has been studied using an excitation source emitting at 193 nm (Freedman *et al.*, 1980). There appear to be two reaction pathways. One pathway involves intersystem crossing from a singlet $\pi\pi^*$ state to a triplet $\sigma\sigma^*$ which homolyzes. For chlorobenzene intersystem crossing occurs from the S₁ $\pi\pi^*$ state whereas for bromo- and iodobenzene S₃, S₂ and S₁ $\pi\pi^*$ states are involved. In the other pathway a distortion of the S₁ $\pi\pi^*$ state occurs as takes place in the formation of prefulvene. This distortion enables electronic energy to enter the phenyl ring as vibrational energy and so lead to homolysis. This concept of a distorted excited state being responsible for homolysis does not appear to have been considered as a possible reaction pathway for solution phase experiments. A study has been made of the vapour phase dechlorination of chlorotoluenes in the presence of ethene (Koso *et al.*, 1979) and it was concluded the homolysis occurs from the triplet state.

There is much less precise information concerning the photophysical parameters for chlorobenzenes in solution. It is known that chlorobenzene and many of its derivatives homolyze on photolysis. Moreover, if benzene is used as solvent, the chlorine atom is replaced by a phenyl group, whereas the use of hydrogen-donating solvents such as methanol leads to dehalogenation. Irradiation of chlorobenzene in benzene leads to biphenyls and in this system the solvent gathers the light. Benzene can act both as a singlet and a triplet sensitizer (Dubois and Wilkinson, 1963). Thus, although the homolysis of chlorobenzenes is sensitized by benzene, one cannot draw any conclusion as to the excited state of chlorobenzene responsible for reaction. To elucidate the mechanism of homolysis of chlorobenzene and other chloroaromatics, sensitization and quenching experiments have been undertaken (Bunce et al., 1980). The results favour the view that the triplet state is responsible for reaction and, in support of this, it was pointed out that the quantum yield for dechlorination is high (0.54). However, the energy of the triplet state (85 kcal mol⁻¹) lies well below that of the aryl-chlorine bond strength (Table 1) and therefore the question arises as to how this energy deficiency is made up. As yet this question has not been satisfactorily answered. That alkyl ketones can sensitize the homolysis of chlorobenzene has been demonstrated (Augustyniak, 1980). Since it has recently been shown that triplet states of carbonyl compounds will form excited complexes with electron deficient alkenes (Maharaj and Winnik, 1982) one cannot be certain whether the sensitization observed by Augustyniak is due purely to energy transfer. A variety of substituted chlorobenzenes undergo homolysis on irradiation in benzene solution, e.g. 4-chloroaniline and 2-, and 4-chlorobenzonitriles (Robinson and Vernon, 1969, 1971). Interestingly 4-chloroacetophenone and 4-chlorobenzophenone display very low photoreactivity even though their triplet yields are close to unity. This lack of reactivity may be due to the lowest triplet states of these compounds being associated with an $n \to \pi^*$ transition rather than a $\pi \to \pi^*$ or $\sigma \to \sigma^*$ transition.

In another study aimed at determining the mechanism whereby halobenzenes homolyze, compounds such as [12] were irradiated in methanol



(Davidson *et al.*, 1980b). It was found that the compounds dechlorinate rather than suffer homolysis of the carbon—bromine bond. This is rather surprising when one considers that the methylene—bromine bond is weaker than the aryl—chlorine bond by ~35 kcal mol⁻¹. The homolysis of the carbon—chlorine bond obviously competes very effectively with energy transfer to the methylene—bromine bond. The triplet state of [12] is of higher energy than the methylene—bromine bond and is of lower energy than that of the aryl—chlorine bond. Thus it was concluded that the excited singlet state of [12] is responsible for homolysis. If by any chance the triplet state of chlorobenzenes can undergo homolysis in solution then this process must have a very high rate constant to compete so effectively with energy transfer.

Another very interesting example of dechlorination competing effectively with other processes is shown by [13] (Eichin *et al.*, 1980). It was found that irradiation of *meso*-[13] in decane gave the *meso* dechlorinated product, dechlorination having competed with homolysis of the benzylic carbon carbon bond. Homolysis of this benzylic bond should be facile since its energy lies below that of both the excited singlet and triplet states of chlorobenzene. The photochemistry of the benzylic compounds [14a] and [14b] has also been investigated (Robinson and Vernon, 1969; Davidson *et al.*, 1980b). Compound [14a] was found to be relatively stable when irradiated in benzene solution but irradiation of [14b] in methanol solution led to dechlorination. Thus in [14b] the dechlorination process competed with both singlet and triplet energy transfer. This result suggests that the excited singlet state of the chloroaromatics must be at least in part responsible for the homolysis.

The observation that benzene can sensitize the homolysis of chlorobenzene (Robinson and Vernon, 1969, 1971) raised the question as to whether a benzene—chlorobenzene exciplex could be involved in the process. This point has been examined by Bunce and Ravanal (1977) who found that [15]



undergoes dechlorination relatively inefficiently. They found that [15] exhibits exciplex emission showing that the two aryl groups can interact intramolecularly. It would appear that exciplex formation leads to energy wastage rather than efficient chemical reactions. By extrapolation it seems reasonable to suggest that irradiation of chlorobenzenes in benzene solution leads to intermolecular exciplex formation. If high concentrations of benzene are employed, termolecular complex formation (one molecule of chlorobenzene and two molecules of benzene) is also likely. One really needs to know the extent to which these complexes lead to deactivation before one can exclude the excited singlet state of the chlorobenzene and benzene play an important part in determining the product distribution has been demonstrated by Kojima *et al.* (1981). Thus irradiation of either neat chlorobenzene or concentrated benzene solutions of chlorobenzene gives a different ratio of the o-, m- and p-chlorobiphenyls than when dilute benzene solutions of the solution for the solution for the solutions of the soluti

chlorobenzene are used. The concentration effect was attributed to the participation of chlorobenzene excimers at high chlorobenzene concentrations. However, Bunce *et al.* (1980) claim that the excited singlet excimer is an energy-wasting intermediate rather than a reactive one.

The formation of exciplexes between chlorobenzene and benzene and its derivatives has been looked at in other contexts. It has been found (Grimshaw and de Silva, 1980a) that the chloro-compound [16a] undergoes photocyclization in cyclohexane solution whereas the bromo- and iodo-compounds



[16b,c] dehalogenate. To rationalize these observations it was suggested that interaction of the chlorine atom in the triplet state of the *cis*-conformer of [16a] with the other benzenoid group leads to an exciplex from which carbon—chlorine bond homolysis occurs with resultant cyclization. If N,Ndiethylaniline is added to the reaction mixture only benzanilide is formed, suggesting that the greater electron-donating ability of the amine has negated the rather weak intramolecular complexing ability. For [16b] and [16c] the carbon—halogen bonds are of lower energy than the triplet state and therefore homolysis can occur in the triplet manifold of the *trans*-conformer, which is the most extensively populated ground-state conformer. For the chlorocompound [16a] the *trans*-conformer is unreactive since the carbon—chlorine bond is of higher energy than the triplet state and the anilino group is not suitably situated spatially to assist dechlorination. Interestingly, the reactivity of [16a] is reduced to zero by the addition of polar solvents to the cyclohexane solution. This suggests that the initially created excited state has some charge-transfer character and that this can be solvated by polar solvents to such an extent that its energy is lowered below that of the intramolecular exciplex formed between the chlorophenyl and anilino groups. The excited state responsible for the reactivity of [16a-c] was assigned to the triplet state on the basis of sensitization and quenching studies. However, it is difficult to tell if some of the reactivity of [16a] is not due to the excited singlet state and whether dissociation of [16b,c] will not be so efficient as to compete with intersystem crossing.

