

was determined at a constant concentration of 1 (0.0127 M) with the diene concentrations varying from 0.0101 to 0.203 M. The quantum yield of isomerization decreased with increasing concentration of the diene and reached a constant quantum yield after the concentration of the diene in the mixture increased above 0.081 M, thus showing some quenching of the singlet state of the halide. The quantum yield of isomerization corrected for singlet quenching was determined by plotting the inverse of the quantum yield of isomerization versus the corresponding pentadiene concentration and extrapolating the linear portion of the curve to

zero concentration of the diene.

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## Photochemistry of Polyhaloarenes. 9. Characterization of the Radical Anion Intermediate in the Photodehalogenation of Polyhalobenzenes

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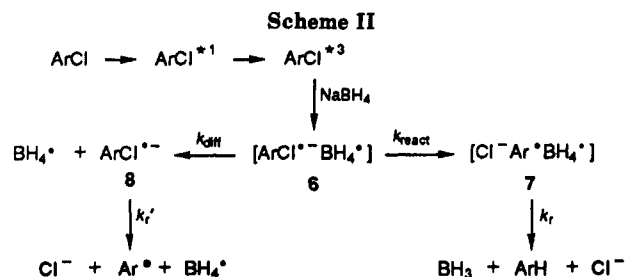
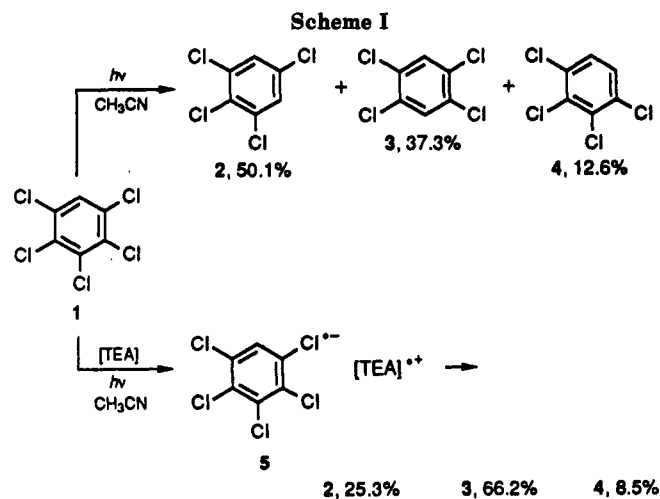
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The product-determining intermediate in the photodehalogenation of polyhalobenzenes has been characterized by generating excimers and radical anions within a micellar core and by formation of corresponding radical anions by electron transfer from lithium *p,p'*-di-*tert*-butylbiphenyl radical anion (LiDBB). The photodechlorination of pentachlorobenzene (1; 254 nm, CH<sub>3</sub>CN) produces 1,2,3,5-tetrachloro- (2), 1,2,4,5-tetrachloro- (3), and 1,2,3,4-tetrachlorobenzene (4). The regiochemistry of this reaction is compared with that observed in the photodechlorination of 1 in a micellar solution of hexadecyltrimethylammonium bromide (CTAB) with occupancy numbers (*n*) principally <2 and ≥2. Further comparisons with photodechlorination of 1 in a micellar CTAB solution (*n* < 2) in the presence of triethylamine, as well as photodechlorination in CH<sub>3</sub>CN in the presence of triethylamine, were used to characterize unencumbered radical anions. The regiochemistries observed in photolytic dehalogenations of 1, 2, 1,2,4-trichlorobenzene, and pentafluorobenzene in the presence of triethylamine are in good agreement with those realized in the radical anion fragmentations induced by electron transfer from LiDBB.

The mechanistic aspects of the photochemistry of monochloroarenes have been studied in detail in the presence of electron donors.<sup>1</sup> Polychlorobenzenes exhibit enhanced and efficient photodechlorination to their corresponding lower homologues in the presence of electron donors.<sup>2,3</sup> This reaction offers a potentiality for development as a powerful tool for toxic waste disposal methods and thus the mechanistic pathways followed are of considerable interest.

