bromide, 1647-26-3; 2-bromo-2-methylbutane, 507-36-8; 2-bromo-2-methylpentane, 4283-80-1; 2-bromo-2,3-dimethylbutane, 594-52-5; 2-bromo-2,4-dimethylpentane, 68573-19-3; 2-bromo-2,4,4-dimethylpentane, 62574-65-6; 2-bromo-2-methyl-3-phenylpropane, 23264-13-3; 1-bromo-1-methylcyclopentane, 19872-99-2; 1-bromo-1-methylcyclohexane, 931-77-1; 1-bromo-1-ethylcyclohexane, 931-95-3; 1-bromo-1-methylcycloheptane, 81012-83-1; 1,2-dibromobutane, 533-98-2; *meso*-2,3-dibromobutane, 5780-13-2; 1,3-dibromobutane, 107-80-2; 2-chlorohexane, 638-28-8; 2-hexyltosylate, 4563-91-1; 2-iodohexane, 18589-27-0; 3-bromohexane, 3377-87-5; 1,8-diazabicyclo[5.4.0]undec-7-ene, 6674-22-2; 1,5-diazabicyclo[4.3.0]non-5-ene, 3001-72-7; 2,2,5,5-tetramethylhexane, 1071-81-4; semiphorone, 5857-71-6.

Photolysis of Aryl Chlorides with Aliphatic Amines

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Kinetic arguments show that the aliphatic amine assisted photodechlorinations of chlorides of the benzene, naphthalene, and biphenyl series take place mainly from the triplet excited state. Deuterium labeling studies have been used to determine the origin of the hydrogen atom which replaces chlorine when 4-chlorobiphenyl is photoreduced. Three pathways are inferred: hydrogen abstraction from the solvent and protonation both within the exciplex (or radical ion pair) and by external proton donors.

The photochemistry of chlorinated aromatic compounds has been studied in some detail because of the importance of some of these compounds as environmental pollutants. In some cases, irradiations in the presence of added substances such as amines and dienes have led to enhanced photolability of the halide, as a result of electron-transfer reactions.

The work described in this paper was undertaken with the long-term goal of evaluating whether this increased photolability could be exploited to develop methods for photochemical destruction of chlorinated pollutants of the chlorobenzene, -naphthalene, and -biphenyl series. We now report studies on the mechanism of the aliphatic amine assisted photolysis of some of these substances.

4-Chlorobiphenyl. Ohashi, Tsujimoto, and Seki[1] studied the photoreduction of 4-chlorobiphenyl in acetonitrile, assisted by triethylamine. They observed that the amine both quenched the fluorescence of the halide and also enhanced its photolability. Scheme I was proposed

Scheme I

$$\mathrm{ArCl} \xrightarrow{h\nu} {}^1\mathrm{ArCl}$$

$${}^1\mathrm{ArCl} \xrightarrow{k_1} \mathrm{ArCl}$$

$${}^1\mathrm{ArCl} + \mathrm{R_3N} \xrightarrow{k_2} [\mathrm{ArCl^{-}\cdot} \ldots \mathrm{R_3N^{+}\cdot}],\ \mathrm{X}$$

$$\mathrm{X} \xrightarrow{k_3} \mathrm{ArCl} + \mathrm{Et_3N}$$

$$\mathrm{X} \xrightarrow{k_4} \text{products}$$

as the mechanism of this photoreduction. Steady-state analysis gives eq 1 and 2 for the influence of amine upon the quantum yields of fluorescence (ϕ_f) and reaction (ϕ_r). In these equations ${}^1\tau$ is the singlet lifetime ($=1/k_1$).

$$(\phi^0/\phi)_f = (I^0/I)_f = 1 + k_2{}^1\tau[\mathrm{R_3N}] \tag{1}$$

$$\frac{1}{\phi_r} = \left(1 + \frac{k_3}{k_4}\right)\left(1 + \frac{1}{k_2{}^1\tau[\mathrm{R_3N}]}\right) \tag{2}$$

According to Scheme I, the quantity $k_2{}^1\tau$ can be evaluated in two independent ways; in acetonitrile solution, Ohashi et al. obtained a value of $k_2{}^1\tau$ of 23 $\mathrm{M^{-1}}$ by fluorescence quenching studies and of 20 $\mathrm{M^{-1}}$ from a study of the variation of ϕ_r with [$\mathrm{Et_3N}$]. They thus proposed Scheme I as an established mechanism for the amine-assisted photodechlorination of 4-chlorobiphenyl, with electron transfer to the excited aryl chloride as the key step. The intermediate exciplex is not seen to fluoresce in solvents such as acetonitrile but is easily observed in alkane media.[2]

Our initial interest in this reaction was directed toward the events following electron transfer. Ohashi et al. show this as expulsion of chloride ion (eq 3 and 4), precedent

$$\mathrm{ArCl^{-}\cdot} \rightarrow \mathrm{Ar\cdot} + \mathrm{Cl^-} \tag{3}$$

$$\mathrm{Ar\cdot} + \mathrm{RH} \rightarrow \mathrm{ArH} + \mathrm{R\cdot} \tag{4}$$

for which is shown by the electroreduction of aryl halides[3] and in one of the chain-propagating steps of the $\mathrm{S_{RN}1}$ mechanism for substitution of aryl halides.[4]

Recent work has shown that eq 5–7 could be a plausible

$$\mathrm{ArCl^{-}\cdot} + \mathrm{H^+} \rightarrow \mathrm{ArClH\cdot} \tag{5}$$

$$\mathrm{ArClH\cdot} \rightarrow \mathrm{ArH} + \mathrm{Cl\cdot} \tag{6}$$

$$\mathrm{Cl\cdot} + \mathrm{RH} \rightarrow \mathrm{HCl} + \mathrm{R\cdot} \tag{7}$$

alternative to the above scheme, because acids can catalyze the photoreduction of aryl halides.[5-7] The intermediate ArClH· is a cyclohexadienyl radical from which aromatization by loss of Cl· should be easy. Since sequences 3 and

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[1] Ohashi, M.; Tsujimoto, K.; Seki, K. *J. Chem. Soc., Chem. Commun.* **1973**, 384.

[2] Bunce, N. J.; Kumar, Y.; Ravanal, L.; Safe, S. *J. Chem. Soc., Perkin Trans. 1* **1978**, 880.

[3] Asirvatham, M. R.; Hawley, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 5024.

[4] E.g.: Rossi, R. A.; de Rossi, R. H.; Lopez, A. F. *J. Am. Chem. Soc.* **1976**, *98*, 1252.

[5] Nordblom, G. D.; Miller, L. L. *J. Agric. Food Chem.* **1974**, *22*, 57 (1974).