A wide variety of substituted dichlorobenzenes has been shown to undergo dechlorination on irradiation in methanol solution (Mansour *et al.*, 1980). Usually monochloro-compounds are the major products. Accurate quantumyield measurements have been made and, unlike chlorobenzene, some of the reactions can be carried out by sensitization using either acetophenone or benzophenone. Quantum yields are temperature dependent and dechlorination does not occur below -70° C. This indicates that electronic excitation is insufficient to cause bond homolysis and that some energy from the surround-ings (as heat) has to be supplied to overcome the activation energy barrier for homolysis.

1,4-Dichlorobenzene on irradiation in the presence of nitrogen oxides leads to the production of nitro-compounds with little evidence of dechlorination (Nojima and Kanno, 1980). This is rather surprising when one considers the relative ease with which chlorobenzenes dechlorinate.

The photochemistry of trichlorobenzenes has been examined (Åkermark et al., 1976; Choudhry et al., 1979). Irradiation of 1,2,4-trichlorobenzene [17] in either cyclohexane or propan-2-ol produces 1,3- and 1,4-dichlorobenzene; loss of a chlorine atom occurs so that the steric compression between the *ortho*-chlorine atoms is relieved. No trace of chlorine loss from the 4-position could be found. The relief of steric congestion must play some part in the energetics of the homolytic process and it is interesting to find that there is some evidence which supports the view that both the excited singlet and triplet states are reactive. Thus it is found that the ratio of the products formed in the reaction is sensitive to the presence of oxygen. In propan-2-ol the ratio of 1,3-dichlorobenzene to 1,4-dichlorobenzene changes from 0.65 in degassed solution to 0.5 in aerated solution. Furthermore the use of acetone as sensitizer leads to a ratio of 3 : 1. These results support the view that the triplet state is involved and, surprisingly, that the triplet state leads to a different product distribution to that from the singlet state. The question of the relative reactivity of excited singlet and triplet states is not



really understood and is the subject of current debate (Henne and Fischer, 1977). The sensitization and quenching experiments on [18] are in agreement but the problems associated with such experiments are highlighted by this example. The fact that the product distribution is unaffected by substrate concentration suggests that only triplet sensitization is occurring. Since the sensitizer also reacts with the solvent and therefore some is probably consumed during the irradiation period, it is difficult to make a quantitative appraisal of the results. In a related piece of work (Choudhry et al., 1979) it was shown that [18] and 1,3,5-trichlorobenzene dechlorinate on irradiation in methanol solution. The product distribution from [18] clearly shows that the relief in strain plays a major part in deciding which is the most favourable chlorine atom to lose. Sensitization experiments, using acetone, and quenching experiments, utilizing isoprene and oxygen, demonstrate that the triplet state of [18] is a reactive intermediate and that 1,3-dichlorobenzene is the favoured product from this species. The results indicate that formation of 1,3-dichlorobenzene is more favoured by reaction of the triplet than the excited singlet state. Why should this be so? The excited singlet state has approximately 15 kcal mol⁻¹ more energy than the triplet state and therefore should exhibit less regioselectivity. Since formation of 1,3-dichlorobenzene is the process leading to the greatest relief of strain, the process presumably has the lowest energy of activation and is consequently the more favoured pathway for the less energetic triplet state.

Measurements of the quantum yields for dechlorination of chloroanisoles and chlorotoluenes has been made (Mansour *et al.*, 1979) (Table 2). If it is assumed that the quantum yields of formation of the excited singlet and triplet states are similar for all the compounds, it appears that chlorotoluenes are more reactive than chloroanisoles. This is what one would expect on the basis of the influence of OMe vs Me upon the polar contribution to the

TABLE	2

Starting compound	Products	Quantum yield
2,6-Dichloroanisole	2-Chloroanisole Anisole	5.24×10^{-3}
3,5-Dichloroanisole	3-Chloroanisole Anisole	7.18×10^{-2}
2,4-Dichlorotoluene	4-Chlorotoluene Toluene	7.59×10^{-3}
2,5-Dichlorotoluene	3-Chlorotoluene Toluene	1.44 × 10 ⁻¹
3,4-Dichlorotoluene	4-Chlorotoluene Toluene	1.10 × 10 ⁻¹

Quantum yields for dechlorination of chloroanisoles and chlorotoluenes in methanol^{α}

^a Mansour et al., 1979

transition state for the homolytic reaction. It is, however, surprising to find that 3,5-dichloroanisole dechlorinates more efficiently than dichloroanisoles bearing a 2-chloro substituent. A similar situation arises with the chlorotoluenes. From the work on trichlorobenzenes (Åkermark *et al.*, 1976; Choudhry *et al.*, 1979) one would have expected that the chlorine atoms in the 2-position would be particularly prone to homolysis. Irradiation of 4-chloroanisole in methanol gives rise to both homolysis (producing anisole) and nucleophilic substitution (Soumillion and De Wolf, 1981). It has been suggested that the substitution reaction involves formation of a radical ion pair, the radical cation of which reacts with methanol to give 1,4-dimethoxybenzene.

The relevance of the strength of the carbon-halogen bond relative to the energy of the excited state undergoing reaction has been examined using compounds [19a-c] (Grimshaw and de Silva, 1980b). These compounds



undergo photocyclization on irradiation in cyclohexane and the quantum yields for this process show a strong wavelength dependence (Table 3). This wavelength effect suggests that dissociation is occurring from either a vibrationally excited first excited singlet state or an upper excited singlet state. The latter could take place if the energy entering the molecule *via* the $\sigma \rightarrow \sigma^*$ transition of the arylhalo group leads solely to dissociation rather than being channelled into the lower lying $\pi \rightarrow \pi^*$ transition.

TABLE 3

Turne di seti sus	Quantum yield ($\times 10^2$)		
wavelength/nm	$\mathbf{X} = \mathbf{Cl}$	X = Br	$\mathbf{X} = \mathbf{I}$
245	1.2	110	460
315	< 0.2	4	90
335	< 0.4	< 0.4	9
370	< 0.1	< 1	< 4

Quantum yields for the photocyclization of [19 a-c]^a

^a Grimshaw and de Silva, 1980b

CHLORINATED BIPHENYLS

The photophysics of these compounds is documented far better than that for the chlorobenzenes. Biphenyl itself is a twisted molecule due to the steric interaction between the hydrogen atoms at the 2,2'- and 6,6'-positions. This twisting leads to a decrease in conjugation. Excitation produces a nonplanar singlet state which relaxes to an excited singlet state having a greater degree of planarity and a planar triplet state. Measurement of the quantum yields of phosphorescence and phosphorescence spectra gives data on the relaxed (planar) triplet state. This relaxed state may however not be a reactive state and one must use caution in using phosphorescence data to interpret chemical reactivity. Table 4 summarizes some of the known photophysical parameters of the chlorinated biphenyls and the quantum yields for dechlorination at room temperature (Bunce et al., 1978; Ruzo et al., 1974, 1975a). Inspection of Table 4 shows that for all the chlorinated biphenyls, intersystem crossing is efficient although they do have a measurable quantum yield of fluorescence. The photoreactive compounds contain a chlorine atom at the 2-position. This substituent will, because of its size, increase the energy of activation for the biphenyl system to achieve planarity. Consequently, its expulsion will lead to a far greater relief of strain than if the chlorine had been substituted at either a 3- or 4-position. Compounds containing a 2-chloro group have a shorter triplet lifetime (calculated from quenching data obtained from experiments using cyclohexa-1,3-diene as a triplet quencher) than those not having a chlorine substituent in an *ortho*-position, and this may be a manifestation of the importance of homolytic carbon—chlorine bond cleavage as a non-radiative decay route. Product studies (Ruzo *et al.*, 1975a; Ruzo and Zabik, 1975) show that it is the *o*-chloro substituents which are lost preferentially.

