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(27) On the basis of HMO calculations.
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Racemization and Bromide-Exchange Studies on 1-Phenylbromoethane and the Question of the Ion-Pair Mechanism for Bimolecular Nucleophilic Substitutions at Saturated Carbon

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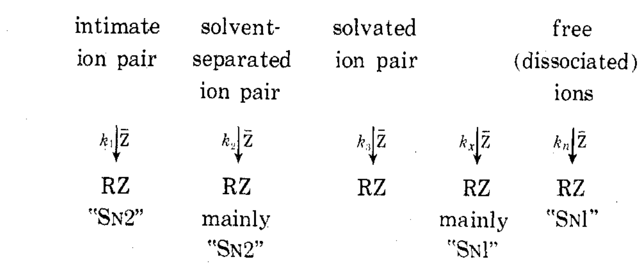
In an effort to determine whether the ion-pair mechanism for nucleophilic substitution at saturated carbon operates in bimolecular reactions, the racemization and bromide–radiobromide exchange of 1-phenylbromoethane were examined in anhydrous acetone containing lithium bromide. Within experimental error, the rate constants and Arrhenius and thermodynamic activation parameters are identical for the racemizations and exchanges. There is no evidence for inversion without exchange or exchange without inversion. Consequently, for the ion-pair mechanism to be operating, all of the ion pairs formed by the substrate and leaving group must be intercepted (or collapse to starting material) before the ions separate sufficiently to allow the alkyl group to turn over and give, on the collapse of the ion pair, inversion without halide exchange. On the other hand, the results are completely consistent with the classical Hughes–Ingold SN2 mechanism.

The observation that the rates of halide–radiohalide exchange and racemization of optically active 1-phenylbromoethane[1] and those of 2-iodooctane[2] were the same within experimental error was the basis for the postulation of the SN2 mechanism for the bimolecular nucleophilic displacement at saturated carbon by Gleave, Hughes, and Ingold.[3] It was the carbonium ion route, the SN1 or unimolecular mechanism of the mechanistic pair, which was the more difficult to establish;[4,5] chemists, on the other hand, readily accepted the concerted nucleophilic attack–leaving group departure of the SN2 mechanism. As Sneen and Larsen point out, however, it is the traditional SN2 reaction pathway which is the less likely.[6] They have proposed an elaboration of the ion-pair scheme of Winstein and his colleagues[7] as a single unified mechanism to replace the SN1–SN2 dichotomy. In their ion-pair mechanism, which is summarized in Scheme I, it is proposed that the initial step is the formation of a contact or intimate ion pair by the substrate with its leaving group. The reaction could show the characteristics of SN2, mixed, or SN1 mechanisms depending upon where in the series of solvation equilibria from intimate ion pair to the free, independently solvated ions nucleophilic attack occurs.

Scheme I



Should such a mechanistic scheme be proven correct, it has wide ramifications not only for all nucleophilic substi-

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Table I
Second-Order Rate Constants for the Racemization of (+)- or (−)-1-Phenylbromoethane in Anhydrous Acetone at Various Temperatures and Lithium Bromide Concentrations

Temp, K	Rate constants[a] × 10^3 mol sec/l. at [LiBr] given				
	0.0100 *M*	0.00500 *M*	0.00200 *M*	0.00100 *M*	0.000500 *M*
298.15	1.334 ± 0.014	1.678 ± 0.004	2.349 ± 0.024	3.005 ± 0.029	3.712 ± 0.024
303.15	2.092 ± 0.010[b]	2.630 ± 0.007[b]	3.645 ± 0.012[b]	4.601 ± 0.057[b]	5.783 ± 0.065[c]
308.15	3.273 ± 0.009[b]	4.091 ± 0.011[b]	5.597 ± 0.019	7.117 ± 0.050[b]	9.229 ± 0.084[c]
313.15	4.929 ± 0.010	6.274 ± 0.039[b]	8.449 ± 0.024	11.116 ± 0.099[b]	14.329 ± 0.110
318.15	7.328 ± 0.056	9.395 ± 0.032	12.705 ± 0.035	16.360 ± 0.070	18.305 ± 0.084