0022-3263/82/1947-1948$01.25/0

Table I. Effect of Amines on Fluorescence and Photolysis of 4-Chlorobiphenyl and 1-Chloronaphthalene

	fluorescence			photolysis			
solvent	[ArCl], M	K_{SV},[f] M^{-1}	K_{SV}(corr), M^{-1}	conditions	$10^3[ArCl]_0$, M	$P(\Delta M)$[b]	$P(\log)$[b]
		4-Chlorobiphenyl/Et_3N					
CH_3CN	1.01×10^{-3}	19.6 ± 0.2		aerated	1.08	86.3	57.4
				aerated	1.08	79.6	44.0
CH_3CN-H_2O (19:1)	9.58×10^{-4}	11.2 ± 0.3		aerated	1.02	102	18.5[c]
				aerated	1.02	92.3	48.6
CH_3CN-H_2O (9:1)	9.07×10^{-4}	8.3 ± 0.1					
C_6H_{12}	2.60×10^{-4}	10.6 ± 0.3		aerated	1.30	43.5	36.9
CH_3OH	2.45×10^{-5}	2.5 ± 0.1	3.0	aerated	1.12	28.4	17.6
	2.45×10^{-4}	2.2 ± 0.1	2.5	degassed	1.16	18.4	9.5
	2.02×10^{-3}	2.4 ± 0.1	2.6	degassed	1.24	16.1	16.4
				degassed	1.09	19.2	10.9
		4-Chlorobiphenyl/Piperidine					
CH_3OH	2.38×10^{-4}	0.67 ± 0.06	0.76	degassed	1.19	2.16	2.15[d]
CH_3CN	2.18×10^{-4}	11.5 ± 0.4	12.7	degassed	1.09	61.1	44.9
		1-Chloronaphthalene/Et_3N					
CH_3OH	3.31×10^{-4}	3.6 ± 0.1	4.2	degassed	1.67	3.5[e]	23.1
	1.81×10^{-3}	3.8 ± 0.1	4.3				
		1-Chloronaphthalene/Piperidine					
CH_3OH	3.31×10^{-4}	0.80 ± 0.05	0.93	degassed	1.67	7.6	13.6[d]

[a] Calculated K_{SV} in degassed solution; see Experimental Section. [b] P = intercept/slope from plot of ϕ_r^{-1} vs. $[\text{amine}]^{-1}$. For the significance of ΔM and log, see text and ref 9. [c] Preliminary run with only five concentrations of Et_3N; large standard deviation on the intercept (see Table III of supplementary material). [d] Omitted data points at low [piperidine] because of correction difficulties for unassisted reaction when the logarithm method is used (see Table III of supplementary material). [e] Intercept very close to zero, hence relatively large standard error (see Table III of supplementary material). [f] Mixtures aerated in all cases.

4 and 5–7 lead to the same products, we have undertaken isotopic labeling experiments in an attempt to distinguish them.

We first repeated the experiments of Ohashi et al.[1] in acetonitrile. The Stern–Volmer constant for quenching the fluorescence of 4-chlorobiphenyl ($K_{SV} \equiv k_2{}^1\tau$ in Scheme I) was 19.6 ± 0.2 M^{-1}, in agreement with the previous value. However, the parameter intercept/slope from the plot of ϕ_r^{-1} vs. $[Et_3N]^{-1}$ (termed P and also $\equiv k_2{}^1\tau$ in Scheme I) was consistently larger than K_{SV}. The result $P > K_{SV}$ was noted also in the solvents cyclohexane, methanol, and aqueous acetonitrile when triethylamine was the amine and in acetonitrile and in methanol when piperidine was used (see Table I).[8]

If it be consistently true that $P > K_{SV}$, the very plausible and attractive Scheme I would be disqualified as a mechanism for the amine-assisted photoreduction of 4-chlorobiphenyl. The next paragraphs examine whether $P > K_{SV}$ is a valid result.

(a) Is the Result an Experimental Artifact? With the parameter P being obtained as the ratio of the intercept and slope, experimental errors are possible. However, the fact that P is *always* greater than K_{SV} would seem to argue against this. Experimentally, the K_{SV} data were obtained in aerated solutions, while most the ϕ_r measurements were done in degassed solutions. Measurements of fluorescence intensities in degassed and aerated solutions allowed K_{SV} values to be corrected to degassed solution; moreover, some of the ϕ_r measurements were made in aerated media (see Table I).

Errors in actinometry were ruled out as follows. (i) In the solvents used in this study, ϕ_r for the reaction in the absence of amine is ca. 10^{-3}; the correction for the unassisted reaction is negligible, at least when triethylamine is the amine. (ii) According to eq 2, the plot of any quantity proportional to ϕ_r^{-1} against $[Et_3N]^{-1}$ should afford the same value of P; this was verified by plotting the areas of the GLC peaks in place of concentrations. The same parameter P was obtained. (iii) The method of calculating ϕ_r could affect the results. Two methods are presented in Table I. The "ΔM" method is the conventional assumption that ϕ_r = moles reacted/einsteins absorbed. Other formulations for ϕ_r may be preferable in situations like this where both reactants and products absorb the light.[9] The "log" method (eq 8) is applicable to the present

$$\phi_r = (M_0 \ln (M_0/M))/I_0t \qquad (8)$$

circumstances where reactant (4-chlorobiphenyl) and product (biphenyl) have similar molar absorptivities. In eq 8, M_0 is the initial concentration of 4-chlorobiphenyl and M its concentration at time t. I_0t is the total photon dose absorbed over the time t.

Another potential experimental problem is competing light absorption by the amine. In acetonitrile, Et_3N has $\epsilon_{254nm} = 61$, compared with 21000 for 4-chlorobiphenyl. At high concentrations of Et_3N, the amine absorbs much of the light, and ϕ_r drops (Figure 1). Even after correction of ϕ_r for the light filtered by Et_3N, the plot was not linear. The data in Table I were obtained below this concentration range, and, in addition, experiments were run in methanol, in which the end absorption is blue shifted and $\epsilon_{254nm} = 3$.

(b) Does Scheme I Omit Important Side Processes? Various competing processes were considered, as follows. (i) The yield of biphenyl is not quantitative but is ca. 70%. Adding eq 9 to Scheme I gives eq 10 for the variation of

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(6) Bunce, N. J.; Kumar, Y.; Ravanal, L. *J. Org. Chem.* **1979**, *44*, 2612.

(7) Smothers, W. K.; Schanze, K. S.; Saltiel, J. *J. Am. Chem. Soc.* **1979**, *101*, 1895.

(8) The value of K_{SV} varies with solvent in the same way as observed by Gebicki, J. *Acta Phys. Pol. A* **1979**, *A55*, 411) for quenching the fluorescence of anthracene by triethylamine. The lower values in solvents such as methanol are ascribed to solvation of the lone-pair electrons on nitrogen by hydrogen bonding.