TABLE 4

Positions of					
substitution	ዋF ^a	ዋ₽ ^a	$\tau_{\rm T} / 10^{-8} {\rm s}$	φr	
2	0.09	0.46		0.39ª	
3	0.07	0.27		0.0011 ^a	
4	0.07	0.60		0.0006 ^a	
2,4	0.02			0.62 ^a	
2,5	0.06			0.13 ^a	
2,21	0.005	0.95		0.16 ^a	
2,4,5	0.11			0.43 ^a	0.05 ^c
2,4,6	0,003			0.14 ^a	0.02 ^c
2,2',4,4'	0.02	0.94	0.78	0.45 ^a	0.10 ^b
2,2',3,3'			0.77	0.007^{a}	
2,2',5,5'	0.0007		0.67	0.0053ª	0.01 ^b
2,2',6,6'			0.70		0.006 ^b
3,3',4,4'	0.08		2.20	0.005ª	
3,3',5,5'	0.02	0.41	1. 9 1	0.0003ª	0.002 ^c
2,2′,4,4′,6,6′	0.003	~1.0			

Photophysical parameters and quantum yields for dechlorination (ϕ_{r}) of chlorinated biphenyls

^a Bunce *et al.*, 1978; φ_r measured using 245 nm radiation with iso-octane as solvent ^b Ruzo *et al.*, 1974; φ_r measured using 300 nm radiation with cyclohexane as solvent

^c Ruzo et al., 1975a; φ_r measured using 300 nm radiation with cyclohexane as solvent

The quenching studies (Bunce *et al.*, 1978; Ruzo *et al.*, 1974) utilizing cyclohexa-1,3-diene suggest that the triplet state is responsible for reaction. However, it has been pointed out (Bunce *et al.*, 1978) that the diene also quenches the excited singlet state of the chlorobiphenyls and it is therefore possible that quenching of both excited singlet and triplet states is occurring. If this had been the case one should have observed some curvature in Stern-Volmer plots and from the published data (Ruzo *et al.*, 1974) this does not seem to be the case. Recently it has been shown (Bunce and Gallacher, 1982) that the kinetics for the 4-chlorobiphenyl/diene system are not amenable to

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a simple kinetic analysis due to the fact that it is impossible to select conditions under which the whole of the incident radiation is absorbed by the biphenyl. Apparently the chloroaromatic reacts with the excited diene, and in the case of 1-chloronaphthalene, cycloadducts were isolated. As a consequence of these findings it is impossible to give a rigorous explanation for the effect of added dienes upon the photochemistry of chloroaromatic compounds. Attempts have been made to employ the heavy atom effect. This method relies upon the ability of an added compound containing a heavy atom (e.g. bromine or iodine) or a heavy atom itself (e.g. xenon) to enhance the rate of intersystem crossing between an excited singlet state and a triplet state. If this occurs, the triplet yield being thereby increased, and if the triplet lifetime is not appreciably shortened, then the yield of triplet product should be increased. The results (Bunce et al., 1978) are not totally convincing but do lend some credence to the view that the triplet state participates in the reaction. Sensitization studies (Bunce et al., 1978) provided very little convincing evidence.

From the fact that the quantum yields for dechlorination are often higher than the quantum yields of fluorescence (Table 4) it has been concluded that the triplet state is the reactive state. The quantum yields of reaction are greater than those of fluorescence only when there is an o-chloro substituent and the evidence presented suggests that the triplet states are involved in the reactions of these compounds. However, within the series of chlorobiphenyls containing an o-chloro substituent there is little correlation between quantum yields of reaction and of phosphorescence and this is not surprising when one considers that the quantum yield of phosphorescence is made up of many rate constants which include the rate constant for reaction. Given that the triplet state is the reactive species, the question arises as to how homolysis of a bond can occur in a compound whose triplet energy lies below the bond dissociation energy. What is not known with any certainty is the bond energy of the carbon-chlorine in bonds in ortho-substituted chlorobiphenyls. As previously pointed out the relief of steric strain caused by homolyzing such a bond may well bring the energy of activation for homolysis below the triplet energy of the biphenyl. Furthermore the triplet energy of a 2-chlorobiphenyl is higher than that of biphenyl itself by 8 kcal mol⁻¹ (Wagner and Scheve, 1977). The fact that the phosphorescence spectrum of 2-chlorobiphenyl (Wagner and Scheve, 1977) shows a broad structureless band whereas that of 4-chlorobiphenyl is structured and similar to that of biphenyl, shows that the o-chloro substituent does affect the geometry of both the ground and excited states. Thus the energetics for the loss of chlorine from the triplet state of an o-chlorobiphenyl may be favourable. For biphenyls bearing chlorine substituents at positions other than the ortho ones, the carbon-chlorine bond strength should be similar to the value given in Table 1. Since the triplet energy of these compounds is around 64 kcal mol⁻¹ (Ruzo *et al.*, 1975a) (slightly higher for the nonplanar triplets) the loss of chlorine is an endothermic process. This would account for the very low quantum yields for dehalogenation of the compounds, and it is possible that the reaction that does occur arises from the first excited singlet state. On irradiation in neutral or alkaline propan-2-ol solution, 2,4,6-trichlorobiphenyl undergoes preferential loss of an *ortho* chlorine (Nishiwaki *et al.*, 1980). Polychlorinated biphenyls also undergo loss of chlorine upon irradiation in alkaline solutions of alcohols (Nishiwaki, 1981) and when they are adsorbed upon silica gel (Occhiucci and Patacchiola, 1982).

CHLORINATED TERPHENYLS

Terphenyls, like biphenyls, are nonplanar compounds. Introduction of chlorine substituents decreases the quantum yield of fluorescence and presumably enhances intersystem crossing (Chittini et al., 1978). Irradiation of chlorinated terphenyls in cyclohexane and in methanol leads to dechlorination. Another significant reaction in methanol is replacement of the chlorine by a methoxyl group, that is to say, nucleophilic substitution is competing with dehalogenation. The quantum yields for dechlorination of compounds bearing an o-chloro substituent are considerably higher than those in which the substituent is in other positions. Evidence presented in favour of the reaction occurring from the triplet state included the finding that the presence of oxygen retards the reaction and the addition of xenon (a heavy atom quencher) enhances the quantum yield for reaction. Sensitization experiments using benzophenone gave inconclusive results. Thus there is some evidence for the participation of the triplet state in the dechlorination reaction although there is the possibility that some reaction does occur from the excited singlet state.

1-CHLORONAPHTHALENE AND RELATED COMPOUNDS

On irradiation in hydrogen-donating solvents such as methanol and cyclohexane, 1-chloronaphthalene gives naphthalene and binaphthyls with φ (disappearance) in the range 2–20 × 10⁻³ (Ruzo *et al.*, 1975b). Photoinduced dechlorination of 2-chloronaphthalene and 1,2-dichloronaphthalene has also been reported. When methanol was used as a solvent formation of methoxynaphthalenes was also observed. Nucleophilic substitution increases in importance when solvents of poor hydrogen-donating ability (e.g. acetonitrile) containing a nucleophile such as water are used. When such solvents are used and nucleophiles are absent, the formation of binaphthyls is enhanced. The fact that the reactions are retarded by the presence of oxygen and that they can apparently be sensitized by benzophenone led to the initial suggestion that reaction occurs via the triplet state. However, in later papers (Bunce *et al.*, 1976, 1980) the reactivity was ascribed to the excited singlet state. If the value for the vinyl—chlorine bond strength from Table 1 is used, reaction from the excited singlet state appears to be endothermic. To overcome this difficulty it was suggested that reaction occurs via an excimer and spectroscopic evidence for such a species was obtained. The most convincing evidence for the participation of an excimer comes from the finding that the quantum yield for dechlorination of 1-chloronaphthalene increases as the concentration of the chloro-compound is increased. Furthermore, the addition of 4-chlorobiphenyl, a nonabsorbing additive, also increases the quantum yield of dechlorination (2).

$$1-NpCl^* + 4 Cl-Biph \rightleftharpoons |1-NpCl/4 Cl-Biph| * \rightarrow Np \cdot + Cl \cdot + 4 Cl-Biph$$
(2)
Hetero-excimer

The formation of binaphthyls from 1-chloronaphthalene is also indicative of excimeric intermediates, as indicated in (3). The breakdown of the excimeric

$$1-NpCl^{*} + ArH \rightarrow Excimer \rightarrow Np \cdot + Cl^{-} + ArH^{\ddagger}$$

$$Np \cdot + R - H \rightarrow NpH + R \cdot$$

$$ArH^{\ddagger} + ArH \rightarrow Ar - Ar$$

$$ArH^{\ddagger} + CH_{3}OH \rightarrow Ar - OCH_{3}$$
(3)

intermediates (formed between two molecules of the chloro-compound or between one molecule of chloro-compound and one molecule of dechlorinated aromatic hydrocarbon) to give radical cations explains the formation of methoxylated products when methanol is used as solvent.