Irradiation of pentachlorobenzene (1) in acetonitrile at 254 nm leads to its dechlorination. At low conversions (15–20%) of 1, 1,2,3,5-tetrachlorobenzene (2) is formed as the major product along with 1,2,4,5- and 1,2,3,4-tetrachlorobenzene (3 and 4, respectively) as minor products (Scheme I).<sup>2,3</sup> In the presence of triethylamine (TEA), irradiation at 254 nm leads to a reversal in the regiochemistry of dechlorination of 1 so that 1,2,4,5-tetrachlorobenzene (3) is now formed as the major product with 2 and 4 generated as minor components as shown in Scheme I.<sup>2,3</sup>

The reversal in regiochemistry in the presence of triethylamine is likely the consequence of reaction of the radical anion of 1 generated through the transfer of an electron from triethylamine to an excited state of 1. The pattern of monodechlorination observed is consistent with that expected from a radical anion of 1, on the basis of a transition state analogous to the intermediate for nucleophilic aromatic substitution.<sup>2</sup> As noted, the regiochemistry of the photodechlorination in the absence of triethylamine



contrasts sharply with that in the presence of triethylamine and the dependence of quantum yield upon substrate concentration and quencher is consistent with product formation via the triplet and triplet excimer as major

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Table I. Relative Ratios of Products from the Irradiation of 1 in Various Media

medium (conc, M)	statistical probability of occupancy for occupancy nos $n = 0-4$					percentage ratio of products		
	0	1	2	3	4	2	3	4
CH <sub>3</sub> CN (0.005)						48.4 ± 0.2	39.5 ± 0.2	12.1 ± 0.1
CH <sub>3</sub> CN (0.071)						40.3 ± 0.6	40.3 ± 0.5	19.4 ± 0.8
CTAB <sup>a</sup> (0.017) <sup>b</sup>	0.673	0.267	0.053	0.007	0.001	49.8 ± 0.7	45.1 ± 0.3	5.10 ± 0.50
CTAB <sup>a</sup> (0.174) <sup>b</sup>	0.018	0.072	0.144	0.194	0.195	43.6 ± 0.6	51.0 ± 0.6	5.40 ± 0.50
CTAB <sup>a</sup> /TEA <sup>c</sup> (0.017) <sup>b</sup>	0.673	0.267	0.053	0.007	0.001	35.0 ± 0.4	55.0 ± 0.6	10.0 ± 0.7
CH <sub>3</sub> CN/TEA (0.005)						26.4 ± 0.3	62.5 ± 0.3	11.1 ± 0.9

<sup>a</sup> Concentration of CTAB in all cases was 0.20 M. <sup>b</sup> Refers to microscopic concentration of 1 (see ref 6). <sup>c</sup> 0.165 M in all cases.

pathways with a minor contribution (2–6%) of direct fission of the singlet.<sup>4</sup> The regiochemistry of dechlorination of 1 thus appeared to offer a sensitive probe with which to determine the nature of the intermediate species involved in related photochemical transformations. We applied this concept in our investigations into the mechanistic aspects of the sodium borohydride mediated photochemistry of 1. An analysis of the variation of quantum yield with BH<sub>4</sub><sup>-</sup> concentration provided the basis for the proposed mechanistic pathway for the photodecomposition of 1 that is shown in Scheme II.<sup>3</sup>

Electron transfer from borohydride to the triplet state of 1 generates the radical anion–radical pair 6, which can either diffuse out of the cage to the naked radical anion 8 and BH<sub>4</sub><sup>-</sup> radical or undergo fragmentation within the cage to form a caged radical pair 7. Similar conclusions have been reached by Kropp and Schuster.<sup>5</sup> Decomposition of 8 should give the three isomers of the tetrachlorobenzenes in a ratio consistent with that expected from a radical anion; i.e., the ratio should be similar to that which was obtained in the presence of triethylamine.

The relative ratios of 2–4 observed at various concentrations of borohydride (e.g., 0.02 M, 44.8% 2, 43.9% 3, and 11.3% 4), however, are closer to those obtained in the absence of triethylamine.<sup>3</sup> This suggested that the reaction proceeds mostly via the intermediate 7. This conclusion is consistent with additional evidence obtained through trapping and deuterium tracer studies.<sup>3</sup> The regiochemistry of dechlorination thus appeared to be very useful in determining the nature of the reactive intermediates involved in such reactions. It became necessary, therefore, to determine the validity and reliability of the proposal that the regiochemistry observed in the presence of triethylamine is indeed that expected for the fragmentation of the radical anion of 1. Generation of the radical anion of 1 through other means and comparison of the regiochemistry with that observed in the presence of triethylamine was clearly the next logical step.

