with 80% ethanol to a strength of 0.1 M. 2,6-Lutidine (0.15 g) was added to each reaction mixture to prevent acid-catalyzed reactions. The solutions were heated for 48 h at 55 °C and then analyzed by GLC with 5% Carbowax 20M on 90–100 mesh ABS (6′ × $^1/_4$″ column) at 115 °C with a helium carrier (0.67 mL/s). Retention times of the solvolysis products and the other reaction components were found to be as follows by the use of pure samples of each component: ethanol, 46 s; water, 72 s; *exo*-2-norbornyl ethyl ether, 112 s; 2,6-lutidine, 160 s; norbornylene, 200 s; and *exo*-norborneol, 533 s. *exo*-2-Norbornyl ethyl ether was prepared by the ethanolysis of *exo*-2-norbornyl *p*-bromobenzenesulfonate in anhydrous ethanol. It was shown that the Carbowax column would give complete separations of mixtures of *endo*- and *exo*-norborneol and that the products were stable to the reaction conditions.

Acknowledgment is made to the donors of the Petroleum Research Fund (Grant PRF16290-B4-C), administered by the American Chemical Society, and to the U.S. Army Research Office (Grant DAAL03-86-K0026) for partial support of this work at the University of Alabama in Huntville. The work at New Mexico State University was supported by the National Science Foundation (Grant CHE-83-04000). We thank R. M. Karaman for determining the thiourea effects on the exo isomer.

Registry No. *endo*-2-Norbornyl *p*-toluenesulfonate, 840-90-4; *exo*-2-norbornyl *p*-toluenesulfonate, 959-42-2; *endo*-2-norbornyl *p*-methoxybenzenesulfonate, 111025-81-1; *exo*-2-norbornyl *p*-methoxybenzenesulfonate, 68488-93-7; *endo*-2-norbornyl *p*-fluorobenzenesulfonate, 111005-78-8; *exo*-2-norbornyl *p*-fluorobenzenesulfonate, 111005-80-2; *endo*-2-norbornyl *p*-chlorobenzenesulfonate, 111005-79-9; *exo*-2-norbornyl *p*-chlorobenzenesulfonate, 111005-81-3; *endo*-2-norbornyl *p*-bromobenzenesulfonate, 840-89-1; *exo*-2-norbornyl *p*-bromobenzenesulfonate, 840-88-0; *endo*-2-norbornyl *p*-nitrobenzenesulfonate, 25716-02-3; *exo*-2-norbornyl *p*-nitrobenzenesulfonate, 111005-82-4.

Photochemistry of Polyhaloarenes. 7. Photodechlorination of Pentachlorobenzene in the Presence of Sodium Borohydride

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The mechanism of photodechlorination of pentachlorobenzene (1) in acetonitrile has been examined. The quantum yield of reaction (Φ_r) has been found to vary with the concentration of 1. A charge-transfer intermediate formed from the triplet excited state of 1 is proposed to explain the observations. Φ_r increases with added $NaBH_4$ and $1/\Phi_r$ varies directly with the inverse of the concentration of the electron-transfer reagent. The regiochemistry, deuterium isotope effects, tracer studies, and quenching analyses are consistent with an electron-transfer process.

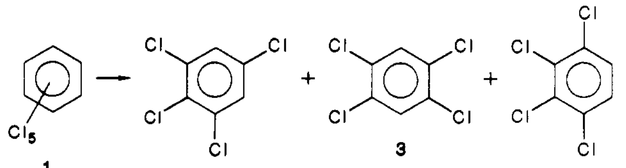
The photochemistry of aromatic halides has been actively investigated, in part, due to their role as environmental pollutants. Attention has been focused on ways to increase their photolability,[1] as a means of their efficient conversion to less toxic substrates, especially in view of the fact that they display significantly enhanced photolability in the presence of electron-transfer agents such as amines[2–5] and dienes.[5]

Increased photolability of chlorobenzene in the presence of sodium borohydride has also been reported by Barltrop and co-workers.[6] A mechanism proposed to explain their observations, however, does not explain the observations reported more recently by Epling[7] for the sodium borohydride mediated photodehalogenation of some chlorotoluenes and polychlorobiphenyls. An understanding of the mechanistic pathway of borohydride-enhanced photodechlorination is important, especially due to its potential in the destruction of polyhaloaromatics.