That chloroaromatic hydrocarbons such as 1-chloronaphthalene can form excited complexes with aromatic hydrocarbons appears to offer an explanation for the observation that the addition of typical triplet quenchers such as cyclohexa-1,3-diene and piperylene in some cases accelerates the reaction rather than retards it and in other cases apparently leads to quenching efficiencies less than diffusion controlled (Ruzo and Bunce, 1975). Enhanced loss of chlorine can be explained if the dienes and the chloro-compound form a hetero-excimer which breaks up to give the radical cation of the diene, chloride ion and a naphthyl radical. However, use of high diene concentrations and a polar solvent alters the course of the reaction and cycloaddition products formed between the diene and the chloro-compound are produced (Bunce and Gallacher, 1982). It is also difficult to rationalize the finding that added electron acceptors such as biacetyl also increase the rate of dechlorination; for example, when the concentration of biacetyl in methanol is increased from $1.7\times 10^{-3}M$ to $5.10^{-2}M$ a 2.27-fold increase in rate is observed.

The photodechlorination of polychlorinated naphthalene in methanol solution has been investigated (Ruzo *et al.*, 1975c). Besides dechlorination, binaphthyl formation and to a lesser extent formation of methoxylated naphthalenes were observed. The formation of these products can be accounted for by the mechanisms given for 1-chloronaphthalene.

9,10-DICHLOROANTHRACENE

Irradiation of this compound in acetonitrile solution containing 2,5-dimethylhexa-2,4-diene or cyclohexa-1,3-diene leads to dechlorination and the formation of 9-chloroanthracene (Smothers *et al.*, 1979). By way of contrast when benzene is used as solvent a cycloaddition reaction takes place to give



[20] (Yang *et al.*, 1975). The formation of [20] has been rationalized in terms of an exciplex intermediate. In polar solvents, interaction of the excited anthracene with conjugated dienes and aromatic hydrocarbons may give rise to full electron transfer. The use of acetonitrile containing deuterium oxide as solvent and 2,5-dimethylhexa-2,4-diene as diene led to the formation of deuteriated 9-chloroanthracene [23]. Not only does the formation of this compound substantiate the view that interaction of the diene with the excited anthracene gives rise to extensive if not complete electron transfer but also demonstrates that the loss of chlorine is not from radical anion [21] but rather from the radical [22].



REACTIONS OF OTHER CHLORINATED AND RELATED COMPOUNDS OF MECHANISTIC INTEREST

The photoinduced decomposition of di- and octachlorobenzofuran in methanol and hexane solutions has been investigated and not surprisingly dechlorination was observed (Hutzinger *et al.*, 1973). Thus in the case of the octachloro compound, hepta-, hexa-, penta- and tetra-chlorobenzofurans were produced upon irradiation with light of wavelength 310 nm. Irradiation of halogenopyridines in benzene gives phenylpyridines (Terashima *et al.*, 1981). The order of reactivity of the halogeno substituents is chlorine < bromine < iodine. Interestingly, the positional reactivity is dependent upon the halogen substituent. Thus for the bromo- and iodo-compounds the positional reactivity is 2 > 3 > 4 whereas for the chloropyridines it is 3 > 2 > 4. Pentachloropyridine undergoes dechlorination to give 2,3,4,6-tetra-chloropyridine on irradiation in ethers (Ager *et al.*, 1972). The reason for this regiospecific loss of chlorine is not known. 4-Bromo- and 4-iodotetra-chloropyridines undergo exclusive loss of bromine and iodine respectively (Bratt *et al.*, 1980) indicating homolysis of the weakest bond in the system.



Pentachloropyridine-N-oxide rearranges to the isocyanate [24]. Its formation was postulated as occurring *via* an intermediate oxaziridine.

A most remarkable reaction has been found to occur when chlorobenzene (Bryce-Smith *et al.*, 1980) and 3-chlorotetrafluoropyridines (Barlow *et al.*, 1979, 1980) are irradiated in the presence of alkenes such as cyclopentene. It was found that the alkene inserted into the carbon—halogen bond to give 1,2-addition products. Use of bromo- and iodobenzene led to the production of unstable 1,2-addition products. Available evidence suggests that aryl radicals are not involved. Thus in the reaction of 3-chlorotetrafluoropyridine with ethylene (Barlow *et al.*, 1979, 1980), telomerization of the ethylene was not observed. Fluorobenzenes, in which homolysis of the carbon—halogen bond dissociation energy, also form 1,2-addition products with alkenes (Bryce-Smith *et al.*, 1980). It is possible that these reactions occur *via* an exciplex with the alkene acting as an electron donor. 2,3,4,5,6-Pentafluorobiphenyl [25] is formed in a related reaction which appears to take place when a mixture of benzene and hexafluorobenzene is irradiated (Bryce-Smith *et al.*, 1979). The yield of this



product is dependent upon the concentration of benzene, the presence of proton donors, and the polarity of the solvent. Increasing the polarity of the solvent leads to an increase in product yield which suggests that an exciplex intermediate is involved. However, use of deuteriated solvents, such as CH_3OD , does not lead to incorporation of deuterium in the product and therefore free radical ions cannot be involved. Quenching studies indicate that triplet hexafluorobenzene is the excited species responsible for reaction. In this reaction homolysis of the carbon—halogen does not appear to take place, but rather to occur from an intermediate *via* an ionic process. This is

somewhat reminiscent of the electrocyclic reactions which produce compounds such as [3] and which give products by elimination of a molecule of hydrogen halide.

The reaction of tetrahalophthalonitriles with aryl ethers is a most interesting reaction because in some cases (e.g. 1,4-dimethoxybenzene) competition between dehalogenation and biaryl formation occurs (Al-Fakhri *et al.*, 1980). The formation of these products is nicely rationalized in terms of the radical ion pair [26]. Thus the formation of the dehalogenated product appears



to follow a similar mechanism to that postulated for the reaction of, for example, 1-chloronaphthalene (Bunce *et al.*, 1976). Irradiation of tetrahalobenzonitriles (the halogen being either chlorine or fluorine) in the presence of ethers leads to [27] (Al-Fakhri and Pratt, 1976) and here again it seems necessary to invoke reaction *via* radical ions in order to explain the loss of fluorine as in the earlier example (Bryce-Smith *et al.*, 1980). The tetrachloropyridazine [28] undergoes a series of rearrangements in preference to homolysis of the carbon—chlorine bond (Fox *et al.*, 1982).