[a] Least-squares values. [b] Average of two runs. [c] Average of three runs.

tution reactions but also for other substitutions, and for elimination and addition reactions among others.[8] The importance of ion pairs in nucleophilic substitutions at saturated carbon is quite well established at or near the unimolecular or dissociated ion extreme of the mechanistic range[9] but not for bimolecular displacements. Hughes et al.[1] reported that both the halide exchange and the racemization of 1-phenylbromoethane in anhydrous acetone with lithium bromide were bimolecular. Since in that system the leaving group and the nucleophile are identical, some of the variables are eliminated. Also as a bulwark of the S_N2 mechanism, what system could be more appropriate for a detailed examination to determine whether ion pairs play a role in bimolecular nucleophilic substitutions at saturated carbon?

Results

The racemization of optically active alkyl halide by halide ion can be represented by the equations

$$(+)\mathrm{RX} + \mathrm{X}^- \xrightarrow{k} (-)\mathrm{RX} + \mathrm{X}^-$$

$$(+)\mathrm{RX} + (-)\mathrm{RX} \underset{\text{or concurrent}}{\xrightarrow{\text{instantaneous}}} (\pm)\mathrm{RX}$$

Note that the inversion of one molecule of, say, the (+) isomer to the (−) isomer not only removes the rotational contribution of one (+) species but cancels that of another, giving two molecules of racemic (±) mixture. The rate expression, eq 1, applies

$$\ln \frac{[\mathrm{RX}]_0}{[\mathrm{RX}]_t} = 2k[\mathrm{X}]t \qquad (1)$$

where $[\mathrm{RX}]_0$ and $[\mathrm{RX}]_t$ are the concentrations of the optically active alkyl halide initially and at time t, k is the rate constant, and [X] the concentration of the halide ion.[10] In practice, the alkyl halide concentration terms were replaced with the angle of rotation of plane polarized light or, more precisely, the recorder output of the recording polarimeter. Good linearity was obtained for 3–6 half-lives, depending upon when the instrument instability became a significant fraction of the rotational value.

For the halide exchange studies, the electrodeposition method developed by Beronius[11] was used. In this method, the solution of inorganic halide (e.g., LiBr) in the solvent (e.g., acetone) containing radiohalide (e.g., $^{82}\mathrm{Br}^-$) is placed in the thermostatted electrolysis cell and a very small portion of the halide electrodeposited on a silver disk as AgX. The activity of that disk is a measure of the $t = 0$ halide activity. A known amount of RX is then added and, at various time intervals, AgX is deposited on fresh silver disks at the same current for the same time as was used for the $t = 0$ electrode. The decreasing activity of subsequent electrodes is then a measure of the amount of radiohalide incorporated into the RX and no longer available for electrodeposition.

The halide exchange reaction can be represented as

$$\mathrm{RX} + \mathrm{X}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RX} + \mathrm{X}^-$$

where k_1 and k_{-1} are the rate constants for the forward and reverse reactions. They are identical and equal to k. Assuming that any isotope effects are negligible, the rate constants for the incorporation of the radiohalide, X*, the process actually studied, will be the same or

$$\mathrm{RX} + \mathrm{X}^{*-} \underset{k}{\overset{k}{\rightleftharpoons}} \mathrm{RX}^* + \mathrm{X}^-$$

and

$$\frac{-\mathrm{d}[\mathrm{X}^*]}{\mathrm{d}t} = k[\mathrm{RX}][\mathrm{X}^*] - k[\mathrm{RX}^*][\mathrm{X}]$$
$$= k([\mathrm{RX}][\mathrm{X}^*] - [\mathrm{RX}^*][\mathrm{X}])$$