## Results and Discussion

**Photochemical Generation of the Aromatic Radical Anion of 1 in Micellar Media.** Two different approaches were used to generate the radical anion of 1. The first method was designed to generate an uncomplexed radical anion of 1 within a micelle using triethylamine as the electron donor. Pentachlorobenzene (1) was dissolved in 0.200 M CTAB (hexadecyltrimethylammonium bromide) solution (bulk concentration of 1, 0.001 M corresponding to a microscopic concentration<sup>6</sup> of 0.017 M). On the basis of Poisson statistics,<sup>7</sup> the number of solute pentachloro-

Table II. Absorption Maxima of Triethylamine in Various Media

solvent	$\lambda_{\max}$ (nm) (log $\epsilon$ )
methanol	206 (2.94)
50% methanol/H <sub>2</sub> O	201 (3.10)
water	192 (3.35)
hexane	208 (3.61)
CTAB <sup>a</sup> /H <sub>2</sub> O	228 (2.08)
KBr <sup>a</sup> /H <sub>2</sub> O	230 (1.93)
TMA <sup>a</sup> /H <sub>2</sub> O	230 (1.90)

<sup>a</sup> 0.008 M in water.

benzene molecules per micelle is expected to be predominantly  $\leq 1$  (Table I). A large excess of triethylamine (0.165 M) dissolved into such a solution is expected to reside mostly in the aqueous phase and around the micellar surface. This premise is supported by absorption spectra studies of triethylamine in different media (Table II). The absorption is solvent dependent with a significant difference in the absorption maxima in, for example, water and hexane. It was assumed that if triethylamine were to reside within the micelle rather than the aqueous phase, its absorption spectra in a CTAB solution would resemble that in hexane rather than that in water. However, the absorption spectra in a 0.08 M solution shows a large bathochromic shift with little resemblance to the spectra in either hexane or water (Table II). It is possible, however, that the large shift in CTAB is due to the increased ionic strength of the medium with respect to water. The absorption spectra in 0.08 M KBr and tetramethylammonium bromide appear to confirm this. Tetramethylammonium bromide was used to mimic the CTAB molecules and the resultant ionic strength or interaction with triethylamine that the polar head of CTAB would generate. The absorption spectra of triethylamine in 0.08 M solutions of CTAB, KBr, and tetramethylammonium bromide are remarkably similar with an absorption maxima at  $\sim 230$  nm. These results thus indicate that triethylamine is located in a region that makes it susceptible to the ionic environment around it rather than within the hydrocarbon environment of the micelle where it would not be expected to be affected by variations in the ionic strength of the aqueous phase. These results are in harmony with the conclusions of Thomas and co-workers,<sup>8a</sup> as well as Erickson and Gillberg,<sup>8b</sup> who have provided spectral evidence that *N,N*-dimethylaniline resides at the micellar water interface in CTAB.

Appropriate amounts of pentachlorobenzene were dissolved in a 0.2 M CTAB solution in order to achieve the occupancy numbers shown in Table I. On irradiation in the presence of triethylamine, electron transfer can take place from the amine residing on the surface to an excited pentachlorobenzene across the micellar interface. This

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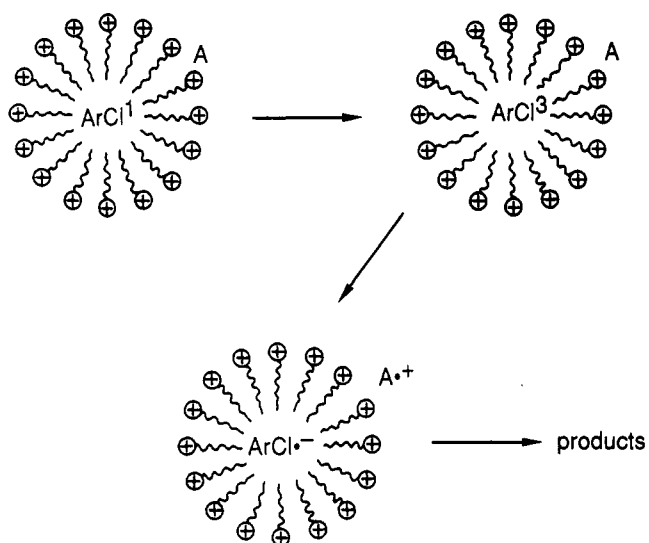
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Scheme III

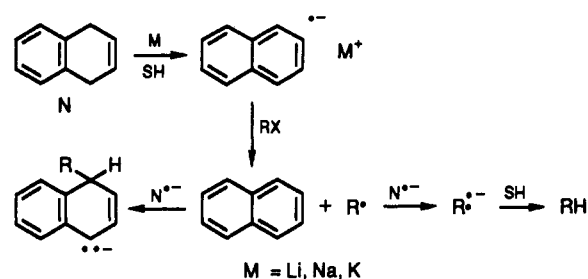


would result in the formation of a radical anion of pentachlorobenzene within the micelle. Since the micellar surface is positively charged, the resultant radical cation of triethylamine will be repelled away from the micellar surface to leave behind an uncomplexed radical anion of 1 within the micelle<sup>9a</sup> as shown in Scheme III.

