Structure and Mechanism in the Photoreduction of Aryl Chlorides in Alkane Solvents

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The photochemical dechlorinations of chlorides of the benzene, naphthalene, and biphenyl series are compared. It is concluded that triplet-state homolysis of the Ar–Cl bond is the preferred reaction pathway provided that the chloro compound has a triplet energy close to the necessary bond-dissociation energy. For 1-chloronaphthalene this is not the case, and an inefficient degradation takes place from the singlet state.

Photolysis of aryl halides in solution generally involves radical intermediates through cleavage of the carbon–halogen bond. In aromatic solvents, this leads to arylation, while reductive dehalogenation is observed in solvents able to donate a hydrogen atom.[1] As noted in a recent review[2] these processes have been widely studied because of the importance of halogenated materials as environmental pollutants.
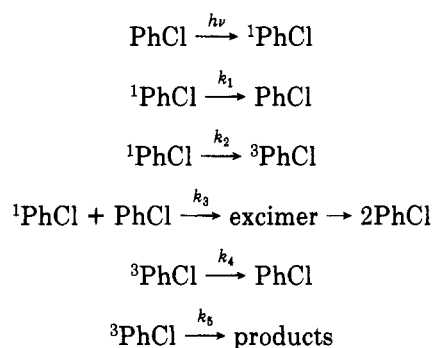
Among aryl chlorides, which are the subject of this paper, reductive dechlorination can proceed by a variety of mechanisms. Homolytic cleavage of the C–Cl bond may occur,[3,4] or the reaction may be initiated by electron transfer[5,6] possibly accompanied by protonation of the excited aryl chloride.[7,8] In this paper, our objective has been to try to discover the factors that make a particular mechanism dominant for an aryl chloride or class of aryl chlorides. To this end, we have studied chlorinated representatives from the benzene, naphthalene, and biphenyl series.

Results and Discussion

Chlorobenzene.[9] In nonpolar solvents, photoreduction of chlorobenzene proceeds by simple homolysis.[3] Even though excimers may be detected spectroscopically in concentrated chlorobenzene solutions at low temperature, they are not involved in the major reaction pathway. This was shown by studying the reaction quantum yield (ϕ_r) as a function of chlorobenzene concentration; ϕ_r decreased as the concentration rose. Thus, either the excimer is completely unreactive or it decomposes with much lower photoefficiency than the monomer. A predominantly excimer route for photolysis leads to ϕ_r increasing with concentration.

The data were analyzed in terms of Scheme I, where the reaction proceeds from the triplet excited state.

Scheme I

$$PhCl \xrightarrow{h\nu} {}^{1}PhCl$$

$${}^{1}PhCl \xrightarrow{k_1} PhCl$$

$${}^{1}PhCl \xrightarrow{k_2} {}^{3}PhCl$$

$${}^{1}PhCl + PhCl \xrightarrow{k_3} excimer \rightarrow 2PhCl$$

$${}^{3}PhCl \xrightarrow{k_4} PhCl$$

$${}^{3}PhCl \xrightarrow{k_5} products$$

Steady-state analysis gives eq 1 for the dependence of

$$\frac{1}{\phi_r} = \left(\frac{k_4 + k_5}{k_5}\right)\left(\frac{k_1 + k_2 + k_3[PhCl]}{k_2}\right) \quad (1)$$

ϕ_r upon the chlorobenzene concentration. The experimental data[9] are described by eq 2. Thus at infinite dilution (no excimer) ϕ_r is expected to be in the range 0.50–0.54.

$$\phi_r^{-1} = (1.94 \pm 0.08) + (21.5 \pm 2.2)[PhCl]; \ r = 0.976 \quad (2)$$

Compound 1, which can form a fluorescent intramolecular excimer [λ_{max}(excimer) = 315 nm in cyclohexane at room temperature], behaves in accordance with the proposed mechanism. At a concentration of 0.01 M in cyclohexane, compound 1 has $\phi_r = 0.01$, to be compared with $\phi_r = 0.42$ for chlorobenzene at 0.02 M in the same solvent.

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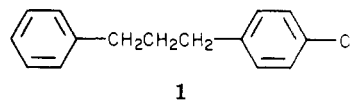
The multiplicity of the excited state was established to be triplet by the following experiments.

(i) Xenon Assistance[10] to the Reaction. Xenon promotes the $S_1 \rightarrow T_1$ intersystem crossing, and at 1 atm pressure of xenon small effects on fluorescence quenching and ϕ_r enhancement were observed.[11]

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(ii) Triplet Quenching of the Reaction. We had no success at quenching the photoreduction of chlorobenzene using 2-octene, even though simple alkenes are reported to quench triplets of benzene derivatives.[12] However, the reaction was quenched by biacetyl, and a plot of ϕ_0/ϕ_Q vs. [biacetyl] afforded the Stern–Volmer quenching constant 250 M^{-1}. With the lifetime of triplet chlorobenzene in cyclohexane measured[11,13] at 5×10^{-7} s, this gives 5×10^8 L mol^{-1} s^{-1} for the bimolecular quenching constant for the interaction of biacetyl with triplet chlorobenzene. Consistent with this conclusion but less compelling is the influence of oxygen on the reaction. Oxygen quenches the fluorescence of chlorobenzene, $(\phi_0/\phi_{O_2})_F = 1.3$, but has a bigger influence on the quantum yield of the reaction, $(\phi_0/\phi_{O_2})_r = 1.7$, both measured in cyclohexane.