Since the total amount of X* is constant,

$$[\mathrm{RX}^*] = [\mathrm{X}^*]_0 - [\mathrm{X}^*]$$

where $[\mathrm{X}^*]_0$ is the initial, or $t = 0$ concentration, of radiohalide as measured by the activity of the first electrode. Substituting and rearranging gives

$$\frac{\mathrm{d}[\mathrm{X}^*]}{-[\mathrm{X}][\mathrm{X}^*]_0 + ([\mathrm{RX}] + [\mathrm{X}])[\mathrm{X}^*]} = -k\,\mathrm{d}t$$

Noting that

$$\int \frac{1}{nx + a}\,\mathrm{d}x = \frac{1}{n} \ln (nx + a) + c$$

allows integration of the expression to

$$\frac{1}{[\mathrm{RX}] + [\mathrm{X}]} \ln \{([\mathrm{RX}] + [\mathrm{X}])[\mathrm{X}^*] - [\mathrm{X}][\mathrm{X}^*]_0\} = -kt + c$$

Rearranging and adding the constant ln [1/([RX] + [X])] to both sides gives

$$\ln \left\{ [\mathrm{X}^*] - \frac{[\mathrm{X}][\mathrm{X}^*]_0}{[\mathrm{RX}] + [\mathrm{X}]} \right\} = -([\mathrm{RX}] + [\mathrm{X}])kt + c'$$

Again ignoring isotope effects, at infinite time the radiohalide will be statistically distributed between inorganic and organic halide so that the $t = \infty$ activity will be given by

$$[\mathrm{X}^*]_\infty = \frac{[\mathrm{X}^*]_0[\mathrm{X}]}{[\mathrm{RX}] + [\mathrm{X}]} \qquad (2)$$

Thus the rate expression becomes

$$\ln \{[\mathrm{X}^*] - [\mathrm{X}^*]_\infty\} = -([\mathrm{RX}] + [\mathrm{X}])kt + c' \qquad (3)$$

Equation 3 can be converted to the form used by other workers[12]

$$\ln \left\{ \frac{[\mathrm{X}^*]}{[\mathrm{X}^*]_\infty} - 1 \right\} = -([\mathrm{RX}] + [\mathrm{X}])kt + C \qquad (4)$$

Slopes of the plot of the ln term of eq 3 or 4 (with $[\mathrm{X}^*]_\infty$

Table II
Second-Order Rate Constants for the Bromide–Radiobromide Exchange of 1-Phenylbromoethane in Anhydrous Acetone at Various Temperatures and Lithium Bromide Concentrations

Temp, K	Rate constant[a] × 10^3 mol sec/l. at [LiBr] given			
	0.0100 *M*	0.00500 *M*	0.00200 *M*	0.000500 *M*
298.15	1.313		2.370 ± 0.026[b]	3.613 ± 0.003[b]
303.15	2.1500 ± 0.0003[c]	2.679 ± 0.020[d]	3.803 ± 0.018[e]	6.321 ± 0.026[e]
308.15	3.3113 ± 0.0001		6.2085 ± 0.0001[b]	9.46 ± 0.23[d]
313.15	5.033		8.330	12.6 ± 2.1[b]

[a] Rate constants were determined graphically. Where least-squares determinations were also done, agreement was within ±0.2%. [b] Average of two runs. [c] Average of three runs. [d] Average of four runs. [e] Average of five runs.

Table III
Activation Parameters at 303.15 K for the Reaction of 1-Phenylbromoethane and Bromide Ion in Anhydrous Acetone[a]

	Arrhenius parameters		Thermodynamic parameters		
	ln *A*	E_a, kJ/mol	$\Delta H^{\ddagger}$, kJ/mol	$-\Delta S^{\ddagger}$, J/deg mol	$\Delta G^{\ddagger}$, kJ/mol
Racemization	20.94 ± 0.14	67.0 ± 0.2	64.199 ± 0.087	79.88 ± 0.67	88.41 ± 0.29
Exchange	20.93 ± 0.15	66.9 ± 0.5	64.083 ± 0.516	80.38 ± 1.06	88.45 ± 0.84