The reaction in CTAB micelles in the absence of triethylamine might be expected to depend on the occupancy number of 1 since the quantum yield of dechlorination of 1 is known to be concentration dependent.<sup>3,4</sup> It had been suggested that at high concentrations of 1, reaction occurs principally via an excimer between an excited triplet-state and ground-state molecule of 1 with fragmentation of the radical anion-like moiety leading to product. Hence, when the concentration of 1 in the micellar solution is adjusted such that the occupancy number is either 0 or 1, the probability of excimer formation, and therefore radical anion-like behavior, would be very remote. Conversely, when the occupancy number is at least 2, the formation of an excimer within the confines of the micelle would be expected. If this hypothesis is true, some difference in the regiochemistry of the products in the two cases would be expected, i.e., in the former case the regiochemistry would reflect the fragmentation pattern of the triplet state while the latter would exhibit a pattern characteristic of excimer formation and reflecting radical anion fragmentation to a degree dependent upon the extent of charge separation. Table I shows the product ratios in various media as well as bulk concentrations (microscopic concentrations for micellar media) under identical irradiation conditions.

The reaction in acetonitrile and the product ratios have been explained previously. In micellar media, in the absence of triethylamine, the dependence of the product ratio on the occupation number, although present, is not very pronounced (entries 3 and 4). The differences in the regiochemistries seem similar to those obtained in solution ( $\text{CH}_3\text{CN}$ ) at the lowest and highest concentrations of 1 (entries 1 and 2, respectively). In the presence of triethylamine under conditions where the occupation number is primarily less than 2, the regiochemistry of dechlorination (entry 5) is distinctly similar to the ratio obtained in solution in the presence of an electron donor (entry 6). The results obtained in the micellar media are very encouraging as they exhibit the expected trend in the product

Scheme IV

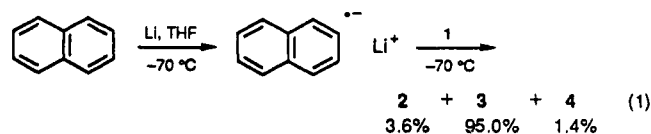


ratios, indicating the validity of using the regiochemistry of dechlorination to understand the nature of the intermediate species.

**Nonphotochemical Generation of Radical Anions of Aromatic Halides.** A second method, involving a nonphotochemical technique, was used for the generation of the radical anion of pentachlorobenzene. Naphthalene is known to react with lithium metal in a variety of solvents to form the corresponding radical anion.<sup>10</sup> When a solution of this radical anion is allowed to react with an alkyl halide, electron transfer to the alkyl halide leads to the formation of an alkyl radical and a halide ion and then after a second electron transfer to the corresponding alkane or organometallic RM. Coupling reactions of alkyl radical with naphthalene radical anion are also observed as shown in Scheme IV.<sup>10</sup>

By use of appropriate donors, it should be possible to generate a radical anion of 1 through transfer of an electron from the preformed radical anion of the donor. An essential condition is that the donors should have reduction potentials higher than that of 1, or conversely, lower electron affinities than 1. Naphthalene and biphenyl are two commonly used precursors that easily react with alkali metals to form the corresponding radical anion. These have half-wave reduction potentials of  $-1.98$  and  $-2.05$  V, respectively<sup>11,12</sup> (relative to a mercury pool anode), which are conveniently higher than those for penta-, tetra- and trichlorobenzenes. The half-wave reduction potentials for 1, 3, and 1,2,4-trichlorobenzene, for example, are  $-1.21$ ,  $-1.45$ , and  $-1.64$  V, respectively<sup>13</sup> (relative to a Hg pool anode). Thus, addition of the chlorobenzene to a solution of the radical anion of naphthalene or biphenyl should lead to the formation of the radical anion of the chlorobenzene through electron transfer from the precursor radical anion.<sup>14</sup>

Treatment of a 0.034 M solution of naphthalene in THF at  $-68$  °C with 1.12 equiv of Li metal in an argon atmosphere resulted in a green solution of the corresponding radical anion. Treatment of this solution with 1 and subsequent quenching with water resulted in the formation of the three isomers of tetrachlorobenzene in the ratios shown (eq 1).