3 Bromo- and iodoaromatics

BROMO- AND IODOBENZENES

As can be seen from Table 1, the carbon—halogen bond strength in these compounds is substantially lower than the aryl—chlorine bond strength and falls below the energy of the excited singlet state for benzenoid compounds. Furthermore the $\sigma \rightarrow \sigma^*$ absorption bands of carbon—bromine bonds have a tail which extends beyond 254 nm. Thus irradiation at short wavelengths such as 254 nm can lead to reaction *via* direct population of the $\sigma \rightarrow \sigma^*$ transition as well as *via* the more classical route involving the $\pi \rightarrow \pi^*$ transition. Which of the two transitions is of lower energy in the singlet manifold has in most cases not been defined. Epr studies of the radical anions derived from simple halogenobenzenes (Andrieux *et al.*, 1979) show that the lowest anti-bonding orbital is σ^* . Introduction of electron-withdrawing groups having —R effects, such as cyano and nitro groups, reduces the energy of the π^* orbital and brings it below the σ^* orbital. It is therefore likely that direct irradiation of bromo- and iodobenzenes leads to cleavage in the excited singlet state, this process competing with intersystem crossing. In the case of iodo-compounds where the bond-dissociation energy is less than the energy of the triplet state, bond homolysis from this state is also likely.

By examination of the excitation spectrum of phosphorescence for a number of iodoaromatics it has proved possible to locate the $S_0 \rightarrow T_n$ absorption band (Marchetti and Kearns, 1967). That irradiation into this band leads to homolysis with comparable efficiency to excitation in the $S_0 \rightarrow S_n$ absorption bands suggest that the triplet state is primarily responsible for homolysis of these compounds.

There is also some evidence for the triplet state of 1,4-dibromobenzene being responsible for homolysis (Pedersen and Lohse, 1979). By means of the technique of flash photolysis excited 1,4-dibromobenzene was shown to react in benzene to give a transient which was identified as a phenylcyclohexadienyl radical, a species generated by attack of a 4-bromophenyl radical upon benzene. The addition of the classical triplet quencher penta-1,3-diene quenches the formation of the cyclohexadienyl radical. This suggests that the diene quenches the triplet state of the bromo-compound so reducing the amount of 4-bromophenyl radicals available for reaction.

Examination of the products of photolysis of a series of 4-bromophenoxyalkyl bromides (Davidson *et al.*, 1980b) showed that the aryl—bromine bond is cleaved in preference to the weaker methylene—bromine bond. It was shown that the homolysis reaction competed with total success against energy transfer to the weaker bond. For this reason it was postulated that homolysis occurred from the singlet manifold. The correctness of this mechanism was verified by the finding that [29] underwent homolysis of the



aryl—bromine bond even though a naphthalene group, capable of deactivating the excited singlet and triplet state of the bromophenyl group, is ideally situated within the molecule.

The competition that exists between excitation into the $\sigma \rightarrow \sigma^*$ transition of the carbon—iodine bond and the $\pi \rightarrow \pi^*$ transition of the aryl group when 254 nm light is used is illustrated by the reactions of [30] and [31] (Davey *et al.*, 1982). In the case of [30], reaction to give [34] is very dependent upon the value of *n*, and, when n > 6, little if any reaction occurs. It was shown that when *n* is as large as 6, energy transfer to the carbon—bromine bond becomes inefficient due to the inability of the methylene chain to coil so as to allow the bromine atom to approach close enough to the aryl group to allow energy transfer to take place. In contrast, the efficiency of the reactions of [31] seems to be far less dependent upon the value of *n*. Examination of the absorption spectra of [31] shows that a measurable percentage of the light absorbed at 254 nm enters the $\sigma \rightarrow \sigma^*$ transition of the carbon—iodine bond.

Since the aryl-iodine bond is so much weaker than the aryl-bromine bond (Table 1), one may expect that the quantum yields of products formed via photolytic cleavage of the halo-compounds should be the greatest for iodo-compounds. This is not found in practice. Irradiation of [33] gives [34] and the quantum yields for reaction of the iodo-compounds are lower than those of the bromo-compound (Grimshaw and de Silva, 1979, 1980c). Certainly the irradiation of iodo-compounds in neat solvents with which aryl radicals can react often leads to very high yields of products via this process (Sharma and Kharasch, 1968; Wolf and Kharasch 1961, 1965; Kharasch, et al., 1966; Matsuura and Omura, 1966; Pinhey and Rigby, 1969), and these reactions usually occur more readily than those for the corresponding bromocompounds. However, the quantum yield of product formation is not a true reflection of the efficiency of the photoinduced homolysis since the recombination of geminate radicals will reduce the efficiency of the productforming reaction. In principle the extent to which cage recombination occurs can be probed by examining the effect of increasing the macroscopic solvent viscosity upon the reaction. In the case of [33], increasing the solvent viscosity caused a decrease in quantum yield of product formation (Grimshaw and de Silva, 1979, 1980c), e.g. for the iodo-compound in hexane ($\eta = 0.28$ cp) $\varphi = 0.35$, whereas in cyclohexane ($\eta = 0.80$ cp) $\varphi = 0.21$. Change in solvent polarity also affects the quantum yields but the fact that within a given type of solvent the quantum yield decreases as the viscosity is increased indicates that recombination of geminate aryl radicals and halogen atoms is an important energy-wasting process.

It has also been shown that the cyclization of compounds such as [33] can be triplet sensitized. The chloro-compound undergoes reaction and if this occurs from the triplet state, the process is endothermic. To account for reactivity of the compounds [33] it was suggested that the triplet state of the arylamine portion of the compound forms an excited complex with the haloarene group and it is this complex which undergoes reaction. A similar argument was used to explain the reactivity of [35] which contrasts with the stability of [36] (Grimshaw and de Silva, 1980d). In the complex formed by [35] the aryl—iodine bond can interact with the arylamino group. This is not the case in [36] and it is believed that this is the reason for the stability of this compound. It is interesting that compound [37] is also photostable. This stability was attributed to light-induced charge transfer occurring as with [35] but with back electron transfer effectively competing with aryl-bromine bond homolysis.



The reported reactions of the isomeric methyl bromobenzoates (Nikishin and Cheltsova, 1968) are of interest in that for these compounds there is a possibility of reaction from an $n \rightarrow \pi^*$ excited state. Photolysis of the esters in benzene solution containing acetone gave low yields of methyl benzoate and high yields of phenylated methyl benzoates. Thus homolysis of the carbon—bromine bond does occur in these compounds. The rate of reaction was greatest for methyl-2-bromobenzoate. In this compound there is considerable steric interaction between the ester group and the bromine substituent. Expulsion of the bromine atom not only relieves the steric congestion but also allows better overlap of the π -system of the ester group with that of the benzene nucleus. As with the chlorobiphenyls (Ruzo *et al.*, 1974, 1975a) the isomer which homolyzes leading to the greatest relief of strain is the most reactive. Surprisingly, the efficiency of the reaction is dependent upon the concentration of acetone. It is hard to tell whether the acetone is acting as a singlet or a triplet sensitizer. One would expect the reaction to occur predominantly from the singlet manifold and to be favoured by population of the $\pi \rightarrow \pi^*$ transition rather than the $n \rightarrow \pi^*$ transition since for a $\pi \rightarrow \pi^*$ transition, energy can be dissipated into vibrational modes one of which is the stretching of the carbon—bromine bond. Photolysis of methyl-4-bromobenzoate in methanol gives methyl benzoate (Davidson and Goodin 1982) but the rate of formation of the product is far from linear. The acceleration observed as the reaction proceeded was attributed to the accumulation of hydrogen bromide which may possibly hydrogen bond to the ester group so raising the energy of the $n \rightarrow \pi^*$ transition relative to the $\pi \rightarrow \pi^*$ transitions. It was shown that the photolysis of methyl-4-bromobenzoate in methanol containing hydrogen bromide is very much more efficient than in the absence of hydrogen bromide. Furthermore the production of methyl benzoate was found to be almost linear with time.