[a] Values given are averages of those obtained at each concentration of lithium bromide reported in Tables I and II. At individual concentrations of lithium bromide, agreement between the parameters of racemization and exchange was normally within the sum of the standard deviations of the two values.

calculated by eq 2) vs. *t* were used to evaluate the rate constants for the exchange reaction. In some runs good linearity was obtained for over 7 half-lives. Nor was the calculated rate constant dependent upon the concentration of the alkyl bromide, since changing the concentration by as much as a factor of 20 left the rate constant unchanged within experimental error.

The rate constants for both the exchanges and the racemizations at the lower concentrations of lithium bromide were quite sensitive to moisture. The maximum rate was found for freshly prepared solutions; a rate that fell off as the acetone–lithium bromide solutions picked up moisture even in tightly stoppered flasks stored in a nitrogen-flushed drybox. Consequently, the rate constants for the lowest concentration of lithium bromide are the least secure of those reported in Tables I and II.

Discussion

From Tables I and II it is apparent that the rate constants for both the exchange and the racemization of 1-phenylbromoethane in anhydrous acetone containing lithium bromide decrease with increasing concentration of lithium bromide. Hughes et al.[1] reported a similar observation. This fall-off has been assigned to ion pairing or association of the lithium bromide.[10] Such association would reduce the activity coefficient of the bromide ion. Because concentrations, not activities, were used in determining the rate constants via eq 1 and 3 or 4, the apparent rate constant decreases as the lithium bromide concentration increases. Normally, to avoid such problems, high constant ionic strengths and concentrations of the cation are used to keep the activity coefficient of the nucleophile constant as its concentration is varied.[10,13] Concentration and activity are then linearly related and the rate constants are independent of the concentration of the ionic reactant. Unfortunately, all of the lithium salts, nitrate, chlorate, perchlorate, picrate, etc., which were tried as inert electrolytes were either not sufficiently soluble in the acetone, were too nucleophilic, or else interfered with the electrodeposition of the silver bromide in the exchange studies.

Other halide salts for which association would be much less, salts like the tetraalkylammonium bromides, do indeed give a much smaller drop-off of rate constant with increasing bromide salt concentration. Thus with tetrabutylammonium bromide at 303.15 K the racemization rate constants at 0.001 and 0.01 *M* were 9.70 and 8.42 × 10^{-13} l./mol sec, respectively.[14] While such salts could have been used in the racemization studies, they would have added the complication of ion exchange treatment to the exchange experiments because the radiobromide was most conveniently made by neutron bombardment of inactive lithium bromide.

Despite the decrease in the apparent rate constant with increasing lithium bromide concentration,[14] the reaction is obviously second order, first order in each of alkyl halide and halide ion. Thus increasing the lithium bromide concentration fivefold from 0.002 to 0.01 *M* increases the rate of the racemization and the exchange reactions by an average factor of 2.86 while the rate constant decreases, on average, to 57% of its former value. A 20-fold concentration change from 0.0005 to 0.01 *M* led to an average rate increase by a factor of 7.28 with an average decrease in second-order rate constant to 36.4% of its former value.

In Table III Arrhenius activation parameters and thermodynamic data are reported. Like the rate constants in Tables I and II, which are apparent values uncorrected for the activity of the bromide ion, the parameters in Table III include contributions due to changes in salt effects and activity coefficients on the temperature dependence of the rates. However, as with the rate constants, comparisons between racemization and exchange reactions which were done under the same reaction conditions are valid.