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Table III. Relative Ratio of Products from the Radical Anion of Pentachlorobenzene (1)

T (°C)	1/T × 10 <sup>2</sup>	log (k <sub>3</sub> /k <sub>2</sub> )	log (k <sub>3</sub> /k <sub>4</sub> )	percentage ratio of products		
				2	3	4
0	0.366	0.988	1.87	16.7 ± 0.9	81.2 ± 2.4	2.10 ± 0.10
-25	0.403	1.11	1.63	12.8 ± 0.1	83.3 ± 0.1	3.90 ± 0.20
-40	0.429	1.35	1.94	8.00 ± 0.50	90.0 ± 1.9	2.00 ± 0.11
-55	0.459	1.50	2.16	5.90 ± 1.12	92.8 ± 0.5	1.30 ± 0.21
-68	0.488	1.76	2.31	3.34 ± 0.43	95.7 ± 0.5	0.96 ± 0.09
45	0.314	0.676 <sup>a</sup>	1.05 <sup>a</sup>	26.4 ± 0.30	62.5 ± 0.3	11.1 ± 0.9
45	0.314	0.683 <sup>b</sup>	1.27 <sup>b</sup>	25.9	62.5	6.67
45	0.314	0.173 <sup>c</sup>	0.772 <sup>c</sup>	50.1 ± 0.7	37.3 ± 0.6	12.6 ± 0.9

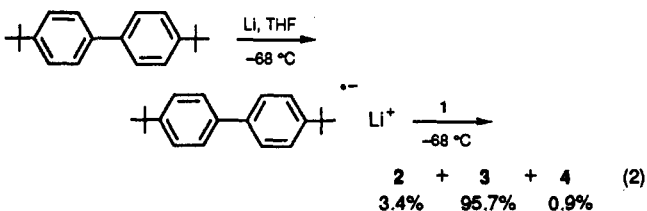
<sup>a</sup> Values obtained from photochemical reaction with triethylamine. <sup>b</sup> Extrapolated values from Arrhenius plots. <sup>c</sup> Values obtained from photochemical reaction without triethylamine.

Table IV. Relative Ratio of Products from the Radical Anion of 1,2,3,5-Tetrachlorobenzene (2)

T (°C)	1/T × 10 <sup>2</sup>	log (k <sub>10</sub> /k <sub>9</sub> )	percentage ratio of products		
			9	10	11
0	0.366	0.960	5.17 ± 0.31	94.2 ± 1.23	0.63 ± 0.01
-25	0.403	1.25	2.80 ± 0.01	97.2 ± 0.50	0.00
-50	0.448	1.11	3.80 ± 0.10	96.2 ± 1.30	0.00
-65	0.481	1.23	2.90 ± 0.50	97.1 ± 0.63	0.00
45	0.314	0.604 <sup>a</sup>	18.8 ± 1.0	75.5 ± 1.40	5.70 ± 0.61
45	0.314	1.166 <sup>b</sup>	5.15	75.5	
45	0.314	-0.166 <sup>c</sup>	59.2 ± 1.5	40.5 ± 1.51	0.30 ± 0.01

<sup>a</sup> Values obtained from photochemical reaction with triethylamine. <sup>b</sup> Extrapolated values from Arrhenius plot. <sup>c</sup> Values obtained from photochemical reaction without triethylamine.

Analysis of the product mixture, however, was difficult owing to several side reactions. In order to avoid these side reactions, presumably arising from coupling reactions between the donor and radical derived from acceptor radical anion, *p,p'*-di-*tert*-butylbiphenyl (DBB) (half-wave reduction potential -2.14 V relative to Hg pool anode)<sup>12</sup> was used as donor. The presence of the *tert*-butyl groups is known to prevent the side reactions encountered with naphthalene.<sup>10</sup> Similar treatment of DBB with Li and subsequent reaction with 1 in THF again gave the three isomers of tetrachlorobenzene as products as shown in eq 2.



In addition, the reaction was free from the side reactions observed in the previous case. Remarkably, the expected major product 3 from the radical anion of 1 is formed almost exclusively at this temperature (-68 °C). Thus, although the product ratios appeared to indicate reaction via the radical anion of 1, the reactivity pattern was not as close as we anticipated. The difference in the temperature of the respective reactions (-68 and 45 °C, re-

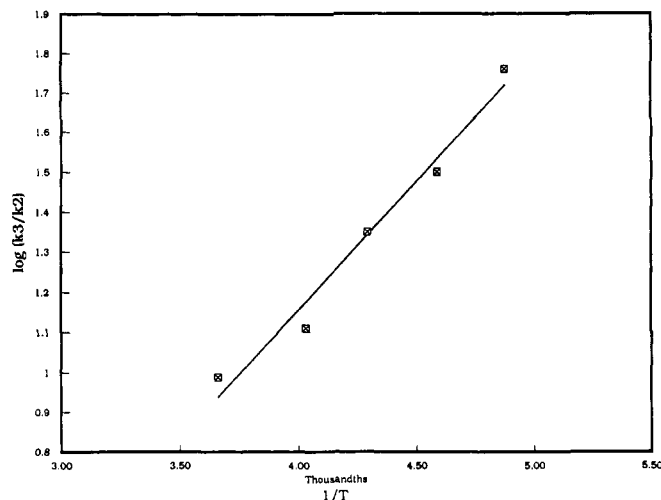


Figure 1. Arrhenius plot for the rates of formation of 3 vs 2.

spectively) appeared to be a possible source for the unexpectedly high yield of 3. A series of reactions was, therefore, carried out at various temperatures between 0 and -68 °C, the results of which are shown in Table III.