The photocyclization of [38] to give [39] is an interesting reaction (Paramasivam *et al.*, 1979) because not only does the thiocarbamate group intramolecularly scavenge the aryl radicals in competition with the reaction of the



radicals with solvent methanol but also reaction occurs solely *via* the homolytic cleavage of the aryl—bromine bond, the weakest carbon—halogen bond. Cleavage of aryl—bromine bonds in preference to aryl—chlorine bonds has also been shown to occur on photolysis of 4-bromo-4'-chlorodiphenylmethane in benzene (Robinson and Vernon, 1970).

Irradiation of 2-bromobenzoyldiphenylphosphine [40] gives products which indicate that there is competition between acyl—phosphorus bond cleavage and aryl—bromine bond homolysis (Dankowski *et al.*, 1979). This gives some indication as to the lability of the acyl—phosphorus bond and in view of the use of acylphosphines and related compounds as photoinitiators for polymerization this would appear to warrant further attention. The



photoaddition of bromobenzene to alkenes carrying electron-withdrawing groups has been accomplished with the aid of cuprous chloride as a catalyst (Mitani *et al.*, 1980). A similar type of reaction, but uncatalyzed, occurs upon irradiation of chlorobenzene (Bryce-Smith *et al.*, 1980) and 3-chlorotetrafluoropyridine (Barlow *et al.*, 1979, 1980) in the presence of alkenes. It has been reported that irradiation of bromobenzene in the presence of nitrogen oxides leads to the formation of a number of nitrophenols but as yet there is little information concerning the mechanism of this reaction (Nojima *et al.*, 1980).

BROMO- AND IODOPOLYCYCLIC AROMATIC HYDROCARBONS

It was noted earlier that the addition of compounds such as cyclohexa-1,3diene and biacetyl accelerated the dechlorination of chloronaphthalene and this was attributed to the operation of a charge-transfer mechanism (Bunce *et al.*, 1976; Ruzo and Bunce, 1975). The presence of such compounds in the reactions of 1-bromonaphthalene and 4-iodobiphenyl did not cause any acceleration and in some cases caused a slight retardation. The observation that carbonyl compounds quench the excited singlet state of aromatic hydrocarbons by an exciplex mechanism makes the use of 1,2-dicarbonyl compounds as triplet quenchers open to question (Busch *et al.*, 1977). The lack of acceleration of dehalogenation of bromo- and iodo-compounds by added dienes etc., suggests that the rate of dehalogenation is very high and this is no doubt a reflection of the relatively weak carbon—halogen bond strengths.

The question of whether the dehalogenation of 1-iodonaphthalene, 4iodobiphenyl and 1-bromonaphthalene occurs from the singlet or triplet manifold has been probed by examining the effect of added lithium halides upon the reactions with methanol as solvent (Ruzo et al., 1977). In all cases the efficiency of retardation by the ions was $I^- > Br^- > CI^-$. Halide ions are known to quench the excited singlet states of aromatic hydrocarbons (Beer et al., 1970; Davidson and Lewis, 1973; Watkins, 1973). The efficiency of quenching is not related to the heavy atom effect but rather to the ease of oxidation of the anions. The quenching does lead to triplet production (Watkins, 1973) and therefore the observed retardation may indicate that the added ions quench the excited singlet state and that reaction occurs from this state. However, it is well known that heavy atom effects can increase the efficiency of intersystem crossing between T \rightarrow S₀. It is known that halide ions do accelerate this process (Najbar and Rodakiewicz-Nowak, 1978), and therefore the quenching effect of the ions may indicate that reaction is occurring from the triplet state. This example illustrates the problems of using external heavy atom effects as a diagnostic tool for investigating reaction mechanisms. In many cases the relative efficiency of $S_1 \longrightarrow T_1$, and

T \longrightarrow S₀ are largely unknown. For some ω -naphthylalkyl halides it has been found that the presence of the halogeno groups leads to an increase in triplet yield (Davidson et al., 1980a) but has little effect upon triplet lifetime. Grieser and Thomas (1980) have used a much more direct method for determining the lability of triplet bromo- and iodonaphthalenes and also biphenyls. They studied the triplet lifetime and yield of these compounds as a function of temperature and in this way were able to obtain energies of activation for homolysis from the triplet state. For 1- and 2-iodonaphthalenes a value of \sim 5 kcal mol⁻¹ was obtained and for 4-bromobiphenyl a value of 16 kcal mol⁻¹. The energy of activation for homolysis of triplet 1-bromonaphthalene could not be obtained due to the high temperatures that are required to assist the homolysis of this species. This particularly simple but elegant way of studying triplet reactivity opens up possibilities for assessing the reality of the involvement of triplet states in the dehalogenation of haloaromatics. By use of nanosecond flash photolysis (Pineault et al., 1981) it was shown that internal conversion and intersystem crossing compete with homolysis of the excited singlet state of 2-iodoanthracene. Little homolysis occurs from the lowest triplet state of this compound. Similarly homolysis occurs from upper triplet states of 9-iodoanthracene (produced by intersystem crossing) but not from the lowest triplet state which has insufficient energy.

The debromination of monobrominated and dibrominated biphenyls has been examined (Bunce *et al.*, 1975) and it is not surprising to find that the 2-bromo-compound is more reactive than the 4-bromo-compound. On irradiation 2,5-dibromobiphenyl loses the bromine which gives the largest release of steric strain to give 3-bromobiphenyl.

Irradiation of 9-bromophenanthrene in hexane solution gives [41] (Weiss et al., 1971). The formation of this product may be rationalized as occurring



by attack of 9-phenanthryl radicals upon the starting material. However, the reaction was carried out in hexane solution and one would expect the 9-phenanthryl radicals to abstract hydrogen from the solvent. The absence of this reaction may be due to the production of the phenanthryl radicals from an excimer composed of two molecules of the bromo-compound.

4 Assisted dehalogenation of halogenoaromatics

AMINE- AND SULPHIDE-ASSISTED DEHALOGENATION OF HALOGENOAROMATICS

There is an extensive literature concerned with the formation of excited complexes between aromatic hydrocarbons and tertiary amines (Davidson, 1975, 1983; Gordon and Ware, 1975; Mataga and Ottolenghi, 1979). In many cases the reduction potentials of haloaromatic hydrocarbons are similar to the parent hydrocarbons (Andrieux et al., 1980) and therefore the excited singlet state of these compounds may well form excited complexes or radical ions with electron donors. The presence of a halogen atom may affect the probability of such reactions occurring by enhancing intersystem crossing to such a degree that the excited singlet state has a very short lifetime and therefore little chance of participating in a bimolecular reaction. If the triplet state does not react with the amine, the addition of amine will have no effect. Another possibility is that the photoinduced homolysis has a very large rate constant thus attenuating the singlet life-time, and consequently reaction with an amine will be inefficient. This appears to be the case for bromobenzene and iodobenzene and related compounds since the dehalogenation reactions are unaffected by the presence of tertiary amines (Davidson and Goodin, 1981). 4-Chlorobenzonitrile, which does not dechlorinate on irradiation in methanol, does dechlorinate when triethylamine is added; the inefficiency of the homolytic reaction allows the bimolecular reaction with the amine to compete. The dechlorination of many chlorinated biphenyls is accelerated by the addition of triethylamine (Bunce et al., 1978; Ruzo et al., 1975a) and it is those compounds with a low quantum yield for dechlorination which show the most marked acceleration. Other compounds which undergo triethylamine-assisted dehalogenation include chlorinated terphenyls (Chittini et al., 1978), where again only the relatively light stable compounds showed the enhancement, 1-chloronaphthalene (Ruzo et al., 1975b; Bunce et al., 1976) and bromobiphenyls (Bunce et al., 1975). In the latter reactions, the addition of triethylamine leads to a much cleaner reaction and, if the quantum yield of biphenyl formation is being measured, the apparent acceleration by the amine is due to the suppression of side reactions.