Pentachlorobenzene (1) was chosen as a model for our mechanistic studies because it is a significant environmental pollutant, and in an earlier study in this laboratory, the photochemistry of this compound was studied, and factors influencing the regiochemistry of its dechlorination were investigated in detail.[4] The nature of the intermediates has been shown to influence the regioselectivity,[4] and we hoped that comparison would reveal the nature of the intermediates and the mechanism pertaining to borohydride-mediated photodechlorinations.

Results

Irradiation of pentachlorobenzene (1) in acetonitrile in the 254-nm range leads to photofragmentation of the C–Cl bonds. At the low conversions maintained (15–20%) for 1, the primary products are the three tetrachloro benzenes 2–4 as shown below. A larger percentage of conversion



1 2 3 4

of 1 leads to the loss of more than one chlorine atom to form tri- and disubstituted chlorobenzenes. The quantum yield of reaction with respect to moles of 1 reacted increased with increasing concentration of 1 over the range 0.005–0.07 M (Table I). Figure 1 shows the variation of the inverse of quantum yield of disappearance of 1 with respect to the inverse of its concentration.

Irradiation of 1 in 94% aqueous acetonitrile and 4 equiv of sodium borohydride led to a significant increase in the rate of photodechlorination. The quantum yield also increased with increasing equivalents of sodium borohydride

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(1) Bunce, N. J. *Chemosphere* **1982**, *11*, 701. Ackerman, D. G.; Scinto, L. L.; Bakshi, P. S.; Delumyea, R. G.; Johnson, R. J.; Richard, G.; Takata, A. M.; Sworzyn, E. M. *Destruction and Disposal of PCB's by Thermal and Non-thermal Methods*; Noyes Data Corp: Park Ridge, New Jersey, 1983. Gilbert, A. *Photochemistry* **1977**, *8*, 385.

(2) Bunce, N. J. *J. Org. Chem.* **1982**, *47*, 1948.

(3) Ohashi, M.; Tsujimoto, K.; Seki, K. J. *J. Chem. Soc., Chem. Commun.* **1973**, 384.

(4) Freeman, P. K.; Srinivasa, R.; Campbell, J.-A.; Deinzer, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 5531.

(5) Bunce, N. J.; Gallacher, J. C. *J. Org. Chem.* **1982**, *47*, 1955.

(6) Barltrop, J. A.; Bradbury, D. *J. Am. Chem. Soc.* **1973**, *95*, 5085.

(7) Epling, G. A.; Florio, E. *J. Chem. Soc., Chem. Commun.* **1986**, 185. Epling, G. A.; Florio, E. *Tetrahedron Lett.* **1986**, *27*, 675.

0022-3263/88/1953-0148$01.50/0

Table I. Quantum Yield of Disappearance of 1[a] and Product Distributions with Increasing Concentration of 1

[ArCl], M	quantum yield,[b] Φ_{ArCl}	percentage ratio of products: 2	3	4
0.005	0.083	48.43 ± 0.15	39.50 ± 0.20	11.98 ± 0.14
0.0068	0.097	46.97 ± 0.50	40.59 ± 0.90	12.43 ± 0.4
0.0088	0.107	46.0 ± 0.01	39.76 ± 1.00	14.2 ± 1.00
0.011	0.107	45.95 ± 0.30	38.53 ± 0.3	17.6 ± 1.14
0.014	0.100	42.85 ± 1.30	39.53 ± 0.3	17.6 ± 1.14
0.019	0.140	43.16 ± 0.46	41.60 ± 1.15	15.23 ± 0.72
0.03	0.193	41.9 ± 1.6	38.26 ± 0.1	19.82 ± 1.7
0.05	0.247	42.63 ± 0.7	42.63 ± 0.9	14.74 ± 0.4
0.071	0.330	40.25 ± 0.6	40.25 ± 0.5	19.51 ± 0.8

[a] In acetonitrile. [b] Average of five runs with respect to potassium ferrioxalate actinometer.

Table II. Variation of Quantum Yield of Disappearance of 1[a] and Product Distributions with Varying Amounts of Sodium Borohydride

[NaBH$_4$], M	quantum yield,[b] Φ_{ArCl}	percentage ratio of products: 2	3	4
0.00	0.083	50.05 ± 0.7	37.32 ± 0.6	12.63 ± 0.9
0.0005	0.097	48.63 ± 2.57	38.57 ± 1.41	12.80 ± 0.2
0.0017	0.132	49.36 ± 0.66	38.39 ± 0.66	12.24 ± 0.2
0.0025	0.157	48.40	40.17	11.43
0.0033	0.194	44.71 ± 0.5	41.56 ± 0.4	13.73 ± 0.3
0.005	0.246	46.01 ± 0.35	42.13 ± 0.24	11.86 ± 0.28
0.010	0.313	46.37 ± 0.8	42.3 ± 1.50	15.5 ± 0.95
0.20	0.40	48.76 ± 1.3	43.92 ± 1.90	15.33 ± 0.6

[a] 0.005 M in 94% aqueous acetontrile. [b] Average of five runs with respect to potassium ferrioxalate actinometer.