(iii) Quantum Yield of Intersystem Crossing (ϕ_{ISC}). With a maximum ϕ_r of 0.54, it should be possible to assign the major reactive state from the triplet yield. The only reported[11] value for ϕ_{ISC} is 0.3; this seems low given that toluene[12] has a ϕ_{ISC} of about 0.5. Our own measurements, based on the biacetyl sensitization technique[14] with suitable corrections (see Experimental Section), yield a value for ϕ_{ISC} of 0.64 ± 0.02. Again, this is consistent with a triplet-state photoreactivity. We note that ϕ_{ISC} ($=k_2/(k_1 + k_2 + k_3[PhCl])$) will be concentration dependent. Our measurements were made at [PhCl] = 5.0×10^{-3} M.

We now consider the energetics of C–Cl bond cleavage. The value of $D(C_6H_5-Cl)$ formerly accepted[15] was 80 kcal/mol, allowing cleavage of triplet chlorobenzene ($E_T \approx 85$ kcal/mol) to proceed with high efficiency. However, the value of this bond energy depends on the value of $\Delta H_f°(C_6H_5\cdot)$ which has been greatly revised. The other quantities needed to compute $D(C_6H_5-Cl)$ are not in dispute: $\Delta H_f°(Cl\cdot(g)) = +28.9$ kcal/mol;[16] $\Delta H_f°(C_6H_5Cl(l)) = +2.8$ kcal/mol;[17] $\Delta H_{vap}°(C_6H_5Cl) = +9.8$ kcal/mol.[18] Recent values for $\Delta H_f°(C_6H_5\cdot)$ include 78.5 kcal/mol (Benson,[16] 1976), 77 kcal/mol (Szilágyi and Bérces,[19] 1970), 72 kcal/mol (Istomin and Lobanov,[20] 1975), and 72.5 kcal/mol (Fujii and Asaba,[21] 1977).

Thus $D(C_6H_5-Cl)$ appears to lie between 85 and 91 kcal/mol, making C–Cl homolysis at best thermoneutral or more likely somewhat endothermic. However, Whiffen[22] showed that ground-state chlorobenzene has a vibrational energy content of some 4.1 kcal/mol; if the figure is comparable in the excited state, bond cleavage might still be able to occur efficiently.

Accepting the triplet nature of the reaction and substituting values of ϕ_r and ϕ_{ISC} into eq 1, we find the ratio $k_5/(k_4 + k_5) \approx 0.8$; in other words, 80% of all triplets formed undergo reaction. Knowing the lifetime of triplet chlorobenzene ($=(k_4 + k_5)^{-1}$), we deduce the first-order rate constant for decomposition (k_5) to be 1.6×10^6 s^{-1}. Finally, using the data of eq 1 and 2, we can determine ϕ_{ISC} at

infinite dilution; the figure obtained is 0.7.

1-Chloronaphthalene. Our studies show this compound to be almost the reverse of chlorobenzene in its behavior. Whereas chlorobenzene degrades efficiently from its triplet state, with excimer formation inhibiting the chemistry, 1-chloronaphthalene reacts much less efficiently from the singlet state. We previously argued that an excimer appears to be reactive;[6] we have now determined the enthalpy of excimer formation by studying the monomer–excimer fluorescence intensity ratio[23] over the temperature range –60 to +25 °C. This was found to be close to –3 kcal/mol in both ether and isooctane and is less than the values recorded previously for other simple naphthalenes.[24] Introduction of the chlorine atom appears to disfavor excimer formation, because the trend is accentuated for 1,5-dichloronaphthalene. For this compound the excimer band is difficult to observe, and the enthalpy of association is less negative than –1 kcal/mol.

Concerning the photodegradation of 1-chloronaphthalene, the relevant questions were as follows: (i) is the reaction singlet in nature; (ii) if so, is the excimer the reactive species?

It is easy to argue against the triplet mechanism on energetic grounds. Simple naphthalenes have $E_T \approx 59$ kcal/mol, making homolysis of the Ar–Cl bond (>80 kcal/mol) unreasonably endothermic even if vibrational contributions are included. However, experimental evidence on this point was more difficult to obtain. An attempt at sensitization by benzophenone indeed led to decomposition of 1-chloronaphthalene, but the reaction products showed[25] that the reaction had taken a different course. We have an indication that the "sensitized" reaction may in fact be an electron-transfer process; benzophenone quenches the fluorescence of 1-chloronaphthalene [$K_{SV} = 150$ M^{-1} in isooctane, after correction of the fluorescence intensities for (i) competing absorption of excitation light by benzophenone and (ii) absorption of emitted light by benzophenone]. Electron transfer would be consistent with the observation that arylation is the predominant reaction when benzophenone is present.