So far terms such as "amine-assisted" and "acceleration of reaction" have been used and taken to indicate that some form of complex is formed between the haloaromatic and the amine. Fluorescence from complexes formed between 1-chloronaphthalene and triethylamine has been observed (Bunce *et al.*, 1976). In many cases the fluorescence of haloaromatics (Bunce *et al.*, 1976, Ohashi *et al.*, 1973) and haloheterocycles (Nasielski *et al.*, 1972) is quenched by triethylamine and, since this cannot be a classic energytransfer process, it is reasonable to assume that the quenching is due to excited complex formation. Thus the observation that the use of highly polar solvents increases the accelerating effect of added amines is often taken as evidence for the participation of complexes or radical ions in these reactions as shown in (4) (Bunce *et al.*, 1976; Davidson and Goodin, 1981; Ohashi *et al.*, 1973). In order to gain more substantial evidence for the participation of

ArHal
$$(S_1) + Et_3 N \rightarrow (ArHal)\overline{\cdot} + Et_3 N\overline{\cdot}$$

 $ArHal\overline{\cdot} \rightarrow Ar \cdot + Hal\overline{\cdot}$ (4)
 $Ar \cdot \xrightarrow{\text{Solvent}} ArH$
 $or Amine$

radical ions, various dehalogenation reactions have been carried out using a mixture of acetonitrile and deuterium oxide as solvent. If the radical ions (e.g. [42]) have a reasonable life-time, and some of these have been determined (Andrieux *et al.*, 1980), then they may be deuteriated which can lead to deuterium incorporation into the product. In many cases deuterium incorporation



has been observed e.g. 1-chloro and 1-bromonaphthalene, 4-chlorobiphenyl and 9-chloroanthracene (Davidson and Goodin, 1981; Bunce, 1982). Somewhat surprisingly, deuterium incorporation into benzonitrile produced from 4-chlorobenzonitrile was not observed even though the addition of

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triethylamine is essential for reaction to occur (Davidson and Goodin, 1981). In none of the reactions studied was deuterium incorporation into the starting material observed. Thus in these cases, once the radical ion of the halocarbon has been formed, it does not revert to starting material. This contrasts with the finding that N,N-dimethyl-4-chlorophenylpropylamine undergoes dechlorination more slowly than 4-chlorophenylpropane (Bunce and Ravanal, 1977) which suggests that the intramolecular excited complex formed between the amine and the chlorophenyl group undergoes efficient back electron transfer. Because of the efficiency of this type of reaction it is often very difficult to obtain spectroscopic evidence for intramolecular exciplexes and radical ions.

Since the formation of excited complexes between aromatic hydrocarbons and amines appears to involve most commonly the excited singlet rather than the triplet state of the hydrocarbon, it has been tacitly assumed that the amine-assisted dechlorination reactions occur via the singlet state of the chloroaromatic. Bunce (1982) has made a careful kinetic study of these reactions and reaches the conclusion that the excited singlet complex formation is an energy-wasting process and that it is the triplet complex which leads to reaction. Flash photolysis studies have now confirmed that the triplet states of chloroaromatic hydrocarbons are quenched by tertiary amines in acetonitrile (Beecroft *et al.*, 1983).

Addition of triethylamine accelerates the dechlorination of 4-chlorobiphenyl (Bunce *et al.*, 1978; Tsujimoto *et al.*, 1975), but surprisingly 3chlorobiphenyl is reduced to give 1,4-dihydro-3-chlorobiphenyl. This reaction is without precedent, although it is known that many polycyclic aromatic hydrocarbons are photoreduced by tertiary amines (Davidson, 1975).

The debromination of bromopyrimidines is reported to be accelerated by the addition of secondary aliphatic amines as well as tertiary amines (Nasielski *et al.*, 1973; Parkányi, 1981) and radical ions have been postulated as intermediates. The higher oxidation potential of secondary amines compared with tertiary amines makes them less likely to participate in electron-transfer reactions. In the case of the reaction question, the ease of reduction of pyrimidines may help the thermodynamics of the process to be balanced.

The fluorescence of aromatic amines such as N,N-dimethylaniline is quenched by haloaromatics such as chloro- and bromobenzene and exciplex fluorescence has been observed (Tosa *et al.*, 1969; Pac *et al.*, 1972; Grodowski and Latowski, 1974; Bunce and Gallacher, 1982). Irradiation of the amine in the presence of halobenzenes produces benzene, biphenyl, phenylated N,N-dimethylanilines and N-methylaniline. These products are formed as a result of the reactions generating aryl radicals.

Sulphides quench the fluorescence of aromatic hydrocarbons and this is attributed to the occurrence of a charge-transfer rather than an energytransfer process. Not surprisingly sulphides such as diethyl sulphide accelerate the dehalogenation of haloaromatic hydrocarbons (Davidson *et al.*, 1982). Furthermore, if the reactions are carried out in the presence of deuterium oxide, deuterium is incorporated into products thus indicating that either radical ions or exciplexes are intermediates.

DEHALOGENATION OF HALOAROMATIC COMPOUNDS ASSISTED BY SODIUM BOROHYDRIDE

The addition of sodium borohydride has been shown to accelerate the photoinduced dechlorination of 3-chloro- and 4-chlorobiphenyl (Tsujimoto *et al.*, 1975). Available evidence suggests that sodium borohydride photoreduces excited 1-cyanonaphthalene by hydride attack (Barltrop and Owers, 1972). Presumably chlorinated aromatic hydrocarbons are reduced by a similar mechanism.

5 Photoinduced nucleophilic substitution haloaromatics

HALOAROMATICS

This vast area has been recently reviewed (Havinga *et al.*, 1975; Havinga and Cornelisse, 1976). There are many examples of the displacement of the halo group by the hydroxide ion and amines (Nijhoff and Havinga, 1965; Joschek and Miller, 1966; Omura and Matsuura, 1971) although in some of these reactions radical processes play a part, e.g. formation of [44]–[46] from [43] (Omura and Matsuura, 1971).



Solvent polarity also seems to play a part in determining the extent of radical vs ionic reaction. Irradiation of aqueous solutions of 3,4-dichloroaniline produces 2-chloro-5-aminophenol and it has been suggested that the dichloro-compound undergoes heterolysis on irradiation to give a phenyl

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cation (Miller *et al.*, 1979). By way of contrast, irradiation of the dichloroaniline in methanol generates 3-chloroaniline as the exclusive product; thus not only does homolysis occur but reaction takes place at a different position in the nucleus. The fact that methanol is a good hydrogen-atom donating solvent, whereas water is very poor in this respect, may also be an important factor. Thus it was noted with 1-chloronaphthalenes that the use of polar solvents that are poor hydrogen atom donors favours nucleophilic substitution (Ruzo *et al.*, 1975b). 4-Chloroanisole is also photosolvolyzed on irradiation in methanol (Soumillion and De Wolf, 1981) but in this case the solvolysis was envisaged as involving the radical cation of the chlorocompound rather than an aryl cation.

A variety of halo-9,10-anthraquinones undergo photosolvolysis to give products which are of use in the synthesis of dyes. Irradiation of 1-chloro-9,10-anthraquinone in concentrated sulphuric acid produces 1-hydroxy-9,10-anthraquinone (Seguchi and Ikeyama, 1980). The 2-chloroquinone is unreactive. However, the 2-chloro-compound does react with pyridine (Loskutov et al., 1981). The mechanism of these reactions is far from clear. A mechanistic study has been made of the aminolysis, by primary amines, of 1-bromo-4-acetylamino-9,10-anthraquinone to give 1,4-diamino-9-10-anthraquinones (Tajima et al., 1979). A triplet charge-transfer state of the quinone was shown to be responsible for reaction. 1-Bromoquinones which do not possess a charge-transfer triplet state as the lowest triplet state are unreactive. Primary amines react with 1-amino-4-bromo-9,10-anthraguinone-2-sulphonate to give a 1,4-diamino-quinone (Inoue et al., 1973, 1975). The reaction is only successful if oxygen is present. This led to the suggestion that the product is formed by reaction of the amine with a "quinone-oxygen" excited complex. There is the possibility that the function of oxygen is to suppress photoreduction of the quinone. This particular quinone does not photoreact with aromatic amines. However, the case is different for 1-amino-2,4-dibromo-9.10-anthraquinone which reacts with both aliphatic and aromatic amines to give 1,4-diamino-2-bromoquinones (Inoue and Hida, 1978; Inoue et al., 1980). The reaction occurs in both the presence and absence of oxygen. In the absence of oxygen, reaction is proposed as occurring via the triplet chargetransfer state and in the presence of oxygen by reaction of the amine with the excited singlet and triplet complexes of the quinone with oxygen.