Comparison of the rate data for racemization in Table I with that for exchange in Table II shows that, as Hughes et al. reported, the rate constants for the two processes are the same within experimental error. The one-to-one nature of the two processes is confirmed by the activation and thermodynamic parameters, the values of which were generally within one standard deviation for racemization and exchange at the same concentration of lithium bromide and, indeed, were independent of the concentration of inorganic halide. These results are consistent with the classical Hughes–Ingold mechanism for the bimolecular nucleophilic displacement at saturated carbon. They are compatible with the Sneen ion-pair mechanism of Scheme I only if nucleophilic attack occurs early in the ionization sequence. It must occur before the separation of the alkyl group and the leaving group is sufficient for the alkyl group to turn over and so give detectable racemization with internal return.

If the ion-pair mechanism is operating, stabilizing the carbonium ion species by the introduction of appropriate substituents on the phenyl group should shift the average point of nucleophilic attack toward the right of Scheme I, perhaps sufficiently so that significant amounts of racemization with internal return can occur. Racemization then should be faster than halide exchange. This possibility is currently under investigation. Some preliminary results for the bromide–radiobromide exchange have already been reported.[15] However, with 1-phenylbromoethane itself, no evidence confirming that the Sneen ion-pair mechanism applies to bimolecular nucleophilic displacements at saturated carbon has been obtained to date.

Experimental Section

Solvent. Just before preparation of the solutions, reagent grade acetone was dried and purified as previously described.[10]

Lithium Bromide. Reagent grade, "Certified" (Fisher) or "Suprapur" (Merck), $LiBr \cdot xH_2O$ was oven dried at 250°C for at least 24 hr and cooled in a desiccator immediately before weighing and preparation of the 0.05000 ± 0.0002 *M* stock solution which, with appropriate dilutions, was used to make the acetone solutions for this study.

(±)-, (+)- and (−)-1-Phenylbromoethane were made from the corresponding 1-phenylethanol as previously described.[10,16] The alkyl bromides showed no detectable hydroxylic absorptions in infrared spectra neat or at high concentration in CCl_4, nor were anomalous signals present in the proton nuclear magnetic resonance spectra or the vapor phase chromatograms of the halides so examined. Spectra (NMR, ir, mass spectrum) and physical properties were consistent with the structure. The 1-phenylbromoethanes were stored under nitrogen in glass ampules in a freezer until needed but even under these conditions the optically active halides very slowly racemized. Fresh material was made every few weeks. Configurational purity was not established but since the racemizations were first order in alkyl bromide, it is of no consequence to this study.

Racemization Studies. The procedure was analogous to that described earlier[10] except that a Perkin-Elmer Model 141 MC polarimeter equipped with a retransmitting potentiometer and a Honeywell Electronik 194 potentiometric recorder was used. All manipulations of solvent and solution were done in a dry nitrogen-filled glove bag. Concentrations of (+)- or (−)-1-phenylbromoethane (i.e., 0.07–0.14 *M*) that gave near full-scale initial recorder pen deflections were used. Results are reported in Table I.

Reactions using $R_4N^+Br^-$, especially tetrabutylammonium bromide, were run analogously. (See paragraph at end of paper regarding supplementary material.)

Exchange Studies. The radiobromide ($^{82}Br^-$) was made by Aktiebolaget Atomenergi, Isotopservice, 611 01 Nykoping 1, Sweden, by irradiating at high neutron flux 0.87 mg of LiBr in a quartz vial. With adequate lead shielding throughout, the vial was opened and its contents extracted with several portions of hot distilled deionized water. The solution was evaporated to dryness, the 15-ml Erlenmeyer flask was then heated to 300°C for several hours and cooled, and the lithium radiobromide taken up in 5 ml of anhydrous acetone. An aliquot (0.1–0.4 ml) of this solution was added to the 50-ml stirrer-equipped Teflon-lined jacketed aluminum electrolysis cell containing the lithium bromide–acetone solution already equilibrated to the desired temperature. After electrodeposition of AgBr (for the initial, or $t = 0$, activity) on two or three electrodes, a weighed amount of (±)-1-phenylbromoethane (to give a solution of $0.35\text{–}7.5 \times 10^{-2}$ *M*) was added and the reaction timer started. Electrolysis was with silver electrode disks 0.4 cm in diameter at a carefully controlled and reproduced constant current of 200–2000 μA for 20–60 sec depending upon the LiBr concentration. Six to ten electrodepositions spread over about 3 half-lives were used.