Quenching studies likewise gave equivocal results. Biacetyl promoted the disappearance of 1-chloronaphthalene, rather than quenching it, as also did oxygen.[26] Experiments conducted with xenon were consistent with a singlet reaction, however; xenon quenched the fluorescence of 1-chloronaphthalene and also quenched the photodecomposition.

The following arguments suggest the involvement of the excimer in the reaction. (i) The reaction quantum yield ϕ_r increases with the concentration of 1-chloronaphthalene.[6,27] (ii) Compound **2**, which forms an intra-
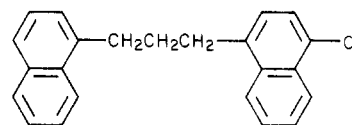
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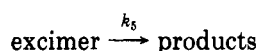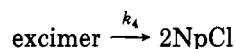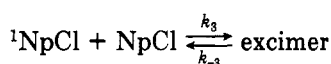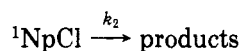(24) B. Stevens, *Adv. Photochem.*, **8**, 161 (1971).

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(26) Attempts to use diene quenchers were unsuccessful. For example, when 1.0×10^{-3} M 1-chloronaphthalene was photolyzed in the presence of 0, 5×10^{-4}, 1×10^{-3}, 2×10^{-3}, 3×10^{-3}, and 5×10^{-3} M 2,5-dimethyl-2,4-hexadiene for 4.5 h, the percent decomposition was 93, 92, 89, 78, and 77%, respectively. However, the percent light absorbed directly by 1-chloronaphthalene at 254 nm was 100, 20, 11, 6, 4, and 2.5%, respectively. Because of the ambiguity in interpreting such data, no attempt was made to photolyze the 1-chloronaphthalene to an appropriately lower conversion.

molecular excimer, is more photolabile than 1-chloronaphthalene. For compound 2 at 0.006 M in cyclohexane, $\phi_r = 0.009$ as compared with $\phi_r = 0.0012$ for an equimolar mixture of naphthalene and 1-chloronaphthalene at the same concentration. (iii) In our preliminary results[6] we found that ϕ_r became smaller at very low concentrations. However, these experiments at low concentrations are very difficult to do: not all the incident light is absorbed, the products absorb light competitively, and the analytical work is less accurate at low concentrations. We therefore undertook a study of the effect of concentration upon ϕ_r in the concentration region where all the light is absorbed.

From Scheme II we can deduce eq 3 for the dependence of ϕ_r on [NpCl]. The reversible formation of the excimer is proposed by following the results for naphthalene.

Scheme II

$$NpCl \xrightarrow{h\nu} {}^1NpCl$$

$$^1NpCl \xrightarrow{k_1} NpCl$$

$$^1NpCl \xrightarrow{k_2} products$$

$$^1NpCl + NpCl \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} excimer$$

$$excimer \xrightarrow{k_4} 2NpCl$$

$$excimer \xrightarrow{k_5} products$$
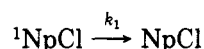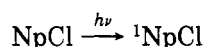
$$\phi_r = \frac{k_2(k_{-3} + k_4 + k_5) + k_3k_5[NpCl]}{(k_1 + k_2)(k_{-3} + k_4 + k_5) + k_3(k_4 + k_5)[NpCl]} \quad (3)$$

The extreme cases are (i) $k_5 = 0$ (unreactive excimer), from which we obtain eq 4, and (ii) $k_2 = 0$ (unreactive monomer), which leads to eq 5.

$$\frac{1}{\phi_r} = \frac{k_3k_4[NpCl]}{k_2(k_{-3} + k_4)} + \frac{k_1 + k_2}{k_2} \quad (4)$$

$$\frac{1}{\phi_r} = \frac{k_1(k_{-3} + k_4 + k_5)}{k_3k_5[NpCl]} + \frac{k_4 + k_5}{k_5} \quad (5)$$

A series of experiments using [NpCl] in the range 1.06×10^{-3}–3.76×10^{-2} M indicated essentially no dependence of ϕ_r upon [NpCl] in this concentration range. Since combinations of rate constants could be such that either of conditions i or ii could be satisfied or that both monomer and excimer react, this experiment does not provide the unequivocal result that was sought. We can say only that the excimer appears to be involved but not that it is the sole reactive intermediate.

Chlorobiphenyls. Previous work in our own[28] and other[4] laboratories has implicated homolysis of the C–Cl bond in the triplet excited state of the chlorobiphenyl. From triplet yields[4,29] the high ϕ_r values for *o*-chlorobiphenyls are consistent only with a reactive triplet. Compounds lacking ortho chlorines generally have $\phi_r < 10^{-3}$, and assignment of the excited state is more difficult, but the excited state is believed to be triplet on the following

grounds: (i) xenon assistance of the reaction;[28] (ii) reaction quenching by biacetyl. Other experiments designed to probe this point give inconclusive results: (i) benzophenone sensitization is very inefficient because ϕ_r is so small;[28] (ii) oxygen does not act as a quencher, but instead, it promotes decomposition.