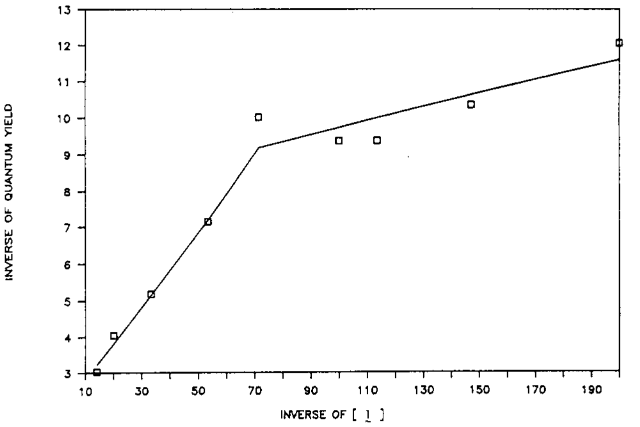

Figure 1. Inverse of quantum yield of disappearance of 1 vs inverse of concentration of 1.

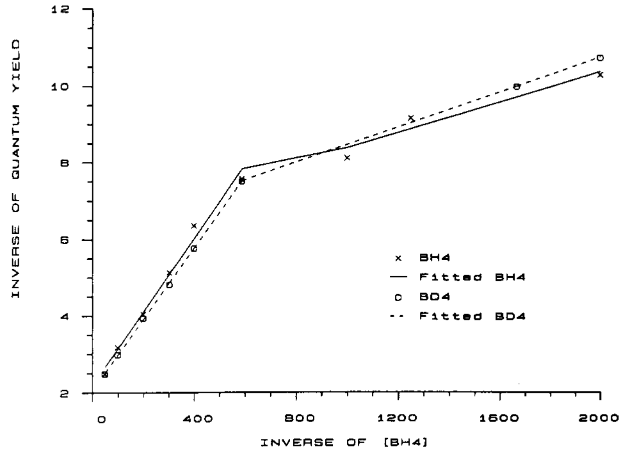

Figure 2. Inverse of quantum yield of disappearance of 1 vs inverse of NaBH$_4$ and NaBD$_4$.

(Table II; Figure 2). Photolysis under identical conditions in the presence of sodium borodeuteride led to the incorporation of 81.6% deuterium in the photoproducts, thus indicating that sodium borohydride is the primary source of hydrogen in these reactions. Most importantly, the quantum yields of disappearance of 1 in the presence of sodium borodeuteride were very similar to those observed with sodium borohydride (Figure 2). Pentachlorobenzene and sodium borohydride did not react in the dark under similar conditions.

The intermediacy of aryl radicals through homolytic cleavage of C–Cl bonds during the photolysis of aryl chlorides in polar and nonpolar solvents has been suggested by a number of workers.[6,8] Barltrop[6] reported efficient quenching of the photodechlorination of chlorobenzene in the presence of sodium borohydride with a well-known phenyl-radical quencher, acrylonitrile.[9] The isolation of 1-chloro-1-cyano-2-phenylethane was cited as evidence for the formation of a phenyl radical through homolytic dissociation of chlorobenzene. However, Epling and coworkers[7] could not quench the NaBH$_4$ mediated reactions of polychloro toluenes and biphenyls either with large amounts of acrylonitrile or with other radical quenchers. Our attempts to quench the photoreaction of 1 in the presence of NaBH$_4$ were also not very sucessful. The quantum yield of product formation (based on formation of 2–4) falls only slightly (Table IV).

