the two chlorostyrene products are formed. The photolysis of 1 in pyridine produces a black solution and a tarlike precipitate after only a few hours of photolysis. In each case TLC of the photolyzed mixtures demonstrates that there is no significant amount of unreacted diazirine present. ¹H NMR spectroscopy of the diazirine prior to photolysis demonstrates the absence of the chlorostyrenes in the starting material.

Low-Temperature IR Spectroscopy. A 2.4 M solution of benzylchlorodiazirine was prepared in 3-methylpentane. The solution was loaded into a CaF_2 low-temperature IR sample cell with a path length of 1 mm and cooled to -175 °C in an Aries low-temperature cell holder. Upon cooling, the solution formed a transparent glass. In the IR spectrophotometer (Perkin-Elmer 1710 FTIR) a background spectrum of the solution prior to photolysis was recorded and saved. The glass was photolyzed with a 150-W Xe arc lamp fitted with a 350-nm filter for varying time intervals. After photolysis, the infrared spectrum exhibits a particularly strong new absorption band centered at approximately 2040 $\rm cm^{-1}.$

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Registry No. 1, 88211-05-6; **3**, 71706-88-2; **3** carbene, 88211-07-8; **4**, 4222-21-3; **4** ylide, 122567-46-8; **4** carbene, 31304-51-5; **5**, 35496-73-2; **5** ylide, 139759-66-3; **5** carbene, 139759-68-5; **6**, 29667-77-4; **6** ylide, 139759-67-4; **6** carbene, 69096-58-8; **7**, 29648-80-4; **7** ylide, 139759-69-6; **7** carbene, 69096-59-9; **9**, 4222-24-6; **9** ylide, 123027-57-6; **9** carbene, 68735-14-8; H₃COD, 1455-13-6; TME, 563-79-1; *E*-BCS, 4110-77-4; *Z*-BCS, 4604-28-8; pyridine, 110-86-1.

Photochemistry of Polyhaloarenes. 12. The Photochemistry of Pentachlorobenzene in Micellar Media¹

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The dependence of the reciprocal of the quantum yield for the photohydrodechlorination of pentachlorobenzene (1) in aqueous 0.100 M hexadecyltrimethylammonium bromide (CTAB) solution upon the reciprocal of the microconcentration of 1 and upon the reciprocal of the probability for excited state 1 reacting with ground-state 1 provides a linear correlation at high microconcentrations of 1. The regiochemistry of the photohydrodechlorination process in CTAB favors formation of 1,2,4,5-tetrachlorobenzene to a significantly smaller extent than is observed in the analogous process in acetonitrile solution in the presence of triethylamine. The bromotetrachlorobenzene byproduct is formed in the photohysis in the following average composition: 1-bromo-2,3,4,5-tetrachloro- (5): 2-bromo-1,3,4,5-tetrachloro- (6): 3-bromo-1,2,4,5-tetrachlorobenzene (7) = 9.7:66.7:23.3. In a trapping experiment carried out during an irradiation of 1 in CH_3CN/H_2O (8:2) in the presence of excess KBr at 254 nm, bromotetrachlorobenzenes (5:6:7) were formed in a ratio of 11.3:66.8:21.9. These experiments are rationalized by proposing that product in these micellar photohydrodechlorination reactions is formed by fission of triplet-state 1 and a competing process which involves conversion of triplet-state 1 to triplet excimer which then undergoes fragmentation.

In recent studies carried out in this laboratory on the photochemistry of polyhaloarenes, attention has been focused on the mechanisms of phototransformations in homogeneous organic solvents,² with the exception of an investigation where micellar media were used to separate the radical cation near the micellar surface (Stern layer) from the radical anion in the interior; the radical cation and anion resulting from electron transfer from the electron donor on the surface to the polyhaloarene in the interior.³ It appeared to us that additional efforts devoted to elucidation of the mechanisms of phototransformation of polyhaloarenes in micellar media were of considerable interest, since photodecomposition in the environment may occur in a micellar environment and since micellar media appear to offer considerable potential in the design of toxic waste disposal systems.