The difference in photolability between the two groups is energetic in origin, but the energies of the excited triplets are hard to determine exactly. Wagner and Scheve[30] have concluded that simple ortho-substituted biphenyls have planar T_1 excited states; since the ground states are nonplanar, the O–O phosphorescence bands and hence the triplet energy cannot be determined spectroscopically. From the high-energy onset of phosphorescence,[30,31] *o*-chlorobiphenyl has had E_T estimated at ~ 72 kcal/mol, while that of the para isomer is ~ 66 kcal/mol. Qualitatively, it is clear that the ortho isomer has the higher energy content and hence is more likely to be able to dissociate efficiently. However, C–Cl bond cleavage is considerably endothermic according to the analysis, even for 2-chlorobiphenyl, yet the compound has $\phi_r = 0.4$.[28] We believe that this is because the triplet energy has been underestimated.

Kaiser[32] has calculated the activation energies for twisting a ground-state chlorobiphenyl through the planar ground state. Thus the total triplet energy of a chlorobiphenyl will be at least the sum of the phosphorescence onset and the ground-state activation term. This adds 1 or 2 kcal/mol to the triplet energy of 4-chlorobiphenyl and brings it up to about 68 kcal/mol, consistent with the fact[30] that 4-chlorobiphenyl accepts triplet energy reversibly from benzophenone ($E_T = 69$ kcal/mol).

For 2-chlorobiphenyl, the ground-state rotation term is larger, and if ~ 5 kcal/mol were added to the 72-kcal/mol phosphorescence onset, then a triplet energy close to D-(Ar–Cl) would be obtained. *o*-Chlorobiphenyls can photolyze with reasonable efficiency,[33] because the vibrational contribution to the total energy would be expected to be at least twice the 4.1 kcal/mol found for chlorobenzene,[22] because a monochlorobiphenyl has 60 normal vibrational modes compared with 30 for chlorobenzene. The extremely inefficient decomposition of 4-chlorobiphenyl can probably be explained similarly. If we assume a C–Cl bond energy near 85 kcal/mol, the triplet energy of 4-chlorobiphenyl falls short by ~ 16 kcal/mol. But since the *average* molecule of 4-chlorobiphenyl has a vibrational energy content of >8 kcal/mol, a small number will have twice this, consistent with a low value of ϕ_r.

Triplet lifetimes of chlorobiphenyls in solution have been reported[4] by using the diene quenching of reaction as a probe. This method assumes that energy transfer from triplet chlorobiphenyl to a diene is diffusion controlled. In our attempts to use this method, we have found that competing light absorption by the diene makes the results completely unreliable. Reaction quenching is indeed observed, but if account is taken of the light actually ab-

(27) The difficulty with the experiment reported in ref 6 is the very small dependence of ϕ_r upon concentration in the convenient range [NpCl] $\geq 10^{-3}$ M. Below this concentration, 1-chloronaphthalene does not absorb all the light, and ϕ_r has to be corrected for this. In addition, the reaction products will absorb a substantial proportion of the light.

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(33) The situation is even more complicated for chlorobiphenyls with more than two ortho chlorines. From the results of Wagner and Scheve,[30] these compounds do not have planar triplets. Hence the phosphorescence onset represents a transition from a nonplanar triplet to a nonplanar ground state, but the nonplanar ground state is presumably not the equilibrium ground state. Three and four ortho chlorines raise the ground-state barrier to ~ 25 and ~ 58 kcal/mol, respectively;[36] thus the rotation energies are large but not easily determined for correction of the phosphorescence energy.

Table I

[PhCl], M	0.008	0.010	0.020	0.031	0.050	0.051	0.071
ϕ_{rel}	1.23	1.18	1.00	0.88	0.79	0.82	0.72

Table II

[biacetyl], M	0	0.001	0.003	0.005	0.008
ϕ_0/ϕ_Q	1.00	1.00	1.26	2.05	2.60

sorbed by the chlorobiphenyl and it is assumed that light absorbed by the diene does not lead to reaction, it is found that the photoreactivity of the chlorobiphenyl is enhanced in the presence of the diene. This is consistent with what was observed previously for 1-chloronaphthalene[6] and 9,10-dichloroanthracene.[7] These studies are reported in the Experimental Section.

Conclusions

Our studies indicate that the degradation pathway of a photoexcited chloroarene is determined mainly by the triplet energy of the chloride. When the triplet energy is comparable with or larger than the C–Cl bond-dissociation energy, homolysis occurs with high efficiency from the triplet. This is the case for chlorobenzene and for o-chlorobiphenyls. When the triplet energy is lower, photodecomposition is very much less efficient. For chlorobiphenyls lacking ortho substituents, an inefficient triplet reaction is observed, but for 1-chloronaphthalene, whose triplet energy is lower still, an inefficient reaction probably involving the singlet excimer is observed. The participation of excimers in the photochemistry is another theme running through this investigation. Excimers are well-known for the simple derivatives of benzene and naphthalene, and they participate in the photochemistry of chlorobenzene and 1-chloronaphthalene. However, excimers of biphenyls are very difficult to observe,[34] and accordingly, they do not appear to participate in the chemistry of chlorobiphenyls. We plan to try to verify these conclusions by studying more highly condensed aryl chlorides and by attempting to observe the corresponding decrease in photoefficiency in the aryl bromide series.