Discussion

The homolytic cleavage leading to aryl radicals can occur from the excited singlet state, which possesses sufficient energy to effect such a cleavage. Exclusive singlet re-

$$\mathrm{ArCl} \rightarrow [\mathrm{ArCl}]^{*1} \rightarrow \mathrm{Ar}^{\bullet} + \mathrm{Cl}^{\bullet} \rightarrow \text{products}$$

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[8] (a) Choudhry, G. G.; Van Den Broecke, J. A.; Webster, G. R. B.; Hutzinger, O. *Environ. Toxicol. and Chem.* **1986**, *5*, 625. (b) Choudhry, G. G.; Hutzinger, O. *Environ. Sci. Technol.* **1984**, *18*, 235. (c) Bunce, N. J.; Bergsma, J. P.; De Graaf, W.; Kumar, Y.; Ravanal, L. *J. Org. Chem.* **1980**, *45*, 3708. (d) Arnold, D. R.; Wong, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 3363. (e) Plimmer, J. R.; Klingebiel, V. I. *J. Agric. Food Chem.* **1976**, *24*, 721.

[9] Koelsch, C. F. *J. Am. Chem. Soc.* **1943**, *65*, 57. Koelsch, C. F.; Boekelheide, V. *J. Am. Chem. Soc.* **1944**, *66*, 412. Kochi, J. K. *J. Am. Chem. Soc.* **1957**, *79*, 2942.

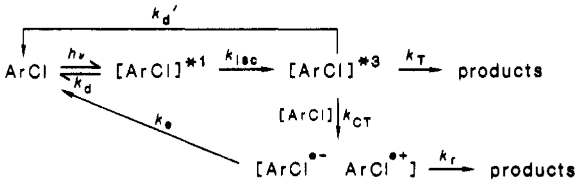
[10] Soumillion, J. Ph.; De Wolf, B. *J. Chem. Soc., Chem. Commun.* **1981**, 436.

Table III. Variation of Quantum Yield of Disappearance of 1[a] with Varying Amounts of Acrylonitrile in the Absence of Sodium Borohydride

[acrylonitrile], M	relative quantum yield of 2 + 3 + 4[b]	percentage ratio of products[b] 2	3	4
0.00	1.00	49.23 ± 1.50	35.38 ± 1.60	15.38 ± 0.50
0.0025	0.97	50.39 ± 1.22	36.09 ± 1.83	13.52 ± 1.00
0.005	1.00	50.68 ± 0.50	35.81 ± 0.41	13.51 ± 0.90
0.0075	1.00	52.55 ± 0.10	34.99 ± 0.55	12.45 ± 0.80
0.01	0.72	50.51 ± 1.60	36.78 ± 0.85	12.71 ± 0.45

[a] 0.005 M in 94% aqueous acetonitrile. [b] Average of three runs.

Scheme I



activity, however, has been ruled out. Reactions attributable to triplet excited state have been reported.[11,12] On the basis of various studies, Bunce et al.[8c,12] concluded that the degradation pathway of photoexcited chloroarene is determined mainly by the triplet energy of the chloride. The quantum yield for intersystem crossing of a number of polychlorobenzenes in cyclohexane was reported as being very efficient (0.4–1.0).[12] This high efficiency of intersystem crossing seems to rule out exclusive singlet reactivity.[12] However, simple C–Cl fission from the triplet state does not fully account for the triplet excitation energies of the polychlorobenzenes (78–80 kcal/mol[13]) and C–Cl bond dissociation energy (85–95 kcal/mol[8c,14]). Homolysis of a triplet excited state could occur if contributions by the vibrational energy content of the ground state[15] and strain relief (2.2 kcal/mol per ortho Cl–Cl interaction[16]) narrow the energy gap sufficiently.

The possibility of electron transfer from the excited triplet state to another molecule in its ground state has also been suggested. Electron transfer may proceed via a triplet excimer[10,12,18,19] to form a radical anion and thereby avoid the energy-demanding homolysis.[10]

The quantum yield for intersystem crossing of 1 in cyclohexane is 0.9.[12] This efficiency does not change appreciably in a polar solvent such as acetonitrile, since Φ_{isc} measured by excitation transfer to biacetyl is 1.0 ± 0.1; thus, photodechlorination should occur almost entirely from the triplet state or via an excimer. Scheme I suggests a possible kinetic scheme for product formation during direct photolysis. From the steady-state assumption, eq 1 may be derived, where $F = k_r/(k_r + k_e)$.

$$\Phi = \Phi_{isc}\left(\frac{k_T + k_{CT}[1]F}{k_T + k_d' + k_{CT}[1]}\right) \qquad (1)$$

At high concentrations, assuming negligible singlet reactivity, if $k_T \ll k_{CT}[\mathrm{ArCl}]F$, k_T may be neglected to simplify eq 1 to eq 2.