Individual electrodes were counted for 3–20 min; the time interval was chosen so that the $t = 0$ electrode would give 30000–1000000 counts. The counts were corrected for background (invariably less then 1% of the $t = 0$ values), for variations in electrodeposition time (rarely more than ±0.1 sec), and for radioactive decay of the ^{82}Br between the time of counting the first and the current electrode of the run. The infinity values were calculated using corrected counts in eq 2. In those runs in which the infinity values were approached, the empirical and calculated values were in good agreement. For example, in one run where the corrected $t = 0$ count (average of two electrodes) was 37229, the calculated infinity value was 3597 while the last electrode (at $t = 66615$ sec) gave 3844 counts, a value only 107% of the calculated infinity value. The last point deviates little from the best line of the $\ln \{[X^*] - [X^*]_\infty\}$ vs. t plot and represents over 7 half-lives of the exchange reaction. The rate constants reported in Table II were generally determined graphically using eq 3 or 4. In those cases where standard least-squares treatment of data was also done, the calculated rate constants were normally within ±0.2% and eq 3, not unexpectedly, gave the smaller standard deviation.

Details of the procedure, electrode preparation, electrolysis cell design, and current source are well presented by Beronius.[11] Results are summarized in Table II. (See paragraph at end of paper regarding supplementary material.)

Control Experiments. To establish that the elimination of hydrogen bromide is much slower than the racemization–exchange reaction, the disappearance of 1-phenylbromoethane (7×10^{-2} *M*) in acetone 0.00, 0.0005, and 0.01 *M* in lithium bromide was followed at 303.15 K by vapor phase chromatography (all-glass system, 4-ft Ucon HB 1500 column, FID, 100°C). In 24 hr there was no detectable change in the concentration nor did any peaks other than acetone and the alkyl halide appear in the chromatograms. The first order or pseudo-first-order rate constants for elimination are considerably less than 1×10^{-9} sec^{-1} under these conditions.[17]

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Registry No.—(±)-1-phenylbromoethane, 38661-81-3; (+)-1-phenylbromoethane, 1459-14-9; (−)-1-phenylbromoethane, 3756-40-9; lithium bromide, 7550-35-8; lithium radiobromide, 57256-21-0; tetrabutylammonium bromide, 1643-19-2.

Supplementary Material Available. Typical data for a racemization and a bromide–radiobromide exchange (1-phenylbromoethane at 303.15 K and [LiBr] = 0.0002000 *M* in acetone) (4 pages). Ordering information is given on any current masthead page.

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Bimolecular Homolytic Substitution at Carbon. A Stereochemical Investigation[1]

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Photochlorination of 1,1-dichlorocyclopropane (1) at 0–5°C in carbon tetrachloride yields 1,1,1,3-tetrachloropropane (2) and 1,1,1,3,3-pentachloropropane (3) as major products, with lesser amounts of 1,1,1,2,3-pentachloropropane (4). Photobromination of 1 yields 1,3-dibromo-1,1-dichloropropane (5) as the only product. Both the chlorination and bromination were shown to be radical processes, accelerated by benzoyl peroxide and azobisisobutyronitrile and inhibited by benzoquinone or darkness. The stereochemistry of the ring opening of 1 was determined from a ^1H NMR analysis of the 1,1,1,3-tetrahalopropane-*2,3*-d_2 isomers produced upon photochlorination and photobromination of 1,1-dichloro-2,3-*trans*-dideuteriocyclopropane (7) and its cis isomer 8. In each case, 7 yielded >96% erythro isomer, and 8 >96% threo isomer. The results clearly demonstrate that attack of both chlorine and bromine atoms on the cyclopropane ring, occurs with essentially complete inversion of configuration. The proposed mechanism involves ring opening via an S_N2-like transition state; attack of the halogen atom is postulated to occur at a minor lobe of the C_1–C_2 hybrid orbital, with concomitant cleavage of the C_1–C_2 bond. Evidence favoring the proposed mechanism over one proceeding via a bridged intermediate or transition state is presented.