Interestingly, the product ratios changed with increasing temperature with the yield of 3 dropping steadily and that of 2 increasing correspondingly. The yield of 4 did not show a pronounced temperature effect. The relative ratios of the products at 45 °C could be calculated with the aid of Arrhenius plots. The log of the ratio of the rates of formation of 3 and 2  $\log (k_3/k_2)$  was plotted against the inverse of absolute temperature of reaction (Figure 1). The ratio of rates is obtained as the ratio of the percentages of 3 and 2 at the respective temperatures corrected for statistical advantages. The relative ratios of products at the photochemical reaction temperature (45 °C) were obtained from this plot (Figure 1) and a similar plot for  $k_3/k_4$  and are shown in Table III. The results are in excellent agreement with the product ratios obtained photochemically in the presence of triethylamine.

Three additional aromatic halides, namely 2, 1,2,4-trichlorobenzene (10), and pentafluorobenzene (15), were also allowed to react in a similar manner to test the generality of this relationship. The results are shown in Tables IV-

Table V. Relative Ratio of Products from the Radical Anion of 1,2,4-Trichlorobenzene (10)

T (°C)	1/T × 10 <sup>2</sup>	log (k <sub>14</sub> /k <sub>13</sub> )	log (k <sub>14</sub> /k <sub>12</sub> )	percentage ratio of products		
				12	13	14
0	0.366	0.805	1.03	7.50 ± 1.30	12.5 ± 0.2	80.0 ± 1.3
-40	0.429	0.897	1.42	3.30 ± 0.02	10.9 ± 0.6	85.8 ± 0.3
-60	0.470	0.943	1.50	2.79 ± 0.51	9.96 ± 0.56	87.2 ± 1.3
-70	0.493	0.974	1.47	2.97 ± 0.23	9.32 ± 0.97	87.7 ± 1.3
45	0.314	0.617 <sup>a</sup>	1.06 <sup>a</sup>	6.50 ± 0.35	18.2 ± 0.1	75.3 ± 0.3
45	0.314	0.741 <sup>b</sup>	0.882 <sup>b</sup>	9.89	13.7	75.3

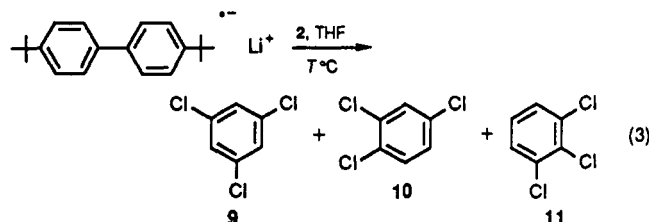
<sup>a</sup> Values obtained from photochemical reaction with triethylamine. <sup>b</sup> Extrapolated values from Arrhenius plot.

Table VI. Relative Ratio of Products from the Radical Anion of Pentafluorobenzene (15)

T (°C)	1/T × 10 <sup>2</sup>	log (k <sub>17</sub> /k <sub>16</sub> )	log (k <sub>17</sub> /k <sub>18</sub> )	percentage ratio of products		
				16	17	18
0	0.366	0.828	0.886	19.1 ± 2.6	64.2 ± 0.6	16.7 ± 0.7
-40	0.429	1.14	0.818	10.0 ± 3.1	69.0 ± 0.3	21.0 ± 0.2
-70	0.493	1.30	0.745	6.85 ± 2.06	68.5 ± 0.6	24.65 ± 0.23
45	0.314	0.974 <sup>a</sup>	1.03 <sup>a</sup>	15.1 ± 0.5	71.6 ± 0.3	13.3 ± 0.7
45	0.314	0.670 <sup>b</sup>	0.941 <sup>b</sup>	30.6	71.6	16.4

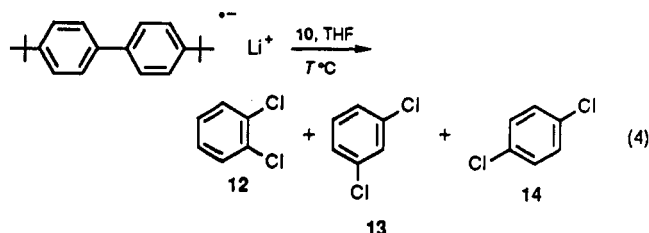
<sup>a</sup> Values obtained from photochemical reaction with triethylamine. <sup>b</sup> Extrapolated values from Arrhenius plot.