Many bromoquinolines and isoquinolines, but not their chloro counterparts, dehalogenate on irradiation in methanol solution containing hydroxide ions (Parkányi and Lee, 1974). The rate of reduction is dependent upon hydroxide ion concentrations but surprisingly the use of a mixture of CH_3OD/D_2O as solvent did not lead to any deuterium incorporation into the product. It was suggested that the hydroxide ion acts as an electron donor so producing the bromoquinoline radical ion which dehalogenates. Hydroxide ions acting as electron donors to excited states is not unknown (Phillips *et al.*, 1969), but it is strange that, if this process does occur, chloroquinolines are unreactive since their reduction potentials are likely to be similar to bromoquinolines.

REACTIONS INVOLVING VINYL CATIONS

Since the photosolvolysis of a number of haloaromatics appears to involve phenyl cations it is instructive to consider the evidence for the formation of vinyl cations in analogous reactions. McNeeley and Kropp (1976) have provided convincing evidence for the formation of vinyl cations *via* the triplet sensitized heterolysis of vinyl halides. A number of arylalkenes (e.g. [47]) give products upon irradiation which can be conveniently rationalized



as arising *via* vinyl cations (Kitamura *et al.*, 1982). The formation of ionic products is favoured by the presence of electron-donating groups in the aryl moieties. The particular mechanism shown for product formation from [47] illustrates the dilemma with regard to the mechanism involving vinyl cations. The cations can be viewed as arising directly from photoinduced heterolysis or as involving electron transfer between geminate radicals produced by photoinduced homolysis. As yet there is no clear indication for a unique pathway. Compelling evidence for the intermediacy of ionic species comes from laser flash photoconductivity experiments with [48] (Schnabel *et al.*, 1980). The closely-related compound [49] undergoes photocyclization to give [50] and this again can best be rationalized as involving vinyl cations (Suzuki



et al., 1981). It appears that the formation of [51] and [52] may well represent one of the few cases of trapping aryl cations by alkenes (Maruyama et al., 1980), and this suggests that it may be worth exploring the reactions with alkenes of those compounds which readily undergo solvolysis.



S_{RN}1 REACTIONS

In the earlier section on the amine- and sulphide-assisted dehalogenation of haloaromatics it was suggested that the radical anion of the haloaromatic is formed and that this cleaves to give an aryl radical and a halide ion. Many anions can act as electron donors for the excited states of haloaromatics and this can set up a chain reaction, as shown in (5). This type of reaction is

$$X^{-} + (ArHal)^{*} \rightarrow X \cdot + (ArHal)^{-}$$

$$(ArHal)^{-} \rightarrow Ar \cdot + Hal^{-}$$

$$Ar \cdot + X^{-} \rightarrow (ArX)^{-}$$

$$(ArX)^{-} + (ArHal)^{*} \rightarrow ArX + (ArHal)^{-}$$
(5)

known as a substitution (S) – radical (R) – nucleophilic (N) reaction, i.e. $S_{RN}I$. Much of the earlier work has been reviewed by Bunnett (1978). A variety of nucleophiles can be used, e.g. enolates, thiolate, arsenate, etc. If the haloaromatic contains more than one type of halogen atom then not surprisingly the most easily lost halogen is iodide followed by bromide with chloride being quite the most stable. Many of the reactions have proved of synthetic value, for example, in the synthesis of isoquinolines (Beugelmans *et al.*, 1982).

Recently an important point of mechanistic interest has been discussed, relating to reaction (6). In some cases it has been found that the anion (ArX).

$$(ArX)\overline{\cdot} + (ArHal)^* \rightarrow ArX + (ArHal)\overline{\cdot}$$
 (6)

can undergo fragmentation in competition with the electron-transfer process; thus in the reaction with thiolate ions [53] there is competition between



formation of the arenethiolate ion [54] and the sulphide [55] (Rossi and Palacios, 1981). Which route takes preference is determined by the nature of R. Thus if R forms a stable radical (benzyl or t-butyl) formation of the arenethiolate ion [54] takes preference. The reactions of haloaromatics with phosphide, arsenide and stibide anions have also been examined (Alonso and

Rossi, 1982). It was found that in accordance with the bond strengths which are in the order aryl—phosphorus > aryl—arsenic > aryl—antimony, the likelihood of the abnormal reaction taking preference increased on going from phosphide to stibide anions. Thus, in the reaction (7) of diphenyl-arsenide anions with an aryl halide, a variety of mixed triarylarsenides were formed. In general, if the σ^* molecular orbital of the aryl—metal bond is of lower energy than that of the radical anion, then the abnormal reaction occurs.

$$ArX + Ph_2As^- \rightarrow Ph_3As + Ph_2ArAs + PhAr_2As + Ar_3As$$
 (7)

REACTIONS OF VINYLIC HALIDES WITH AROMATIC COMPOUNDS

A number of aromatic and heterocyclic compounds have been found to react with vinylic halides on irradiation; for example methoxynaphthalene reacts with the uracil [56] (Matsuura *et al.*, 1980). It has been proposed that the



bromouracil [56] reacts with the excited aromatic hydrocarbon to give a charge-transfer complex as indicated in (8). Other hydrocarbons, e.g. pyrene,

$$ArH^{*} + BrU \rightarrow [ArH^{\dagger} BrU^{-}]^{*}$$

$$[ArH^{\dagger} Bru^{-}]^{*} \rightarrow Br^{-} + U \cdot + ArH^{\dagger} \qquad (8)$$

$$U \cdot + ArH^{\dagger} \rightarrow Ar - U + H^{+}$$

react with 5-halouridines to give adducts such as [57] (Saito *et al.*, 1980). Such adducts are highly fluorescent and are potentially useful fluorescence probes. Uracils and uridines also react with tryptophan in the presence of a



triplet sensitizer such as acetone. In this way, products such as [58] and [59] can be obtained (Ito *et al.*, 1980). It was suggested (Matsuura *et al.*, 1980) that these reactions occur *via* the triplet state of the uracil and uridine. The mechanism of the reaction is dependent upon the type of halouracil or uridine



used. Use of iodo-compounds leads to reaction via homolysis of the carbon iodine bond followed by attack of the uracyl and uridyl radicals so produced upon the tryptophan. The bromo-compounds react by forming a chargetransfer complex with the tryptophan whereas the chloro-compounds react via a heterolytic process. The electron transfer can be sensitized by incorporating electron donors such as 2-methoxynaphthalene into the reaction (Ito *et al.*, 1979) giving the reaction sequence (9).

$$(BrU)^{*}T_{1} + NpOMe \rightarrow BrU^{-} + NpOMe^{+}$$

$$NpOMe^{+} + Try \rightarrow Try^{+} + NpOMe \qquad (9)$$

$$Try^{+} + BrU^{-} \rightarrow Products$$

NpOME = 1-Methoxynaphthalene; Try = Tryptophan

Dihalogenomaleimides (e.g. [60]) react with indoles (Matsuo et al., 1976;



Wald *et al.*, 1980) and with furans and thiophens (Wamhoff and Hupe, 1978). These reactions are thought to involve excited charge-transfer complexes.

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