$$\frac{1}{\Phi} = \frac{1}{F\Phi_{isc}} + \frac{k_d'}{F\Phi_{isc}k_{CT}}\left(\frac{1}{[1]}\right) \qquad (2)$$

Figure 1 is a plot of the inverse of quantum yield of disappearance of 1 versus the inverse of concentration of 1. At high concentrations, a linear plot is obtained, which, at lower concentrations, dips downward as is to be expected if k_T competes with k_{CT}. Excited-state complexation thus enhances the photodecomposition of 1 in acetonitrile. This result differs from a previous report by Bunce et al.[12] that the importance of excimer formation is reduced with the extent of chlorination of benzene, becoming unimportant for tetra-, penta-, and hexachlorobenzenes in cyclohexane. This difference may be attributed to an increased rate of excimer formation in the more polar solvent combined with product formation from excimer being more efficient than product formation from triplet.[18] The intercept in Figure 1 ($1/F\Phi_{isc} = 1.8$) suggests that about 55% (assuming $\Phi_{isc} = 1.0$) of the charge-transfer complex goes to products; the rest decomposes to the starting material. At low concentrations, therefore, it seems likely that excimer contribution is considerably reduced.

In the presence of $NaBH_4$, 1 reacts very rapidly. According to Barltrop,[6] in the case of chlorobenzene, initiation involves homolysis of the C–Cl bond and is followed by a chain in which the phenyl radical abstracts hydrogen from BH_4^- forming benzene and $BH_3^\bullet$; the $BH_3^\bullet$ then transfers an electron to chlorobenzene which fragments to form a phenyl radical. Ohashi and co-workers[20] suggested a hydride transfer to the excited aryl halide instead of an aryl radical. Epling et al.[7] have also suggested a hydride transfer without the intermediacy of a radical.

Substitution of hydrogen for chlorine may take place via a $S_{RN}1$ mechanism.[21,22] A starting point for this process might be a ground-state complex, which could absorb light to yield a radical anion–radical pair (reaction 3).

$$\mathrm{ArCl} + \mathrm{BH_4}^- \rightarrow (\mathrm{ArCl{-}BH_4})^- \xrightarrow{h\nu} (\mathrm{ArCl})^{\bullet-}\mathrm{BH_4}^\bullet \qquad (3)$$

This step appears unlikely as the UV spectrum of 1 in $NaBH_4$ solutions remains unchanged from that in the absence of sodium borohydride. It is more likely that an electron is transferred to an excited state of 1 (reaction 4).

$$[\mathrm{ArCl}]^* + \mathrm{BH_4}^- \rightarrow \underset{\mathbf{5}}{[\mathrm{ArCl}^{\bullet-}\mathrm{BH_4}^\bullet]} \rightarrow \mathrm{Ar}^\bullet + \mathrm{Cl}^- + \mathrm{BH_4}^\bullet \qquad (4)$$

The radical anion–radical complex 5 could easily decompose further into an aryl radical and chloride ion.

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(11) Åbermark, B.; Baeckström, P.; Westlin, U. E.; Göthe, R.; Wachtmeister, C. A. *Acta Chem. Scand., Ser. B* **1976**, *B30*, 49.

(12) Bunce, N. J.; Hayes, P. J.; Lemke, M. E. *Can. J. Chem.* **1983**, *61*, 1103.

(13) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(14) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516. Szwarc, M.; Williams, D. *J. Chem. Phys.* **1952**, *20*, 1171.

(15) Whiffen, D. H. *J. Chem. Soc.* **1956**, 1350.

(16) Benson, S. W., *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; p 281.

(17) Ruzo, L. O.; Bunce, N. J.; Safe, S. *Can. J. Chem.* **1975**, *53*, 688. Bunce, N. J.; Pilon, P.; Ruzo, L. O.; Sturch, D. J. *J. Org. Chem.* **1976**, *41*, 3023.

(18) Bunce, N. J.; Ravanal, L. *J. Am. Chem. Soc.* **1977**, *99*, 4150.

(19) Lim, E. C.; Chakrabarti, S. K. *Mol. Phys.* **1967**, *13*, 293.

(20) Tsujimoto, K.; Tasaka, S.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1975**, 758.

(21) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

(22) Rossi, A. R.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph 178; American Chemical Society: Washington, DC, 1983.