VI. In the case of 2, the isomers of the trichlorobenzenes 9–11 are formed (eq 3).



Isomer 10 is expected to be the major product,<sup>2</sup> produced via the radical anion of 2, and is indeed observed to be so. However, unlike 1 the reaction temperature did not affect the product ratios to as large a degree. As a result of the very small quantities of 11 it is not possible to estimate a value for 11 formed at 45 °C by extrapolation of the corresponding Arrhenius plot. However, the trend in the relative rates for generation of 9 and 10 (Table IV) corresponds to that observed photochemically and contrasts with that found in direct irradiation in the absence of triethylamine.

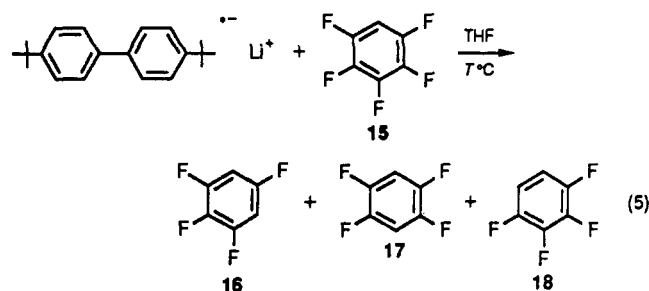
A similar reaction was observed in the reductive fission of 1,2,4-trichlorobenzene (10), which formed the expected *p*-dichlorobenzene (14) as the major product at all temperatures along with the ortho and meta isomers 12 and 13 (eq 4, Table V). Unlike 1,2,3,5-tetrachlorobenzene (2),



however, the product ratio showed a clear dependence on the temperature of the reaction as in the case of 1. A plot of the log of the ratios of the rate of formation of 14 vs 12 and 13, respectively, against the inverse of the absolute temperature of the reaction showed a linear relationship. The extrapolated value for the ratio of rates of formation of 14 to 12 and 13, respectively, at the photochemical reaction temperature (45 °C) shows good agreement (Table V).

Pentafluorobenzene (15) was chosen in order to test the reaction on a distinctly different aromatic halide and to compare the outcome with the results obtained in our earlier photochemical study.<sup>15</sup> Treatment of 15 under the conditions used for the chlorides described previously resulted in a very rapid reaction leading to the formation of tetra-, tri-, and fluorobenzene. The difluorobenzenes could not be detected. In order to avoid forming polyfluorobenzenes other than the tetra isomers, only 0.2 equiv of a solution of the preformed radical anion of DBB was added to a solution of 15. The reverse addition helped to

cut down on the extent of formation of daughter products of the tetrafluoro isomers to ~10%. However, subsequently, the three tetra isomers were found to react at relative rates nearly identical with DBB radical anion, so no corrections were required for the relative ratios of the tetra isomers formed in the radical exchange reaction. The reaction, as before, gave the expected product 17 as the major product with 16 and 18 as the minor products at all temperatures (eq 5). Arrhenius plots gave



the extrapolated values at the photochemical reaction temperature as shown in Table VI. The relative ratios obtained from the Arrhenius plot correlate very well for 17 vs 18. The ratio obtained for 16 does seem a little high, but overall the regiochemistry is in reasonable agreement with that observed photochemically.

These results show that a radical anion of the corresponding polyhaloarene may be generated conveniently using lithium di-*tert*-butylbiphenylide. The polyhaloarene radical anion undergoes fragmentation to aryl radical and halide with hydrogen abstraction by the radical leading to the corresponding reduced aromatic halide. The log of the relative rates of formation of any two isomers exhibits an Arrhenius relationship with the inverse of temperature, thus allowing the calculation of the expected ratio at the photochemical reaction temperature. Overall, the relative ratios at this elevated temperature correlate well with those obtained photochemically in the presence of the electron donor triethylamine, thus suggesting that the products in both cases are formed through a common intermediate, namely a radical anion.

The results thus vindicate the basic premise that the nature of the intermediate species may be characterized from the regiochemistry of dehalogenation. Furthermore, it seems reasonable to ascribe the regiochemistry observed to that of an unencumbered radical anion or solvent-separated species in the radical anion reductions and the triethylamine photochemical runs. Various studies on lithium biphenylide have shown that the radical anion and lithium cation exist both as contact ion pairs and solvent-separated ion pairs in THF although at or below 20 °C they exist mostly as solvent-separated ion pairs.<sup>14,16</sup> In the case of the exciplex between the radical anion of 1 and (Et)<sub>3</sub>N<sup>+</sup>, various studies of pyrene and aliphatic or aromatic amine exciplexes<sup>17,18</sup> and related excited singlet