(9) Bunce, N. J. *J. Photochem.* **1981**, *15*, 1.

$$\mathrm{ArCl^{-}\cdot + Et_3N^{+}\cdot \xrightarrow{k_5} other\ products} \tag{9}$$

$$\frac{1}{\phi_r} = \left(1 + \frac{k_3}{(k_4 + k_5)}\right)\left(1 + \frac{1}{k_2{}^1\tau[\mathrm{R_3N}]}\right) \tag{10}$$

ϕ_r with Et_3N. Again $P = K_{SV}$, and the problem remains. (ii) Radical ion formation may be reversible, and/or not all the product may originate with the caged ion pair X (eq 11–14). The usual analysis gives eq 15, but once again

$$\mathrm{X \xrightarrow{k_{-2}} {}^1ArCl + R_3N} \tag{11}$$

$$\mathrm{X \xrightarrow{k_6} free\ radical\ ions,\ Y} \tag{12}$$

$$\mathrm{Y \xrightarrow{k_7} unproductive} \tag{13}$$

$$\mathrm{Y \xrightarrow{k_8} products} \tag{14}$$

P and K_{SV} are predicted to be equal, with the value $k_2{}^1\tau(k_3 + k_4)/(k_{-2} + k_3 + k_4)$.

$$\frac{1}{\phi_r} = \left(\frac{(k_7 + k_8)}{(k_4k_7 + k_4k_8 + k_6k_8)}\right)\left((k_3 + k_4) + \frac{(k_{-2} + k_3 + k_4)}{k_2{}^1\tau[\mathrm{R_3N}]}\right) \tag{15}$$

From the above arguments, we conclude that $P > K_{SV}$ is a genuine result and that Scheme I, or simple modifications thereof, cannot account for this. The problem would be resolved if the reaction occurred from the triplet excited state, at least in part. Then there would be no need for $k_r{}^3\tau$ to be equal to $k_2{}^1\tau$.

Scheme II is an example of this kind of mechanism, in

Scheme II

$$\mathrm{ArCl \xrightarrow{h\nu} {}^1ArCl}$$

$$\mathrm{{}^1ArCl \xrightarrow{k_1} ArCl}$$

$$\mathrm{{}^1ArCl + R_3N \xrightarrow{k_2} {}^1[ArCl^{-}\cdot + R_3N^{+}\cdot]}$$

$$\mathrm{{}^1ArCl \xrightarrow{k_9} {}^3ArCl}$$

$$\mathrm{{}^3ArCl \xrightarrow{k_{10}} ArCl}$$

$$\mathrm{{}^3ArCl + R_3N \xrightarrow{k_{11}} {}^3[ArCl^{-}\cdot + R_3N^{+}\cdot],\ Z}$$

$$\mathrm{Z \xrightarrow{k_{12}} ArCl + R_3N}$$

$$\mathrm{Z \xrightarrow{k_{13}} products}$$

which it is assumed for simplicity that only the triplet state leads to reaction. Note that merely allowing intersystem crossing in the exciplex and subsequent reaction still leaves $P = K_{SV}$; fluorescence quenching and reaction must be completely uncoupled.

The expression for the variation of ϕ_r with $[R_3N]$ is given by eq 16a or 16b. Provided that $k_9 > k_2[R_3N]$, a plot of

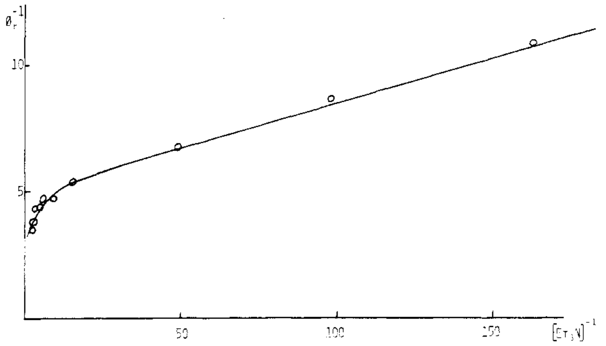

Figure 1. Plot of $\phi_r{}^{-1}$ against $[Et_3N]^{-1}$ for the photolysis of 4-chlorobiphenyl with triethylamine in acetonitrile. The quantum yields are corrected for light absorption by amine, assuming that the amine only acts as a filter.

$$\frac{1}{\phi_r} = \left(1 + \frac{k_{12}}{k_{13}}\right)\left(1 + \frac{k_{10}}{k_{11}[\mathrm{R_3N}]}\right)\left(1 + \frac{k_1}{k_9} + \frac{k_2[\mathrm{R_3N}]}{k_9}\right) \tag{16a}$$

$$\frac{1}{\phi_r} = \left(1 + \frac{k_{12}}{k_{13}}\right)\left(1 + \frac{1}{k_{11}{}^3\tau[\mathrm{R_3N}]}\right)\frac{1}{\phi_{\mathrm{ISC}}} \tag{16b}$$

$\phi_r{}^{-1}$ vs. $[Et_3N]^{-1}$ will be linear at moderate amine concentrations. Scheme II and its relatives therefore provide an explanation for $P > K_{SV}$.

We cannot argue that Scheme II is *the* reaction mechanism. The possibility of reaction through both singlet and triplet pathways cannot be excluded, and indeed is likely in that we do not observe reaction quenching when $[Et_3N]$ becomes so large that almost all singlets are quenched (except in acetonitrile; see above).

Is there any independent evidence to support a triplet mechanism for photodechlorination? Ohashi et al. noted no quenching of photoreduction in acetonitrile when 1,3-pentadiene was present. They took this as evidence for a singlet reaction. However, since we have shown that this diene actually promotes the photodegradation of 4-chlorobiphenyl, this argument must be set aside.[10] Quenching of photodechlorination was observed in amine-assisted reactions carried out in the presence of biacetyl, and a Stern–Volmer quenching constant of 30 M^{-1} was found. Although this value seems rather small for quenching a triplet state, it may be due to the rapid competitive quenching of the state by amine or to the fact that not all of the reaction proceeds from the triplet state.

There is evidence in a related system that dehalogenation does not always involve the singlet state. Russian workers[11,12] have studied the photodehalogenation of 9,10-dihaloanthracenes assisted by diethylamine and triethylamine. With diethylamine excellent agreement between K_{SV} and the intercept/slope parameter P was obtained, consistent with the mechanism of Scheme I. However, when triethylamine was used, the result $K_{SV} > P$ was obtained, and so this simple mechanism does not operate. Our arguments above would suggest a change of excited-state multiplicity as a likely possibility.

We turn now to the deuterium labeling studies. In the absence of amine, the photoreduction of 4-chlorobiphenyl proceeds via simple homolysis; in CH_3OD solvent, no

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[10] Bunce, N. J.; Gallacher, J. C. *J. Org. Chem.*, following paper in this issue.

[11] Kulis, Y. Y.; Poletaeva, I. Y.; Kuz'min, M. G. *J. Org. Chem. USSR (Engl. Transl.)* **1973**, *9*, 1242.

[12] Soloveichik, O. M.; Ivanov, V. L. *J. Org. Chem. USSR (Engl. Transl.)* **1974**, *10*, 2416.