Experimental Section

Procedures for fluorescence, degassing samples, photochemical equipment and analysis by gas chromatography have been described in detail previously.[28] All reactions were carried out in the absence of air, except as noted. For the determination of fluorescence intensities in the presence or absence of gases such as Xe or O_2, the measurements were made in the same 8-mm-o.d. quartz ampules as were used for photolysis. The equipment was the MPF-2A spectrofluorometer together with the phosphorescence accessory, which was redesigned to accommodate this size of ampule. The following compounds were used as internal standards for gas chromatographic analysis: chlorobenzene, cyclooctane; 1-chloronaphthalene, pentadecane; chlorobiphenyls, octadecane. The column used was 8 ft × $^1/_8$ in., 10% OV101 on 80/100-mesh Chromosorb W, operated at 40 °C (chlorobenzene), 150 °C (1-chloronaphthalene), and 165–200 °C (chlorobiphenyls).

Effect of Concentration on the Quantum Yield of Decomposition of Chlorobenzene. The quantum yields were all determined at conversions where the amount of chlorobenzene reacted had been shown experimentally to be directly proportional to light absorbed. The data of ref 9 and the new data obtained in this study were normalized against the photoreactivity of 0.02 M chlorobenzene in cyclohexane. This gave the results shown in Table I. Then ϕ_r was carefully determined for a 1.98 × 10^{-2} M solution against a ferrioxalate actinometer.[35] Because the RPR 2537 lamps are not monochromatic, the actinometry was done as follows. The chlorobenzene solutions, in the usual 8-mm-o.d. evacuated quartz ampules, were held in 20-mm quartz test tubes

which contained cyclohexane. Actinometer 1 samples contained 0.1 M potassium ferrioxalate in 0.05 M H_2SO_4; these ampules were similarly placed in 20-mm quartz test tubes containing cyclohexane. Actinometer 2 samples were also 0.1 M potassium ferrioxalate but were placed in 20-mm quartz test tubes containing chlorobenzene in cyclohexane (0.05 M). Then the light absorbed by chlorobenzene is calculated from the difference between actinometers 1 and 2. After photolysis, the procedure of Hatchard and Parker[35] was modified by taking a 1.0-mL aliquot of the actinometer to which was added 0.1% phenanthroline solution (20 mL) and acetate buffer (10 mL), and this was made up to a 100-mL total volume with water, prior to reading of the absorbance due to the Fe^{2+}-phenanthroline complex at 510 nm. For 0.0198 M chlorobenzene in cyclohexane, ϕ_r was determined as 0.41, and from this the results of eq 1 are derived.

Preparation of 1-(p-Chlorophenyl)-3-phenylpropane (1). A Grignard reagent was prepared from 1-bromo-2-phenylethane, and to this was added dropwise an equimolar quantity of p-chlorobenzaldehyde. The crude secondary alcohol (ν_{OH} 3400 cm^{-1}) was oxidized (dichromate)[36] to the ketone ($\nu_{C=O}$ 1680 cm^{-1}) which was obtained in 74% yield: mp 74–75 °C; NMR (CCl$_4$) δ 3.0 (m, 4 H), 7.0–7.9 (m, 9 H); mass spectrum, m/e 244 (M$^+$). Anal. Calcd: C, 73.62; H, 5.35. Found: C, 73.56; H, 5.56. Reduction[37] afforded the product 1 as an almost colorless oil: bp 216–219 °C (20 mm); NMR (CCl$_4$) δ 1.7–2.2 (m, 2 H), 2.3–2.8 (m, 4 H), 6.8–7.5 (m, 9 H); mass spectrum, m/e 230 (M$^+$). Anal. Calcd: C, 78.08; H, 6.55. Found: C, 77.79; H, 6.74.

Photolysis of Chlorobenzene in the Presence of Xenon. The method was described previously.[28] Fluorescence intensities of the solutions to be photolyzed, which contained chlorobenzene (0.0236 M) in cyclohexane with and without ca. 1 atm of xenon, were 19 ± 1 and 15 ± 1. The ratio of reaction quantum yields ϕ(Xe)/ϕ(no Xe) was 1.14.

Photolysis of Chlorobenzene with Triplet Quenchers. When 2-octene was used as the quencher, the solutions contained chlorobenzene (0.02 M) in cyclohexane with and without 2-octene (0.02 M). 2-Octene quenches the fluorescence of chlorobenzene only weakly (K_{SV} = 1.7 M^{-1}), so that at this concentration, only 3% of the singlets are quenched. The ratio of reaction quantum yields ϕ(octene)/ϕ_0 was 0.94. A series of duplicate reaction mixtures containing chlorobenzene (0.02 M) in cyclohexane together with biacetyl (0–0.008 M) gave the results shown in Table II. The slope of the graph of ϕ_0/ϕ_Q vs. [biacetyl] was 250 M^{-1}; this is probably an underestimate on account of the photolability of biacetyl itself.