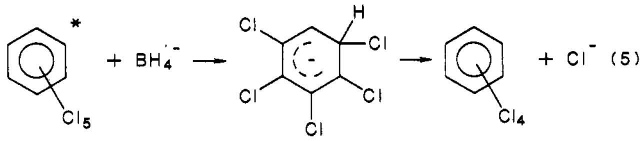
Table IV. Variation of Quantum Yield of Disappearance of 1[a] with Varying Amounts of Acrylonitrile in the Presence of Sodium Borohydride[b]

[acrylonitrile], M	relative quantum yield of 2 + 3 + 4	percentage ratio of products[b,c] 2	3	4
0.00	1.00	44.56 ± 0.95	41.19 ± 0.80	14.24 ± 0.95
0.0025	0.94	50.88 ± 0.65	34.63 ± 1.40	14.49 ± 0.35
0.0050	0.90	52.00 ± 0.10	36.00 ± 0.60	12.00 ± 0.10
0.010	0.81	54.00 ± 0.80	33.13 ± 0.45	12.88 ± 0.20
0.020	0.77	55.80 ± 0.60	31.70 ± 0.50	12.50 ± 0.42

[a] 0.005 M in 94% aqueous acetonitrile. [b] 0.20 M. [c] Average of three runs.

Quenching studies with acrylonitrile do show a small quenching of product formation, presumably due to quenching of the aryl radical (Table IV). However, it is not clear if acrylonitrile can quench an aryl radical with four chlorine substituents since no quenching, except at high concentration of acrylonitrile, was observed in the absence of $NaBH_4$ (Table III).

Direct attack of the excited halide by hydride ions is another possibility as suggested by Epling[7] and Ohashi[20] (reaction 5).



Deuterium studies and regiochemistry of photodechlorination of 1 have given valuable insight into the possible nature of the intermediate(s) involved in borohydride-mediated photodechlorination. Irradiation of 1 with varying equivalents of $NaBD_4$ led to the incorporation of 81.6% deuterium in the products 2–4. This confirmed earlier reports that $NaBH_4$ is the major source of hydrogen.[6,20] The quantum yield of the reaction with $NaBD_4$ is very similar to that obtained with $NaBH_4$ (Figure 2). Hydrogen transfer must therefore take place after a bimolecular product determining step. If reaction 5 were to occur as shown, direct addition of hydride versus deuteride should involve a significant primary isotope effect. Absence of such an isotope effect argues against reaction 5.

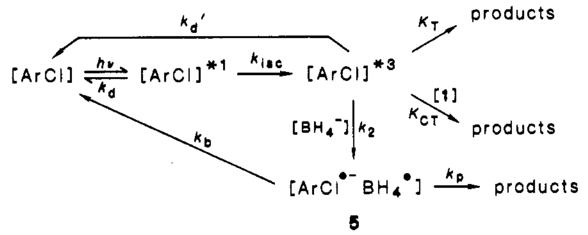
The dependence of quantum yield on the concentration of borohydride suggests that it is involved in the bimolecular product determining step. On the basis of the reactions of nucleophiles with aryl chlorides that proceed via a $S_{RN}1$ pathway,[21,22] the following kinetic scheme is proposed for $NaBH_4$-mediated photodechlorinations (Scheme II).

The expression for the quantum yield is similar to eq 1 except that an additional contribution to the quantum yield, $k_2[BH_4^-]G$, would be included as charge transfer now takes place from the borohydride to an excited state of 1. Competing charge transfer from excited 1 to ground state 1 is expected at the concentration employed for 1 (0.005 M); however, it is assumed that as $[BH_4^-]$ is increased there is a point where $k_2[BH_4^-]G \gg k_{CT}[1]F + k_T$. Equation 2 may therefore be rewritten as eq 6 for large concentrations of $NaBH_4$, where $G = k_p/(k_p + k_b)$.

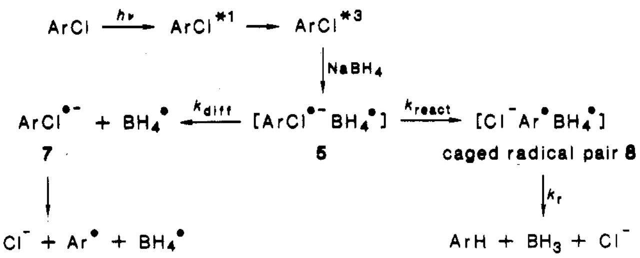
$$\frac{1}{\Phi} = \frac{1}{G\Phi_{isc}} + \frac{k_d'}{G\Phi_{isc}k_2[BH_4^-]} \qquad (6)$$

Figure 2 shows the variation in the inverse of quantum yield of disappearance of 1 with the inverse of borohydride concentration. At high concentrations, there is an excellent correlation with eq 6. The downward dip in the graph at lower concentrations of borohydride is indicative of competing reaction from the triplet state.