Table II. Deuterium Incorporation into Biphenyl upon Amine-Assisted Photoreduction[a]

amine	solvent	d_1 in ArH[b]
Et_3N	C_6D_{12}	21
Et_3N	CD_3CN	16
Et_3N	$CD_3CN + D_2O$	32
Et_3N	$CH_3CN + D_2O$	27
Et_3N	CH_3OD	23
Et_3N	CD_3OD	52
Et_3N	CD_3OD/Et_3ND^+	61
Et_2ND	C_6H_{12}	25
piperidine	CD_3CN	21
Et_2ND	CH_3CN	4[c]
Et_2ND	CD_3CN	28[c]
piperidine	CD_3OD	73
Et_2ND	CH_3OD	19[c]
Et_2ND	CD_3OD	64[c]
Et_3N[d]	CH_3OD	34
Et_3N[d]	CD_3OD	48

[a] Average of duplicate reactions; original data in Table VI of supplementary material. [b] For a sample calculation, see the Experimental Section. [c] Average of two different duplicates run under different conditions (see Table VI of supplementary material). [d] Substrate was 1-chloronaphthalene.

deuterium is incorporated into the biphenyl product, as expected from previous studies.[5]

The data obtained in the presence of amines are recorded in Table II. We first consider the cases where triethylamine was used and draw the conclusion that both hydrogen abstraction (eq 3 and 4) and proton transfer (eq 5–7) are involved. Proton transfer is evident from the experiments using CH_3OD and CH_3CN/D_2O as solvents; it is notable that the presence of Et_3ND^+ enhances the extent of deuterium incorporation into the product. However, the ammonium salt does not influence either K_{SV} or P in kinetic experiments, showing that proton transfer follows the rate-limiting step of the reaction.

Hydrogen abstraction is documented by the experiments in C_6D_{12} and CD_3CN and by the increase in the formation of biphenyl-d in CD_3OD compared with CH_3OD and in CD_3CN/D_2O compared with CH_3CN/D_2O. Even in these fully deuterated media, not all the biphenyl contains a deuterium atom; this indicates that hydrogen donation from the amine is occurring. Since the concentration of amine is low, the implication is that hydrogen must be transferred within the solvent cage. This could occur either by hydrogen abstraction (eq 17a) or, more probably, by

$$(CH_3CH_2NEt_2^{+\cdot}, ArCl^{-\cdot}) \rightarrow CH_3CH{=}NEt_2^+ + ArH + Cl^- \quad (17a)$$

$$(CH_3CH_2NEt_2^{+\cdot}, ArCl^{-\cdot}) \rightarrow CH_3\dot{C}HNEt_2 + ArH + Cl\cdot \quad (17b)$$

proton transfer (eq 17b), by analogy with the mechanisms documented for the electron-transfer-assisted photoreactions of triethylamine with naphthalene,[13] benzene,[14] and aromatic nitrocompounds.[15] Thus three processes for the origin of the incoming hydrogen in ArH can be discerned: hydrogen abstraction from the solvent, protonation by the solvent, and hydrogen transfer, probably protonation, within the exciplex or the radical ion pair.

When secondary amines were used, the isotopic studies were less clear-cut, because the lower ϕ_r for secondary as compared with tertiary amines means that relatively more direct photolysis, and hence hydrogen abstraction, occurs. With this reservation, the results parallel those with triethylamine, and we see hydrogen abstraction (e.g., in CD_3CN), proton transfer (e.g., in CH_3OD), and evidence for abstraction from the amine within the solvent cage (in CD_3OD). In contrast with the photoreduction of anthracene by secondary amines in cyclohexane solution,[16] the photodechlorination studied here results in very little removal of the N–H proton from the secondary amine. This is because the transfer of the N–H proton has been associated specifically with reaction within an exciplex, i.e., 1 → 2. In polar solvents, dissociation occurs instead, and

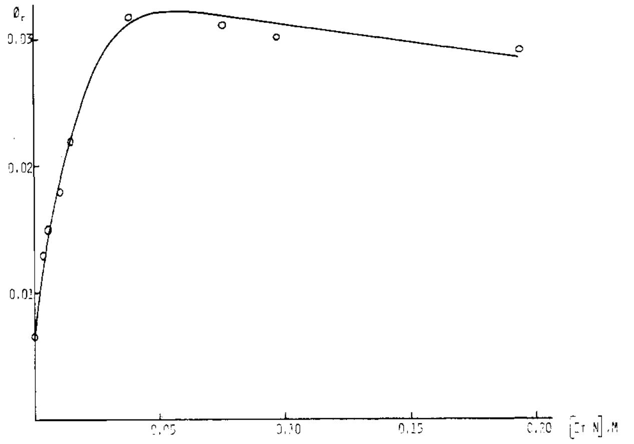

Figure 2. Variation of the quantum yield of disappearance of 2,2′,5,5′-tetrachlorobiphenyl as a function of triethylamine concentration in methanol as solvent.

$$\underset{1}{(ArCl^{\delta-}\ Et_2NH^{\delta+})} \qquad \underset{2}{(ArClH\cdot\ Et_2N\cdot)}$$

the chemistry is similar to that with Et_3N. A larger amount of deuteration was observed in cyclohexane solution, consistent with the results in the anthracene series.[16]

Our deuteration experiments are complemented by those recently reported by Davidson and Goodin,[17] who photolyzed a variety of aryl chlorides and bromides in the presence of Et_3N using CH_3CN/D_2O as the solvent. For the 4-halobiphenyls, the 1-halonaphthalenes, and the 9-haloanthracenes, inter alia, deuterium became incorporated into the photoreduction product. For these halides it was concluded that the photoreduction involves protonation of a radical anion, at least in part.

Other Chlorobiphenyls. Biphenyls chlorinated more heavily than 4-chlorobiphenyl also undergo amine-assisted photoreduction. These polychlorinated derivatives pass into the triplet state with high efficiency,[18,19] and so this observation is much more easily radionalized if the amine-assisted photodechlorination can occur at least partly through the triplet.

Figure 2 shows a set of data for the photoreduction of 2,2′,5,5′-tetrachlorobiphenyl in cyclohexane assisted by triethylamine. In terms of eq 16a, we can interpret this two-part curve as follows. At low $[Et_3N]$, singlet quenching is relatively unimportant ($K_{SV} = 6\ M^{-1}$ in isooctane[2]), and ϕ_r increases with $[Et_3N]$. After correction for the unassisted reaction, a reasonably linear plot of ϕ_r^{-1} vs. $[Et_3N]^{-1}$

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[13] Barltrop, J. A.; Owers, R. J. *J. Chem. Soc. Chem. Commun.* 1462 (1970).

[14] Bellas, M.; Bryce-Smith, D.; Clarke, M. T.; Gilbert, A.; Klunklin, G.; Krestonosich, S.; Manning, C.; Wilson, S. *J. Chem. Soc., Perkin Trans 1* **1977**, 2571.

[15] Döpp, D.; Müller, D. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 297.

[16] Yang, N. C.; Libman, J. *J. Am. Chem. Soc.* **1973**, *95*, 5783.

[17] Davidson, R. S.; Goodin, J. W. *Tetrahedron Lett.* **1981**, 163.

[18] Dreeskamp, H.; Hutzinger, O.; Zander, M. *Z. Naturforsch. A* **1972**, *27A*, 756.

[19] Ruzo, L. O.; Zabik, M. J.; Schuetz, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 3809.