Bimolecular homolytic substitution (S_H2) reactions represent one of the most common reaction pathways available to free radicals.[3] Examples of S_H2 displacements at multivalent atoms are well documented, and have been recently reviewed.[4] Unfortunately, few studies have examined the particular case of an S_H2 displacement at saturated carbon, leaving the mechanism and stereochemistry the subject of speculation.

Theoretical and experimental approaches to this problem[5–15] have not predicted a favored stereochemical path. A simple Hückel MO approach predicted that the reaction might have a low degree of stereospecificity.[6] Initial experimental attempts to detect an S_H2 displacement on carbon by iodine atoms, by observing racemization of optically active *sec*-butyl iodide in either liquid or vapor phase, were unsuccessful.[7,8] Displacement occurred instead on iodine,[9,10] yielding the *sec*-butyl radical and molecular iodine which on recombination gave racemic products. A similar result has recently been reported for methyl iodide,[11] as well as for bromine exchange in bromotrichloromethane.[12] Several attempts to detect an intramolecular S_H2 (S_Hi) reaction have also been unsuccessful,[13,14] although Kaplan[15] has proposed an S_Hi reaction to explain the formation of cyclopropane and cyclopentane from decomposition of 1,3-diiodopropane and 1,5-diiodopentane.

It has become increasingly apparent that the only unambiguous examples of S_H2 displacements on carbon are radical induced cleavages of the strained carbon–carbon bonds of cyclopropanes. Examples of cyclopropane ring openings under free-radical chlorination,[16] bromination,[17] and iodination[18] are well known. Ring opening of perfluorocyclobutane by fluorine atoms has recently been reported.[19]

The stereochemistry of the radical induced cyclopropane ring opening would be of interest since both nucleophilic[20] and electrophilic[21] ring openings have been studied in some detail. Only a few studies, however, have examined the stereochemistry of the radical induced ring opening, and all have been subject to varying degrees of steric and electronic bias. Applequist and Searle demonstrated that radical attack with inversion is possible. Bromination of 9,10-dehydrodianthracene occurs with inversion at both centers.[22] Attack with retention, however, is sterically restricted. Chlorination of nortricyclene gives *exo,exo*-2,6-dichloronorborane,[23] presumed to arise by initial attack with inversion followed by exo chain transfer. Reaction of bromotrichloromethane with dibenzotricyclo[3.3.0.$0^{2,8}$]-3,6-octadiene occurs with inversion of configuration by the trichloromethyl radical.[24] More recently, Shea and Skell[25] have shown that photobromination of 2,4-dehydroadamantane occurs with inversion at one center and randomly at the other, yielding a mixture of (a,e)- and (e,e)-2,4-dibromoadamantane. In all of the above examples the cyclopropane ring is part of a structurally more complex polycyclic system, and thus may not be stereochemically indicative of a monocyclic system.

We have previously reported[1] the first example where the stereochemistry of the ring opening of a monocyclic cyclopropane was determined; reaction of chlorine atoms with 1,1-dichlorocyclopropane (1) proceeds with >96% inversion of configuration. Our complete results on the photochlorination and photobromination of 1 are presented herein. As our work in this area was being completed, Maynes and Applequist[26] described the ring opening of *cis*- and *trans*-1,2,3-trimethylcyclopropane upon photobromination, the only other monocyclic systems examined to date. Photobromination of the cis isomer gave equal amounts of (*S*)-*meso*- and *dl*-3-methyl-2,4-dibromopentane, while the trans isomer gave the (*R*)-meso, (*S*)-meso, and *dl* products. The results demonstrate that attack at one carbon occurs with inversion of configuration, while bromination at the second carbon occurs nonstereospecifically.