states of EDA complexes<sup>17,19,20</sup> provide evidence that an initially formed contact ion pair would rapidly relax to a solvent separated ion pair ( $k_1 \approx 10^9 \text{ s}^{-1}$ ), which, in turn, would rapidly dissociate to free ions ( $k_2 \approx 10^9 \text{ s}^{-1}$ ) in acetonitrile. Thus, within 2 ns most of the contact ion pairs in the present case might reasonably be expected to be converted to either solvent-separated ion pairs or to free ions. The conclusion that unencumbered radical anion or solvent-separated radical anion/cation are product-determining intermediates for the fragmentation processes observed is reinforced by our results in CTAB/ $\text{Et}_3\text{N}$  where the radical anion is created as an unencumbered radical anion. The nearly exclusive formation of a single dehalogenated product in the reactions of LiDBB with pentafluorobenzene and 1,2,3,5-tetrachlorobenzene at low temperatures is noteworthy. The fact that the expected major regioisomer can be predicted with precision allows for possible useful exploitation of this reaction.

### 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. The tetrahydrofuran used was freshly distilled from sodium benzophenone anion before each use. The lithium ribbon (Foote Mineral Co.) used for the radical anion reactions was >99%. Deionized, double-distilled water (potassium permanganate) was used in the micellar reactions.

**General Procedure for Photolysis.** All the samples for irradiation were prepared and irradiated as described earlier.<sup>2,3</sup> Micellar solutions were prepared by dissolving appropriate amounts of 1 in 0.2 M solution CTAB under vigorous stirring.

**General Procedure for Radical Anion Reactions.** The radical anions of naphthalene and *p,p'*-di-*tert*-butylbiphenyl

(DTBB) were prepared in THF according to the procedure described earlier.<sup>10</sup> Typically, 20 mL of 0.05 M solution of DTBB (0.001 mol) in THF at the appropriate temperature was treated with 0.001 mol of lithium metal. After the mixture was stirred for 4 h, a solution containing 0.2 equiv of the halide in 1–2 mL of THF was syringed into the green radical anion solution of DTBB and purged with water after 10 min. In the case of pentafluorobenzene (15), 0.2 equiv of the radical anion solution, with respect to  $6 \times 10^{-4}$  mol of 15, was transferred under argon into a solution of 15 cooled to the appropriate temperature in order to minimize the formation of isomers other than 16–18.

**Product Analysis.** The photolysis mixtures were analyzed by GLC on a Varian 3300 capillary gas chromatograph equipped with an FID, a 30 m  $\times$  0.25 mm DB-WAX 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 a detector temperature of 250 °C. Helium was used as carrier gas at 30 mL/min.

The reaction mixtures from micellar irradiations were extracted with pentane after dilution of the soapy solution. The recovery efficiency was typically ~90%. The product ratios were analyzed as in the previous text. Dodecane and hexadecane were used as internal standards.

The products from the radical anion reductions were analyzed after extracting the products from the THF–water mixture with pentane (recovery efficiency 85–90%) under the GLC conditions described previously. The pentane and residual THF were removed in a rotary evaporator before analysis. However, 15 and the products thereof were analyzed under different conditions. The extreme volatility of these aromatic fluorides necessitated the removal of pentane in a spinning band column. The removal of the residual THF, however, was not possible under these circumstances. The capillary column used to analyze the ratio of products was a combination of a DB-5 and DB-WAX (both 30 m  $\times$  0.25 mm). The GLC column conditions for this analysis employed the following column temperature program: 30 °C for 35 min and raised to 180 °C at a rate of 20 °C/min with injection and detector temperatures as in the previous text.

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## MM2 Model for the Intramolecular Additions of Acyl-Substituted Radicals to Alkenes

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The modified MM2 force field devised earlier to calculate transition states for intramolecular radical additions (Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* 1987, 52, 959) has been extended to include acyl-substituted radicals. Calculations of the regioselectivities and stereoselectivities of the radical cyclizations are in good agreement with experimental results. The calculations show that the C(acyl)–C(rad)–C(alkene) attack angle and the geometric preference for planarity of the C(O)CH<sub>2</sub>• radical, which is maintained in the transition structures for additions, cause the regioselectivities of acyl-substituted radical cyclizations to differ from those of alkyl radical cyclizations.

### Introduction

Intramolecular additions of radicals to carbon–carbon double bonds to form five- and six-membered rings is a topic of intense current interest in synthetic organic chemistry.<sup>1–5</sup> Such cyclizations are usually kinetically

controlled.<sup>1</sup> The 5-hexenyl radical cyclizes with high regioselectivity<sup>4</sup> to give the five-membered ring (5-*exo* clo-

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