Scheme I k_{sd} $arcl \xrightarrow{hv} arcl^{*1} \xrightarrow{k_1} products$ k_{isc} k_{td} k_{rcl}^{*3} k_{r} k_{p} $[arcl^{\cdot\delta^{-}} arcl^{\cdot\delta+1}]$

Photolysis of pentachlorobenzene (1) in acetonitrile at 254 nm at low conversions generates the three tetrachlorobenzene isomers (2, 3, and 4). Our recent analysis of the intersystem crossing yield and the quantum yield dependence upon substrate concentration, concentration of sensitizer and quencher, and intensity of light is consistent with three pathways to product: fission of singlet (k_1) , fission of triplet (k_T) , and fragmentation via the triplet excimer (k_p) (Scheme I). The major pathways to product

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are fission of the triplet and fragmentation via the excimer, as singlet fragmentation is responsible for only 2-6% of the product composition. Are these same pathways operative in micellar media? One would anticipate that concentration of the substrate molecules within micelles would enhance excimer formation, assuming that differences in polarity are small or unimportant relative to our reference solvent, acetonitrile.

Results and Discussion

Our initial experimental approach focused on the dependence of the quantum yield for photohydrodechlorination of pentachlorobenzene on the concentration of pentachlorobenzene within the micelle (the microconcentration) in a micellar solution of hexadecyltrimethylammonium bromide (CTAB).⁴ Pentachlorobenzene (1) was irradiated in 0.100 M CTAB aqueous solution at 254 nm for 2 min. The major dechlorinated products were the tetrachlorobenzenes (2-4) with an accompanying trace of trichlorobenzenes. Bromotetrachlorobenzenes were observed as byproducts. The quantum yield dependence upon microconcentration and the resulting regiochemistry of hydrodechlorination are summarized in Table I. Building on our results in homogeneous solution, the mechanism for photohydrodehalogenation is represented in Scheme II. Since very little direct formation of product by fission of singlet state 1 was observed in homogeneous solution, and since in the present case, in addition to the internal heavy atom effect of five chlorines there is the external heavy atom effect of the bromide ions in the Stern layer, it was assumed that fission of singlet did not contribute to product formation. Wolff has reported,8 for example, that the triplet quentum yield of several aromatic compounds was increased greatly when the surfactant was changed from CTAC (hexadecyltrimethylammonium chloride) to CTAB. Thus, assuming ϕ_{isc} is 1.00, the steady-state assumption for the mechanism illustrated in Scheme II leads to eq 1 for the concentration region where $k_2(1)F \gg k_{\rm s}.$

$$\frac{1}{\phi} = \frac{1}{F} + \frac{k_{\rm td}}{Fk_2(1)} \qquad F = \frac{k_{\rm p}}{k_{\rm p} + k_{\rm e}} \tag{1}$$

A plot of $1/\phi$ vs $1/C_m$ is provided in Figure 1. The linear correlation of $1/\phi$ with $1/C_m$ is excellent (r = 0.995) at high concentrations of pentachlorobenzene. However, as C_m decreases and $1/C_m$ increases, the plot begins to flatten out suggesting that there is a pathway to product which is independent of concentration. This is consistent with product formation via the triplet excimer at high

- 39, 531

Table I. Quantum Yields of Formation of Tetrachlorobenzenes and Product Distributions at Various **Concentrations of Pentachlorobenzene**

local concn	quantum vield	percentage ratio of products ^b		
of 1 $(C_m)^a$	$(\phi)^b$	2	3	4
0.0173	0.0781 ± 0.002	49.8 ± 0.4	45.1 ± 0.3	5.2 ± 0.5
0.0230	0.0833 ± 0.003	49.0 ± 0.5	45.0 ± 0.7	6.0 ± 0.2
0.0288	0.0877 ± 0.005	47.7 ± 0.2	46.4 ± 0.4	5.9 ± 0.3
0.0576	0.102 ± 0.003	46.1 ± 0.4	47.5 ± 0.4	6.3 ± 0.1
0.0721	0.113 ± 0.005	45.6 ± 0.6	48.0 ± 0.6	6.4 ± 0.1
0.0794	0.122 ± 0.004	46.2 ± 0.2	47.7 ± 0.1	6.7 ± 0.2
0.0908	0.321 ± 0.007	46.2 ± 0.4	47.1 ± 0.6	6.7 ± 0.2
0.114	0.143 ± 0.003	45.3 ± 0.7	48.1 ± 0.6	6.5 ± 0.2
0.154	0.162 ± 0.006	45.5 ± 0.4	47.7 ± 0.2	6.8 ± 0.4

^a The microscopic concentration was calculated using the partial specific volumes of CH₂ and CH₃ groups in the hydrocarbon chain of CTAB.⁴⁻⁶ ^b The average was calculated from three samples at each concentration which were irradiated independently with azoxybenzene as an actinometer.⁷



Inverse of the microconcentration of 1

Figure 1. Plot of the inverse of the quantum yield versus the reciprocal of the microconcentration of pentachlorobenzene in CTAB solution.

concentrations and homolytic fission of the triplet at low concentrations.