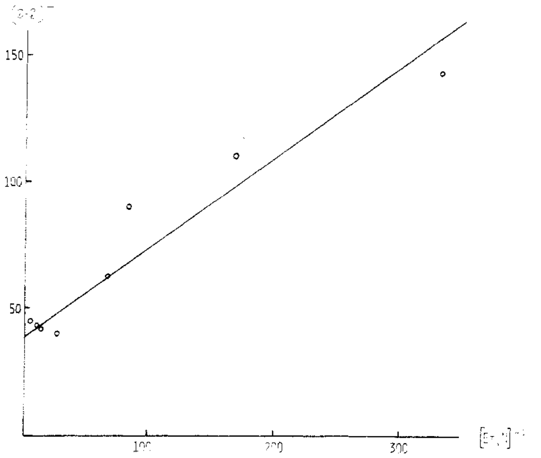

Figure 3. Plot of ϕ_r^{-1} against $[Et_3N]^{-1}$ for the photolysis of 2,2′,5,5′-tetrachlorobiphenyl with triethylamine in methanol. The quantum yields are corrected for the reaction in the absence of amine.

is obtained (Figure 3), consistent with this interpretation. The fall in the value of ϕ_r at higher $[Et_3N]$ may then be attributed to singlet quenching.

For 2,4,6-trichlorobiphenyl, the value of ϕ_r for the unassisted reaction (0.21)[9] is much greater than that for the 2,2′,5,5′-tetrachloro compound (6×10^{-3}). Now no amine-assisted reaction is seen, and triethylamine acts as a quencher. The slope of the graph $\phi_r^0/\phi_r^{Et_3N}$ vs. $[Et_3N]$ is 7 M^{-1}, in excellent agreement with K_{SV} for fluorescence quenching.[2] In this instance, triethylamine quenches the reaction by reducing the stock of reactive triplets.

1-Chloronaphthalene. The behavior we observed parallels that of 4-chlorobiphenyl in all respects. For two amines (triethylamine and piperidine) and different solvents, the parameters *P* are consistently higher than the corresponding K_{SV}. This invariable relationship eliminates the possibility of a chance difference between K_{SV} and *P* due to experimental or analytical problems. These data are also found in Table I. Deuterium labeling studies, while not as extensive as those carried out for 4-chlorobiphenyl, are again consistent with the notion that part of the hydrogen source is H^+ (eq 5–7) and part H· (eq 3 and 4), with a large portion of the (H) originating with the amine. Table II carries a summary of these results.

We therefore conclude that 1-chloronaphthalene, like 4-chlorobiphenyl, undergoes the amine-assisted photoreduction at least in part through its triplet state. The hydrogen introduced into the product naphthalene arises in part from protonation and in part from hydrogen abstraction from the bulk solvent.

Chlorobenzene. Unlike 4-chlorobiphenyl and 1-chloronaphthalene, chlorobenzene undergoes an efficient unassisted photodehalogenation. This reaction occurs from the triplet state, with formation of a singlet excimer being an unproductive side reaction.[20]

In order that all the light should be absorbed, photolyses of chlorobenzene in standard reaction ampules must be carried out at [PhCl] > ca. 0.01 M, 10 times higher than the concentrations of chlorobiphenyls and chloronaphthalene that were used. At these concentrations in cyclohexane solution, $Et_3NH^+Cl^-$ precipitated from solution when Et_3N was present. Very large apparent quenching constants were found at low $[Et_3N]$, but higher amine concentrations had no further effect on ϕ_r; significantly, the break occurred near the amine concentration that would be sufficient to react with all the HCl liberated in the reaction. Typical data are given in the Experimental Section.

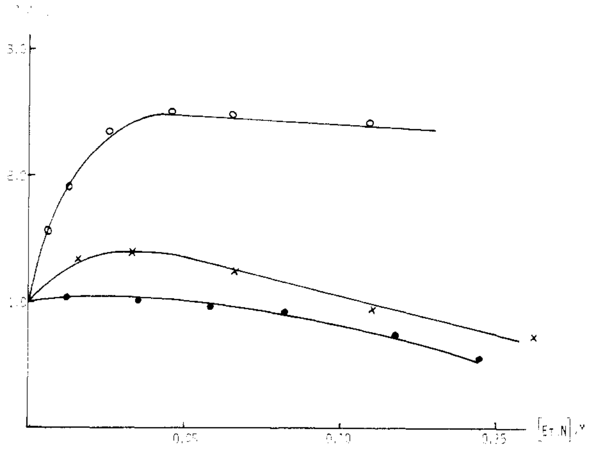

Figure 4. Variation of the quantum yield of disappearance of chlorobenzene with amines. Data are relative to the quantum yield at zero amine concentration being unity: ○, solvent C_6H_{12}–CH_3CN (1:9), triethylamine; ×, solvent C_6H_{12}, triethylamine; ●, solvent CH_3OH, piperidine.

Precipitation did not occur at [PhCl] = 1×10^{-3} M, and the results of Figure 4 were obtained at this concentration. Because not all the light was absorbed, these results were corrected to absolute quantum yields by using the value for chlorobenzene at 1×10^{-3} M from ref 20 (0.51). The reaction was also studied in methanol and in 1:9 v/v cyclohexane/acetonitrile, in which media the amine hydrochloride is soluble. In all three solvents, ϕ_r was observed to increase at low $[Et_3N]$ but fell again as the amine concentration increased further.

The cyclohexane–acetonitrile mixed solvent was also used to study the behavior of 1-(dimethylamino)-3-(*p*-chlorophenyl)propane (**3**), which is able to form an intramolecular exciplex.[21] As might be anticipated from the intermolecular results, this compound was much more photolabile than chlorobenzene; at [c] = 0.020 M, PhCl had ϕ_r = 0.16 in the absence of amine, and ϕ_r = 0.35 at $[Et_3N]$ = 0.20 M (Figure 4), while **3** had ϕ_r = 0.66.

The kinetic Schemes III and IV were tested for consistency with the shapes of the curves in Figure 4. (Note that at constant [PhCl], the step represented by k_1 includes excimer formation.)

Scheme III

$$\mathrm{ArCl} \xrightarrow{h\nu} {}^1\mathrm{ArCl}$$

$${}^1\mathrm{ArCl} \xrightarrow{k_1} \mathrm{ArCl}$$

$${}^1\mathrm{ArCl} + \mathrm{R_3N} \xrightarrow{k_2} \mathrm{X}$$

$$\mathrm{X} \xrightarrow{k_3} \mathrm{ArCl} + \mathrm{R_3N}$$

$$\mathrm{X} \xrightarrow{k_4} \text{products}$$

$${}^1\mathrm{ArCl} \xrightarrow{k_9} {}^3\mathrm{ArCl}$$

$${}^3\mathrm{ArCl} \xrightarrow{k_{10}} \mathrm{ArCl}$$

$${}^3\mathrm{ArCl} \xrightarrow{k_{14}} \text{products}$$

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[20] Bunce, N. J.; Bergsma, J. P.; Bergsma, M. D.; DeGraaf, W.; Kumar, Y.; Ravanal, L. *J. Org. Chem.* **1980**, *45*, 3708.

[21] Bunce, N. J.; Ravanal, L. *J. Am. Chem. Soc.* **1977**, *99*, 4150.