Scheme II



Scheme III



Regioselectivity of photodechlorination of 1 provides a valuable clue to the fate of 5. The regiochemistry of the photodechlorination of 1 was recently reported.[4] The excited state of 1 forms a charge-transfer complex with triethylamine (TEA) in acetonitrile as shown in reaction 7 to give 6, which yields products 3, 2, and 4 in the relative

$$[\mathrm{ArCl}]^* + \mathrm{TEA} \rightarrow \underset{6}{[\mathrm{ArCl}]^{\bullet-}[\mathrm{TEA}^{\bullet+}]} \rightarrow 3 + 2 + 4 \qquad (7)$$

ratio of 8:3:1, respectively. The direct photolysis of 1 in the absence of electron donors gives the same products in the ratio 3:4:1 respectively. This change in regiochemistry of the major product was rationalized by the I_π repulsion theory for orientation in aromatic nucleophilic substitution, which was viewed as consistent with the fragmentation of a radical anion.

Table II shows the relative ratios of the products 2–4. Unlike the dramatic reversal in regioselectivity (between 2 and 3) observed with triethylamine as electron donor, with $NaBH_4$, 3 increases only slightly by approximately 5%. The product distribution is thus not very different from that obtained by the direct photolysis of 1 under identical conditions in the absence of $NaBH_4$ (Table I, entry 1). This is possible if intermediate 5 (Scheme II) decomposes as shown in Scheme III.[22]

The radical anion–radical pair in the initial charge-transfer complex 5 may either diffuse away to give a free (uncomplexed) radical anion of 1 (7) or decompose to form an aryl radical and a radical derived from the borohydride and held within a cage as shown in 8. The product ratios rule out any substantial involvement of 7,[4] although the slight increase in formation of 3 may be attributed to a contribution of 7. Deuterium incorporation results, which show significant contribution of hydrogen from the borohydride in a step subsequent to bimolecular involvement of BH_4^-, strongly suggests the participation of **8**. In-cage transfer of hydrogen at this stage can explain the lack of a primary isotope effect.

Acrylonitrile quenches the borohydride reactions to a very small extent. It is likely that aryl radicals are formed when **7** fragments. In the case of **8**, the caged radical pair may abstract a hydrogen from within the cage or diffuse into the solvent in the form of a radical. It is likely that acrylonitrile, which appears to be an inefficient quencher of the aryl radical generated from **1**, has a lower rate of quenching than the rate of hydrogen transfer from the borohydride in **8** within the radical pair cage.

Experimental Section

General Procedures. Reagent grade acetonitrile (Baker Chemical Co.) was freshly distilled from phosphorus pentoxide, and its purity was greater than 99% by GLC analysis. Sodium borohydride and borodeuteride (Aldrich) were 99% and 98 atom %, respectively.

General Procedure for Photolysis. Irradiations of **1** were carried out in a Rayonet merry-go-round reactor (The Southern New England Co.) equipped with eight 2537-Å lamps. A steady stream of air was passed into the reactor to maintain a constant temperature of 40 °C. The photolysis samples (1 mL) were placed in quartz tubes (Ace Glass, 170 mm × 15 mm), each screwed to a nylon adapter bushing containg a Pyrex glass sliding stopper valve, and degassed through three or four freeze–pump–thaw cycles. The tubes were sealed under vacuum and irradiated at 254 nm for 6 min. Quantum yields of products were determined by using the potassium ferrioxalate[14] actinometer.

Product Analysis. The photolysis mixtures were analyzed by GLC on a Varian 3300 capillary gas chromatograph equipped with an FID with a 30 m × 0.25 mm DB-225 capillary column (J & W Scientific Inc.) and a Varian 4290 integrator. The column was held at 60 °C for 5 min and raised to 180 °C at a rate of 5 °C/min with an injection port temperature of 200 °C and detector temperature of 250 °C. Helium was used as carrier gas at 30 mL/min. The photoproducts were identified by comparing their retention times with those of commercially obtained authentic samples. The mass spectral analyses were carried out with a Finnigan 4023 mass spectrometer equipped with a Finnigan 9610 gas chromatograph. Dodecane was used as an internal standard in the determination of yields of products.