The fluorescence intensity in the presence and absence of O_2 was determined for a 2.35 × 10^{-3} M solution of chlorobenzene in cyclohexane with two aerated and two degassed ampules. Eight determinations of the fluorescence intensity (excitation 267 nm, emission 286 nm, range = 6, excitation and emission slits 7 nm) were as follows: degassed, 31.8 ± 0.1 and 32.2 ± 0.1; aerated, 24.6 ± 0.2 and 23.7 ± 0.2. Four determinations of the ratio of the quantum yield with and without oxygen using 0.020 M solutions gave the value ϕ_0/ϕ_{O_2} = 1.7 ± 0.2.

Quantum Yield of Intersystem Crossing of Chlorobenzene. The determinations were made in cyclohexane solution, with the samples contained in the same degassed 8-mm-o.d. quartz ampules used for photolysis. Instead of two freeze–pump–thaw cycles with a mechanical pump, four such cycles were used, with an oil diffusion pump being used for the last two cycles.

The extinction maxima of toluene and chlorobenzene in cyclohexane are almost equal (ϵ 240). Toluene has λ_{max} 255.5, 261.5, 269.5 nm; the maxima for chlorobenzene are 258, 264.5, and 272 nm. At three wavelengths, equal concentrations of the two aromatics have equal absorbances: 264, 268, and 271 nm. These wavelengths were used as excitation wavelengths. Biacetyl has λ_{max} 276 nm (ϵ 17).

(34) K. A. Zachariasse, W. Kühnle and A. Weller, *Chem. Phys. Lett.*, **59**, 375 (1978).

(35) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

(36) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, 1967, p 1059.

(37) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

Table III

Ph₂CO, M	0	5 × 10⁻⁴	1 × 10⁻³	1.5 × 10⁻³	2 × 10⁻³	3 × 10⁻³
measured I_F	58	51	46	38	34	27
I_F corrected for Ph₂CO absorption at 295 nm	58	51	47	39	35	28
I_F corrected for Ph₂CO absorption at 340 nm	58	54	53	47	45	40

Table IV

[biacetyl], M	0	0.0009	0.0019	0.0028	0.0038	0.0047
% reacted	28	36	36	44	41	41

The working solutions of the aromatics were 5.0×10^{-4} M. In addition they contained biacetyl (0.5×10^{-3}–4.0×10^{-3} M). A curve of phosphorescence intensity (520 nm) was prepared for solutions of biacetyl in cyclohexane alone. The intensity of biacetyl phosphorescence at 520 nm was obtained by scanning through the excitation and taking readings at excitation wavelengths 264, 268, and 271 nm. The instrument was used in ratio mode with filter "29" in place to avoid the problem of second-order scattering. The raw intensity data were corrected (i) for biacetyl fluorescence by opening the tubes to admit air and repeating the reading (the correction was very small) and (ii) by correcting for the phosphorescence intensity of biacetyl alone (this correction was significant). The value of ϕ_{ISC} obtained was dependent on the excitation wavelength: 264 nm, 0.60; 268 nm, 0.62; 271 nm, 0.69. Excitation maxima for the aromatic alone were 268 nm (PhCl) and 265 nm (PhCH₃). The average of the three determinations gave $\phi_{ISC} = 0.64$ in comparison with toluene for which $\phi_{ISC} = 0.53$.[14] Because several corrections must be made to extract ϕ_{ISC} from the raw data, we do not attach significance to the apparent change in ϕ_{ISC} with excitation wavelength.

Preparation of 1-(4-Chloro-1-naphthyl)-3-(1-naphthyl)-propane (2). 4-Chloro-1-acetonaphthone was prepared by the method of Jacobs et al.[38] and after purification through the picrate was condensed with 1-naphthaldehyde in the presence of base to afford 1-(4-chloro-1-naphthyl)-3-(1-naphthyl)-2-propen-1-one. Mild hydrogenation (Pd/C in alcohol) afforded the corresponding saturated ketone [m/e 344 M⁺(^{35}Cl)] which was reduced[36] to the dinaphthylpropane 2. This was purified by chromatography over alumina to give a colorless oil with a noticeable green-blue fluorescence. GLC analysis, however, indicated that it contained ~10% of the dechloro compound, 1,3-dinaphthylpropane, and the mixture was not resolvable by TLC. The ϕ_r values reported in the text are corrected for light absorption by this impurity, with the assumption of equal molar absorptivities of the chloride and the parent hydrocarbon.

Quenching of 1-Chloronaphthalene Fluorescence by Benzophenone. The solutions contained 1-chloronaphthalene (5.0×10^{-3} M) and benzophenone ((0–3.0) × 10⁻³ M). Excitation was at 295 nm, with the fluorescence intensity measured at 340 nm. From the absorbances of the two compounds at 295 nm and the absorbance of benzophenone at 340 nm, the raw fluorescence intensities were corrected for the light not absorbed by 1-chloronaphthalene and the fluorescence absorbed by benzophenone (see Table III).