Scheme IV

$$\mathrm{ArCl} \xrightarrow{h\nu} {}^1\mathrm{ArCl}$$

$${}^1\mathrm{ArCl} \xrightarrow{k_1} \mathrm{ArCl}$$

$${}^1\mathrm{ArCl} + \mathrm{R_3N} \xrightarrow{k_2} \mathrm{X} \rightarrow \mathrm{ArCl} + \mathrm{R_3N}$$

$${}^1\mathrm{ArCl} \xrightarrow{k_9} {}^3\mathrm{ArCl}$$

$${}^3\mathrm{ArCl} \xrightarrow{k_{10}} \mathrm{ArCl}$$

$${}^3\mathrm{ArCl} \xrightarrow{k_{14}} \text{products}$$

$$[\mathrm{R_3N}] + {}^3\mathrm{ArCl} \xrightarrow{k_{11}} \mathrm{Y}$$

$$\mathrm{Y} \xrightarrow{k_{12}} \mathrm{ArCl} + \mathrm{R_3N}$$

$$\mathrm{Y} \xrightarrow{k_{13}} \text{products}$$

Schemes III and IV lead, respectively to eq 18 and 19 for the dependence of ϕ_r upon [amine].

$$\frac{\phi_r}{\phi_r{}^0} = \left(1 + \frac{k_2k_4(k_{10} + k_{14})[\mathrm{R_3N}]}{k_9k_{14}(k_3 + k_4)}\right)\left(\frac{1}{1 + k_2{}^1\tau[\mathrm{R_3N}]}\right) \tag{18}$$

$$\frac{\phi_r}{\phi_r{}^0} = \left(1 + \frac{k_{11}k_{13}[\mathrm{R_3N}]}{k_{14}(k_{12} + k_{13})}\right) \times \left(\frac{1}{(1 + k_{11}{}^3\tau[\mathrm{R_3N}])(1 + k_2{}^1\tau[\mathrm{R_3N}]}\right) \tag{19}$$

The form of the curves in Figure 4 is incompatible with eq 18, which is of the form $y = (1 + ax)/(1 + bx)$ and which predicts a monotonic increase or decrease of y as x increases, depending upon whether a is greater or less than b. Scheme III, involving increased photolability resulting from electron transfer in the singlet state, is thus excluded from consideration. Scheme IV, involving electron transfer in the triplet state, is compatible with $\phi_r/\phi_r{}^0$ rising to a maximum and then decreasing. Thus we conclude once again that the product-forming interaction of the aryl chloride with amine occurs from the triplet excited state of the aromatic compound.

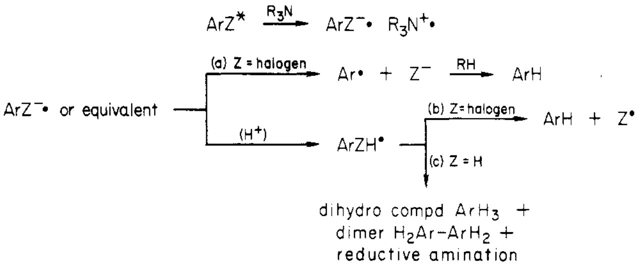
The physical explanation of eq 19 is as follows. At low [$\mathrm{Et_3N}$] singlet quenching is relatively unimportant; triplet formation is not significantly impeded, and the triplet ion pair decomposes to product more efficiently than the free triplet state, i.e., $k_{13}/k_{12} > k_{14}/k_{10}$. Thus ϕ_r increases with [$\mathrm{Et_3N}$] until singlet quenching becomes important, at which point ϕ_r decreases again because the stock of reactive triplets is becoming smaller.

Conclusions

The kinetic studies show that the photodehalogenation of aryl chlorides assisted by amines proceeds from the triplet state more commonly than has previously been recognized. On the basis of the deuteration studies, three modes of reaction can follow electron transfer from the amine to the halide. These are (i) loss of $\mathrm{X^-}$ followed by hydrogen abstraction, (ii) protonation by an external proton donor, and (iii) protonation within the exciplex or ion pair.

These conclusions suggest that the amine-assisted photodehalogenation of an aryl halide is mechanistically very closely related to the reductive addition of an amine to the parent arene.[13,14,16] This is shown as Scheme V. Indeed, when fluorine is the halogen, elimination of fluorine does not occur, path c of Scheme V is followed, and aryl fluorides show the same photochemistry with amines as the parent hydrocarbons.[22] Rare instances where pathway c is followed for aryl chlorides have also been noted.[23,24]

Scheme V



Experimental Section

Procedures and equipment for photolysis, fluorescence, and GLC analysis have been described previously.[2] Solvents were of spectroscopic grade and were checked for spurious absorptions or emissions before use. Reactions were carried out by using quartz ampules (8 mm o.d.) which were connected to Pyrex by a graded seal for evacuation, where necessary, on a standard vacuum line. GC/MS results were obtained by using a VG 7070F mass spectrometer interfaced to a Perkin-Elmer Sigma III gas chromatograph with a 6-ft column of 2.5% SE-30 on acid-washed Chromosorb W and operated isothermally at 165 °C.

Kinetic Experiments with 4-Chlorobiphenyl and 1-Chloronaphthalene. Table III[25] gives the equations upon which the data of Table I are based.

Interrelation of Experiments Carried Out in the Presence and Absence of Air. The ratio of the fluorescence intensities in the absence and presence of air was taken to be equal to the ratio of the lifetimes in the absence and presence of air.[26] For each determination several 8-mm ampules were made up, both aerated and degassed. These ampules fitted a custom-built holder in the fluorometer. Intensity readings were taken at a minimum of ten rotational positions of the ampules to allow for any irregularities in the ampules. The ratios obtained were used to produce the K_{SV} (corrected) values in Table I from the K_{SV} (aerated) data.

Photoreduction of 4-Chlorobiphenyl in the Presence of Biacetyl. The following stock solutions were prepared in methanol: A, 4-chlorobiphenyl (1.97×10^{-3} M), triethylamine (0.100 M), and the reference GLC standard (pentadecane); B, freshly distilled biacetyl (1.11×10^{-2} M). The working solutions were prepared as shown in Table IV.

The ampules were degassed and sealed and irradiated at 254 nm for 2 min. Analysis by GLC (OV-101, 165 °C) gave the results shown in Table V. A plot of $(\phi°/\phi)_r$ against [biacetyl] had a slope of $\sim 30\ \mathrm{M^{-1}}$. The small increase in the yield of biphenyl as the [biacetyl] increases in unexplained. Interestingly, a plot of [extra biphenyl]$^{-1}$ vs. [biacetyl]$^{-1}$ is linear, suggesting that biacetyl may function in some way to stimulate biphenyl production in addition to its effect on quenching triplets of 4-chlorobiphenyl (cf. the effect of benzophenone[20]).

Deuteration Studies. The deuterated solvents were obtained from Stohler Isotope Chemicals. Diethylamine-*N-d* was purchased from Merck Sharpe and Dohme, Inc. The raw data upon which the results of Table II were based are presented as Table VI in

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[22] Gilbert, A.; Krestonosich, S. *J. Chem. Soc., Perkin Trans 1* **1980**, 1393.