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Registry No. 1, 608-93-5; $NaBH_4$, 16940-66-2.

Bicyclopropylidene: Cycloadditions onto a Unique Olefin

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Bicyclopropylidene (1) is capable of undergoing cycloadditions in at least six different modes, depending on the nature of the cycloaddend. In analogy to its [2 + 2] cyclodimerization, 1 adds in a [2 + 2] and [2 + 4] fashion to 1,3-dienes, most probably via diradical intermediates to a large extent. A concerted mode of formation is likely for at least fractions of the [2 + 4] cycloadducts **11**, **14**, **17**, and **45** and the [2 + 2] cycloadducts **22** and **23** of chloroketenes. **1** readily undergoes cycloaddition to electron-deficient olefins, both with σ- and π-electron-withdrawing groups, to give cyclobutane derivatives **18–20** and **24** via 1,4-diradical intermediates all retaining the two cyclopropyl groups of **1**. Chlorosulfonyl isocyanate (CSI), *N*-phenyltriazolinedione (PTAD), and tetracyanoethylene (TCNE), all known for their propensity to form zwitterionic intermediates with electron-rich olefins, yield three types of products with **1** in different proportions. All three arise from the same type of initial 1,4-dipolar intermediates **25**, **29**, and **36** and ring closure yields **27** and **35**, while cyclopropyl to cyclobutyl ring enlargement and cyclopropylcarbinyl to homoallyl ring opening with subsequent closure lead to **32**, **40** and **31**, **41** respectively. The products **33**, **51**, and **59**, obtained from **1** upon photooxidation and ozonolysis, can also best be rationalized by assuming zwitterionic intermediates. This body of results helps to constitute a plausible and general scheme for the classification of various $[2\pi]$-cycloaddends according to their preferred reaction modes.

Cross-conjugated polyenes, such as fulvene and fulvalenes, can partake in diverse modes of cycloadditions (i.e., [2 + 2], [4 + 2], [6 + 2], [8 + 2], [14 + 2], etc.), depending on the nature of the olefinic reaction partner.[1-3] Normal monoalkenes, on the other hand, are confined to only two types of pericyclic reactions, namely, the $[_\pi 2_s + _\pi 2_a]$ and [2 + 4] including the 1,3-dipolar cycloadditions.[4,5] Thermal cyclodimerizations of alkenes are rare, because the orbital symmetry conservation rules preclude a concerted $[2_s + 2_s]$ reaction, and the $[2_s + 2_a]$ transition state is energetically unfavorable; the relatively facile thermal cyclodimerizations of fluoroalkenes have been explained by a stepwise mechanism involving diradical intermediates which are stabilized by the fluoro substituents.[6,7] Methylenecyclopropane[8] and its 1,1-dihalo- and 1-halo-substituted derivatives[9a] as well as the cyclopropylideneacetates[9b] behave in an entirely analogous manner: they all give head to head dimers upon heating, and the 1,1-dichloro derivative also cycloadds to 1,3-butadiene in a [2 + 2] mode. The role of the cyclopropane ring on the high propensity of methylenecyclopropanes to undergo cyclo-

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(1) Dunn, L. C.; Chang, Y.-M.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 7095 and references cited therein.

(2) Prinzbach, H. *Pure Appl. Chem.* **1971**, *28*, 281.

(3) Erden, I.; Kaufmann, D. *Tetrahedron Lett.* **1981**, 215.

(4) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, 1970.

(5) Fleming, I. *Grenzorbitale und Reaktionen organischer Verbindungen*; Verlag Chemie: Weinheim, Germany, 1979.

(6) Sharts, C. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1961**, *83*, 871.

(7) Sharts, C. M.; Roberts, J. D. *Org. React.* (*N.Y.*) **1962**, *12*, 1.

(8) Binger, P. *Angew. Chem.* **1972**, *84*, 483; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 433.

(9) (a) Dolbier, W. R., Jr.; Lomas, D.; Tarrant, P. *J. Am. Chem. Soc.* **1968**, *90*, 3594. Bottini, A. T.; Cabral, L. J. *Tetrahedron* **1978**, *34*, 3187; (b) de Meijere, A.; Wenck, H.; Seyed-Mahdavi, F.; Viehe, H. G.; Gallez, V.; Erden, I. *Tetrahedron* **1986**, *42*, 1291. Liese, Th.; Teichmann, S.; de Meijere, A. submitted for publication in *Synthesis*.