Photolysis of 1-Chloronaphthalene with Biacetyl. Cyclohexane solutions of 1-chloronaphthalene (8.4×10^{-4} M) were photolyzed in the presence of varying amounts of biacetyl (Table IV). The solutions were photolyzed for 39 min by using a photon flux of ~5×10^{16} quanta/s. After the reaction, all the biacetyl had reacted in all ampules.

Reaction of 1-Chloronaphthalene in the Presence of Air. The fluorescence of 1-chloronaphthalene was quenched 11% in aerated isooctane solution as compared with a degassed solution (λ(excitation) = 295 nm, λ(emission) = 335 nm, [NpCl] = $5.0 \times$

(38) T. L. Jacobs, S. Winstein, J. W. Ralls, and J. H. Robson, *J. Org. Chem.*, **11**, 27 (1946).

Table V

[NpCl], M	1.06 × 10⁻³	2.65 × 10⁻³	5.3 × 10⁻³	9.4 × 10⁻³	1.88 × 10⁻²	3.76 × 10⁻²
no. of expts	4	4	4	2	2	2
ϕ_r	2.9 × 10⁻³	3.1 × 10⁻³	3.0 × 10⁻³	2.7 × 10⁻³	2.8 × 10⁻³	2.7 × 10⁻³

Table VI

[biacetyl], M	0	0.0005	0.0017	0.0029	0.0039	0.0056
(ϕ_0/ϕ) disappearance	1.00	1.05	1.09	0.95	1.12	1.22
(ϕ_0/ϕ) appearance of biphenyl	1.00	1.07	1.06	1.25	1.12	1.33

Table VII

[C₆H₈], M	0	0.0034	0.0069	0.0103	0.0172
(ϕ_0/ϕ)_r	1.00	1.27	1.61	1.91	2.56
A_{TCB}	0.13	0.13	0.13	0.13	0.13
$A_{C_6H_8}$	0	0.51	1.04	1.55	2.58
% light absorbed by TCB	100	20	11	8	5

Table VIII

4-Chlorobiphenyl (Irradiation Time 3.5 h)

diene, M	0	0.001	0.002	0.003	0.005
% reacted	65	67	83	92	98
% light adsorbed by chlorobiphenyl	100	57	40	31	21

2,4,6-Trichlorobiphenyl (Irradiation Time 2 min)

diene, M	0	0.0005	0.001	0.002	0.003	0.005
% reacted	85	61	46	33	27	21
% light absorbed by chlorobiphenyl	100	26	15	8	5	3

2,2',5,5'-Tetrachlorobiphenyl (Irradiation Time 1.0 h)

diene, M	0	0.0005	0.001	0.002	0.003	0.005
% reacted	62	46	37	21	13	9
% light absorbed by chlorobiphenyl	100	18	10	5	4	2

10^{-3} M) and 25% when [NpCl] = 1.0×10^{-3} M. The quantum yield of disappearance of 1-chloronaphthalene was enhanced 10% in the presence of air ([C₁₀H₇Cl] = 5×10^{-3} M).

Reaction of 1-Chloronaphthalene in the Presence of Xenon. The ampules contained 1-chloronaphthalene (0.013 M) in isooctane, with and without xenon (~1 atm). Xenon quenched the fluorescence by 15% and depressed ϕ_r by 22%.

Quantum Yield of Reaction of 1-Chloronaphthalene at High Concentration. The ampules contained 1-chloronaphthalene (1.06×10^{-3}–3.76×10^{-2} M) and the GLC standard in cyclohexane. They were irradiated for various times to give appropriate conversions for GLC analysis. The results are given in Table V.

Photolysis of 4-Chlorobiphenyl with Biacetyl. As in the case of 1-chloronaphthalene, the irradiation times were so long that all the biacetyl had reacted at the end of the photolysis. In cyclohexane, no quenching was observed when 4-chlorobiphenyl (1.3×10^{-3} M) was irradiated with biacetyl (0–0.006 M). In methanol, irradiation of 4-chlorobiphenyl (1.1×10^{-3} M) with biacetyl gave the results shown in Table VI. Because of the poor quality of the data, presumably because all the quencher had reacted, no attempt was made to interpret the slopes of the graphs of ϕ_0/ϕ vs. [biacetyl].

Photolysis of 4-Chlorobiphenyl in an Aerated Solution. In cyclohexane solution, air reduced the intensity of 4-chlorobiphenyl fluorescence by 30% as compared with only 15% in isooctane, at 4-chlorobiphenyl concentrations of 1.22×10^{-4} and 1.0×10^{-3} M, respectively. At 0.001 M 4-chlorobiphenyl air caused

an increase in the rate of photodegradation of 4-chlorobiphenyl in isooctane by a factor of 2.8.