[23] Tsujimoto, K.; Tasaka, S.; Ohashi, M. *J. Chem. Soc. Chem. Commun.* **1975**, 758.

[24] Bryce-Smith, D.; Gilbert, A.; Krestonosich, S. *Tetrahedron Lett.* **1977**, 285.

[25] Supplementary material.

[26] Bunce, N. J.; Bergsma, M. D. *J. Org. Chem.* **1980**, *45*, 2083.

Table IV

solution	ampule no. 1	2	3	4	5	6
A, mL	1.0	1.0	1.0	1.0	1.0	1.0
B, mL	0	0	0.2	0.4	0.6	1.0
CH_3OH, mL	1.0	1.0	0.8	0.6	0.4	0

Table V

parameter	ampule no. 1, 2	3	4	5	6
10^4[4-ClBp remaining], M	5.04	5.03	5.23	5.33	5.67
10^4[BpH formed], M	2.73	2.84	2.99	3.06	3.18

Table VII

compd	relative intensity *m/e* 154	*m/e* 155	% d_1
authentic $C_{12}H_{10}$	100	13.5	0^a
authentic $C_{12}H_9D$	49.9	100	100^a
unknown 1	100	35.6	21.6
unknown 2	100	33.4	19.7

[a] Assumed.

the supplementary material. A typical experiment is recorded in full below.

Photolysis of 4-Chlorobiphenyl with Triethylamine in Cyclohexane-d_{12}. The two solutions contained 4-chlorobiphenyl (1.3 mg, 1.2 mg), triethylamine (4.5 mg, 5.3 mg), and cyclohexane-d_{12} (1.0 mL). They were evacuated, sealed, and irradiated at 254 nm for 10 min. No reference standard was used in these experiments, and hence the percent conversion from experiment to experiment was not recorded. For the GC/MS analysis, attention was focussed on the peaks at *m/e* 154 and 155. The experimental solutions were compared with authentic biphenyl and authentic biphenyl-*d* (prepared by photolysis of 4-bromobiphenyl in C_6D_{12}). From the reference materials it was concluded that the monodeuterated fraction d_1 in the unknowns was given by eq 20 (see Table VII) where *R* is the ratio of intensities of *m/e*

$$d_1 = \frac{100R - 13}{87 + 50R} \tag{20}$$

155/154.

Effect of an Amine and Its Conjugate Acid upon Photoreduction. The experiments are recorded for the system 4-chlorobiphenyl-triethylamine/triethylammonium cation. Experiments with 1-chloronaphthalene/triethylamine and 4-chlorobiphenyl/piperidine gave similar results. All were run in methanol.

Triethylamine hydrochloride was prepared by passing dry HCl into a solution of triethylamine in cyclohexane, followed by filtering and drying. The stock solutions, in methanol, were as follows: A, 4-chlorobiphenyl (2.42×10^{-3} M), triethylamine (0.089 M), and the GLC reference standard (hexadecane); B, triethylamine hydrochloride (0.093 M). For the fluorescence studies, six solutions were prepared in 10-mL volumetric flasks by using 1.0 mL of solution A, volumes (0–8 mL) of solution B, and methanol. No quenching of the fluorescence of 4-chlorobiphenyl was observed.

For the photolyses, the ampules contained solution A (1.0 mL), solution B (0–1.0 mL), and methanol (total volume 2.0 mL). Photolysis at 254 nm for 2 minutes gave the results shown in Table VIII.

Table VIII

$10^2[Et_3NH^+]$, M	0	0.46	1.39	2.31	3.24	4.63
10^4[4-ClBp remaining], M	7.4	7.3	7.5	7.5	7.2	7.3
10^4[BpH formed], M	2.9	2.7	2.5	2.5	2.4	2.5

Table IX

	Run 1, [PhCl] = 0.020 M					
$[Et_3N]$, M	0	0.001	0.002	0.003	0.004	
% PhCl reacted	90	69	33	28	15	
	Run 2, [PhCl] = 0.020 M					
$[Et_3N]$, M	0	0.002	0.005	0.010	0.020	
% PhCl reacted	90	71	30	30	25	
	Run 3, [PhCl] = 0.012 M					
$[Et_3N]$, M	0	0.0009	0.0017	0.0034	0.0060	0.0085
% PhCl reacted	34	23	17	17	17	16

For the deuteration studies, two solutions were photolyzed. Each contained 4-chlorobiphenyl (1.2 mg) and 1.0 mL of a solution prepared from acetic acid-*d* (7.4 mg), triethylamine (22.8 mg), and CD_3OD (2.5 mL). The degassed and sealed ampules were irradiated at 254 nm for 10 min and analyzed by GC/MS. The intensities of the *m/e* 155 and 154 signals were as follows: solution 1, 94.3 and 100; solution 2, 100 and 84.1. The percents of monodeuteration in the samples were estimated to be 66% (solution 1) and 55% (solution 2).

Triethylamine-Assisted Photolysis of Chlorobenzene. (a) In Cyclohexane Solution with [PhCl] ≥ 0.01 M. Fluorescence quenching by triethylamine was observed: $K_{SV} = 3.6\ M^{-1}$, $[Et_3N] = 0–0.2$ M. At higher concentrations the plot showed curvative, and in the range $[Et_3N] = 0–1.0$ M the data gave a good linear fit of $(I^0/I)_f$ vs. $[Et_3N]^2$. Absorption spectroscopy showed that this was due to end absorption by triethylamine.

Several runs were made to determine ϕ_r in the presence of different amounts of triethylamine. Precipitation of $Et_3N{\cdot}HCl$ was generally noted. Some typical results are shown in Table IX.

(b) In Cyclohexane with [PhCl] ≈ 10^{-3} M. The stock solutions were (A) chlorobenzene (1.98×10^{-3} M) plus GLC reference standard (cyclooctane) in cyclohexane and (B) triethylamine (0.43 M) in cyclohexane. The results shown in Table X were obtained.

(c) In Cyclohexane/Acetonitrile (1:9 v/v). The fluorescence quenching constant K_{SV} was 23 M^{-1} ([PhCl] = 1.94×10^{-3} M, $[Et_3N]$ = 0–0.26 M). Quantum yields of reaction are given in Table XI for photolyses of PhCl (9.7×10^{-3} M).

(d) In Methanol. K_{SV} was 1.8 M^{-1} ($[Et_3N]$ = 0–0.5 M). The results of the photolyses are given in Table XII. The concentration of chlorobenzene in the solutions to be photolyzed was 1.11×10^{-2} M.