**Studies with Chlorobiphenyls in the Presence of Dienes.
(i) Literature Reports[4,39] in Methanol with 1,3-Cyclohexadiene.** Quenching of the photodegradation of several chlorobiphenyls, by using cyclohexadiene and illumination at 290–300 nm, was used to estimate triplet lifetimes.[4] We found that 1,3-cyclohexadiene has λ_{max} = 256 nm in methanol (ϵ 9000) and ϵ_{290nm} = 150. We take as an example the reaction of 2,2',6,6'-tetrachlorobiphenyl (TCB) with diene, as this represents an extreme case. In cyclohexane,[39] ϵ_{290nm} is given as 50. The data from Table 20 of ref 39 for reaction quenching are given in Table VII together with some absorption data, with the assumption of a 1-cm path length. Thus we see that competing light absorption by the diene more than compensates for any reduction in ϕ_r and hence that the data are not readily interpreted.

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(39) L. O. Ruzo, Thesis, Michigan State University, 1974.

(ii) Reaction of Chlorobiphenyls at 254 nm in Cyclohexane in the Presence of 2,5-Dimethyl-2,4-hexadiene. The extinction coefficients at 254 nm for the indicated compounds were as follows: 2,5-dimethyl-2,4-hexadiene, 16 000; 4-chlorobiphenyl, 21 500; 2,4,6-trichlorobiphenyl, 2800; 2,2',5,5'-tetrachlorobiphenyl, 1700. The solutions to be irradiated contained 1.0 × 10⁻³ M chlorobiphenyl and varying amounts of diene. Because some of the conversions are high, the data are given as the percent of compound reacted (Table VIII).

Diels–Alder Addition of 1,1'-Thiocarbonylbis(1,2,4-triazole) to Dienes. A Useful Preparation of Bicyclic Sulfides and Related Derivatives[1]

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1,1'-Thiocarbonylbis(1,2,4-triazole) adds in a Diels–Alder fashion to a variety of dienes to give high yields of bicyclic sulfides. Alcoholysis of some of these derivatives provided cis-3,5-fused mercapto esters.

We recently reported the synthesis and properties of 1,1'-thiocarbonylbis(1,2,4-triazole) (1).[1] As a thiocarbonyl
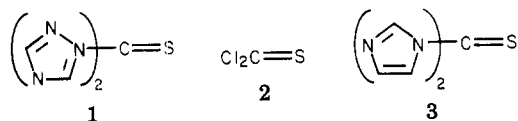

transfer reagent 1 appears to be superior in many ways to the parent thiophosgene (2) or the 1,1'-thiocarbonyldiimidazole analogues (3).[2] For instance, reagent 1 reacts with primary amines in a selective fashion,[3] thus permitting the facile synthesis of unsymmetrically substituted thioureas.[1] This unexpected chemistry prompted us to explore its behavior as a dienophile. Parent thiophosgene (2) is well-known to react with various dienes to give cyclic and bicyclic adducts such as 4.[4] In general, however, these
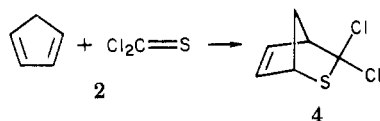
derivatives are unstable and must be stored in the cold. For instance, sulfide 4 decomposes to a black tar if not kept at dry ice temperatures.[4a,c]

We have found that triazole reagent 1 not only adds smoothly and in excellent yield (isolated ca. 90%) to a variety of dienes[5] but also provides crystalline adducts which are moisture stable at room temperature. Thus, further chemistry can be carried out directly, which is not the case with the thiophosgene derivatives.[4c] While a variety of thiocarbonyl dienophiles have been investigated,[4a,6] none appear to give consistently high yields of stable adducts as reagent 1. For example, 2,3-dimethyl-1,3-butadiene reacts with 1 to give 5 in 99% isolated yield.
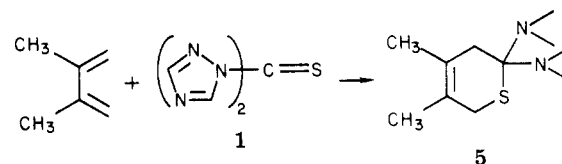
(1) Thiocarbonyl Transfer Reagent Chemistry, Part 2. For Part 1 see: Larsen, C.; Steliou, K.; Harpp, D. N. *J. Org. Chem.* **1978**, *43*, 337.

(2) For a recent paper on this and related derivatives, see: Walter, W.; Radke, M. *Justus Liebigs Ann. Chem.* **1979**, 1756.

(3) When 2 and 3 are treated with amines, the monosubstituted derivatives (*N*-thiocarbamoyl chloride or imidazole) are unstable and are converted to isothiocyanates. A similar versatility of 1 vs. 2 or 3 obtains for a variety of reactions of 1 with several nucleophiles: Larsen, C.; Harpp, D. N., manuscripts in preparation.

(4) (a) Middleton, W. J. *J. Org. Chem.* **1965**, *30*, 1390. (b) Laban, G.; Mayer, R. *Z. Chem.* **1967**, *7*, 227. (c) Johnson, C. R.; Keiser, J. E.; Sharp, J. C. *J. Org. Chem.* **1969**, *34*, 860. (d) Reich, H. J.; Trend, J. E. *Ibid.* **1973**, *38*, 2637.

(5) 1,3-Cyclooctadiene and furan did not react with reagent 1.

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(7) Allgeier, H.; Winkler, T. *Tetrahedron Lett.* **1976**, 215.