Preparation of 1-(*p*-Chlorophenyl)-3-(dimethylamino)-propane (3). *p*-Chloroacetophenone was prepared by Friedel–Crafts acylation of chlorobenzene with acetic anhydride/$AlCl_3$. This was subjected to a Mannich reaction with paraformaldehyde, dimethylamine hydrochloride, and HCl in absolute alcohol. The Mannich base was reduced with sodium borohydride in a phosphate buffer at pH 7.0, affording 1-(*p*-chlorophenyl)-3-(dimethylamino)-1-propanol as a pale yellow oil: NMR (CCl_4) δ 7.2 (s, 4 H), 6.0 (s, OH), 4.6 (t, 1 H), 2.4 (m, 2 H), 2.1 (s, 6 H), 1.7 (m, 2 H). Dehydration with 50% aqueous sulfuric acid at reflux yielded 1-(*p*-chlorophenyl)-3-(dimethylamino)propene [NMR (CCl_4) δ 7.2 (s, 4 H), 6.0 (m, 2 H), 3.0 (d, 2 H), 2.1 (s, 6 H)], which was hydrogenated to the saturated derivative **3** by using Pd/C in glacial acetic acid. Anal. Calcd: C, 66.82; H, 8.15. Found: C, 66.50; H, 7.79; mol wt 197 [$M^+(^{35}Cl)$].

Table X

$[Et_3N]$, M	0	0.016	0.033	0.066	0.110	0.162	0.216
ϕ/ϕ^0	1.0	1.36, 1.33	1.30, 1.49	1.18, 1.30	0.87, 1.01	0.67, 0.77	0.41, 0.51
ϕ_r (av)	0.51	0.68	0.71	0.63	0.48	0.37	0.23
fraction of singlets quenched by Et_3N	0	0.06	0.11	0.19	0.29	0.37	0.44

Table XI

$[Et_3N]$, M	0	0.007	0.013	0.026	0.046	0.066	0.109
ϕ_r	0.16	0.25	0.31	0.38	0.40	0.39	0.38

Table XII

$[Et_3N]$, M	ϕ_r	% light absorbed by Et_3N	% singlets quenched by Et_3N
0	0.25	0	0
0.022	0.26	3	4
0.027	0.26	4	5
0.056	0.26	8	9
0.111	0.27	14	17
0.167	0.28	19	23
0.174	0.28	21	24
0.223	0.30	24	29
0.347	0.30	34	38
0.521	0.26	45	48
0.694	0.21	50	56

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Registry No. 3, 27107-82-0; 2,2′,5,5′-tetrachlorobiphenyl, 35693-99-3; 4-chlorobiphenyl, 2051-62-9; 1-chloronaphthalene, 90-13-1; chlorobenzene, 108-90-7; 1-(*p*-chlorophenyl)-3-(dimethylamino)-1-propanol, 16254-21-0; 1-(*p*-chlorophenyl)-3-(dimethylamino)-propene,, 81012-73-9.

Supplementary Material Available: Original kinetic data (Table III) and deuterium incorporation data (Table VI) for the photolysis of 4-chlorobiphenyl and of 1-chloronaphthalene with aliphatic amines are available (5 pages). Ordering information is given on any current masthead page.

Photolysis of Aryl Chlorides with Dienes and with Aromatic Amines

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Simple dienes quench the fluorescence of 1-chloronaphthalene and 4-chlorobiphenyl with a concurrent singlet-state photochemical reaction, which does not involve dechlorination. Similar chemistry is brought about when the diene is initially excited. Chlorobiphenyls quench the fluorescence of *N*,*N*-dimethylaniline with concomitant photodechlorination of the aryl chloride. Attempts to extend this reaction to amines having longer wavelength absorption were unsuccessful.

In the accompanying paper,[1] the photolysis of aryl chlorides in the presence of aliphatic amines was examined. A mechanism was proposed in which initial light absorption by the aryl halide was followed by interaction of the amine with both the singlet and triplet excited states of the halide. While the singlet-state process led to fluorescence quenching, the triplet-state interaction was mainly responsible for the amine-assisted photodechlorination. At least two pathways were involved in the later steps of the reaction; following electron transfer to the aryl halide, both hydrogen abstraction from the solvent and, where possible, proton transfer were responsible for the formation of the reduced product (Scheme I).

Scheme I

$$\mathrm{ArCl} \xrightarrow{h\nu} {}^1\mathrm{ArCl}$$

$${}^1\mathrm{ArCl} \rightarrow \mathrm{ArCl}$$

$$\mathrm{R_3N} + {}^1\mathrm{ArCl} \rightarrow {}^1(\mathrm{R_3N}\cdot\mathrm{ArCl}) \rightarrow \mathrm{R_3N} + \mathrm{ArCl}$$

$${}^1\mathrm{ArCl} \rightarrow {}^3\mathrm{ArCl}$$

$${}^3\mathrm{ArCl} \rightarrow \mathrm{ArCl}$$

$$\mathrm{R_3N} + {}^3\mathrm{ArCl} \rightarrow {}^3(\mathrm{R_3N}\cdot\mathrm{ArCl}) \leftrightarrow (\mathrm{R_3N}^{+}\cdot\ \mathrm{ArCl}^{-}\cdot)$$

$$\mathrm{ArCl}^{-}\cdot \rightarrow \mathrm{Cl}^{-} + \mathrm{Ar}\cdot \xrightarrow{\mathrm{RH}} \mathrm{ArH}$$

$$(\mathrm{H}^{+}) + \mathrm{ArCl}^{-}\cdot \rightarrow \mathrm{ArClH}\cdot \rightarrow \mathrm{ArH} + \mathrm{Cl}\cdot$$

In this paper we extend our studies to dienes and to aromatic amines.

Photolysis with Dienes

The effect of dienes on the efficiency of photodegradation of aryl halides is rather confused. Some systems appear to show increased photolability when dienes are present, while for others the reverse effect is observed. In the former category, Smothers, Schanze, and Saltiel[2] have studied the photodechlorination of 9,10-dichloroanthracene assisted by 2,5-dimethyl-2,4-hexadiene; they present evidence for reaction proceeding from a singlet exciplex and triplex, where the complexes have charge-transfer character, $\mathrm{diene}^{+}\cdot\ldots\mathrm{ArCl}^{-}\cdot$.

On the other hand, Ruzo, Zabik, and Schuetz[3] observed that 1,3-cyclohexadiene retarded the photodecomposition of certain polychlorinated biphenyls. They argued that a reactive triplet state was involved and used the method to estimate the triplet lifetimes of the PCB molecules in solution. Later, we found that dienes also quench the singlet states of many PCB molecules;[4] further, in the particular case of 1,3-cyclohexadiene, the diene absorbs the incident light competitively with the aryl halide.[5] If we

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[1] Bunce, N. J. *J. Org. Chem.*, preceding paper in this issue.

[2] Smothers, W. K.; Schanze, K. S.; Saltiel, J. *J. Am. Chem. Soc.* **1979**, *101*, 1895.

[3] Ruzo, L. O.; Zabik, M. J.; Schuetz, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 3809.

[4] Bunce, N. J.; Kumar, Y.; Ravanal, L.; and Safe, S. *J. Chem. Soc., Perkin Trans. 2* **1978**, 880.

[5] Bunce, N. J.; Bergsma, J. P.; Bergsma, M. D.; DeGraaf, W.; Kumar, Y.; Ravanal, L. *J. Org. Chem.* **1980**, *45*, 3708.

0022-3263/82/1947-1955$01.25/0