It may, however, be more accurate to use an approach based upon the statistics of pentachlorobenzene distribution in the CTAB solution rather than one based upon the microconcentration in the micelle.⁹⁻¹³ Poisson statistics are appropriate for micellar systems with the assumption that the probability of a solute molecular entering a micelle is not affected by the presence of solute molecules already

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Figure 2. Plot of the inverse of the quantum yield versus the reciprocal of the total probability of encounters between excitedand ground-state pentachlorobenzene in CTAB solution.

 Table II. Regiochemistry of the Photohydrodechlorination of 1 in Solution

	percentage ratio of products			
medium (concn M)	2	3	4	ref
CH ₃ CN (0.005)	48.4 ± 0.2	39.5 ± 0.2	12.1 ± 0.1	3
$CH_{3}CN$ (0.071)	40.3 ± 0.6	40.3 ± 0.5	19.4 ± 0.8	3
CH ₃ CN/Et ₃ N ^a (0.005)	26.4 ± 0.3	62.5 单 0.3	11.1 🜒 0.9	3

^a0.165 M in triethylamine.

in the micelle. On this basis, the distribution of pentachlorobenzene is given by eq 2 where P_n is the probability

$$P_n = \frac{S^n}{n!} e^{-S} \tag{2}$$

$$P = \sum (n-1)P_n \tag{3}$$

of finding a micelle containing n solute molecules and S is the average number of solute molecules per micelle. The total probability of encounters between excited- and ground-state haloarene is given in eq 3.

The rate of excimer formation should be proportional to the total probability, and thus a plot of the reciprocal of the quantum yield vs 1/P should be linear in the region where excimer formation is dominant. A plot of $1/\phi$ versus 1/P is illustrated in Figure 2, and, as anticipated, a linear plot at high probability is revealed with the plot becoming concave downward as one moves along the x axis to values of low probability. As we have reported earlier, the regiochemistry of the hydrodechlorination does not change as dramatically in favor of the formation of 3 with increasing concentration as one would expect if the mechanism were to change from fission of triplet to fragmentation of a triplet excimer in which the charge transfer is essentially complete. This is based upon comparison of the regiochemistry in the present case with that of the photoreduction of pentachlorobenzene in the presence of triethylamine, which is viewed as proceeding through a solvent separated radical anion-radical cation pair (Table II).

Unexpectedly in the photolysis of pentachlorobenzene in CTAB, bromotetrachlorobenzenes (5, 6, and 7) were formed as byproducts, which were identified by GC-MS



Table III. Distributions of Byproduct Bromotetrachlorobenzene at Three Concentrations of 1

local concn	percentage ratio of products ^a			
of 1 $(C_{\rm m})$	5	6	7	
0.0230	10.0 ± 0.4	66.0 ± 2.8	22.8 ± 2.2	
0.0288	9.9 单 0.4	66.0 ± 0.3	24.2 ± 0.8	
0.0721	9.1 单 0.3	68.1 ± 1.7	22.8 ± 1.7	

^a Average of three runs with standard deviation.





comparison with authentic standards. The composition of the bromotetrachlorobenzene fraction at three different concentrations of 1 is listed in Table III. The byproducts are formed in substantial amount, increasing from 20%to 40% of the total product fraction as the concentration of pentachlorobenzene is increased from lowest to highest concentration.

The bromide ion apparently has trapped the excimer. One might consider homolysis of the C-Cl bond in the triplet, followed by electron transfer from the aryl radical to chlorine, to generate aryl cation which then reacts with bromide ion, using as a model the mechanism put forward to explain the phenol products from the photolysis of 4-chlorobiphenyl in water.¹⁴ However, this mechanism seems unlikely, since the excited chloroarene is in the micellar interior and such a mechanism has not been observed in hydrocarbon solvents. In addition, this suggestion would not be consistent with the fact that the bromotetrachlorobenzene fraction increases with increasing amounts of reactant and thus with an increasing rate of excimer formation. We favor, instead, a mechanism similar to that put forward by Soumillion and Wolf, who reported that photoreduction and photosubstitution occurred simultaneously in the irradiation of chlorobenzene and chloroanisoles in the presence and absence of acetone sensitizer in methyl alcohol.¹⁵ Subsequent to excimer formation, bromide ion reacts with the radical cationic moiety of the excimer to produce a pentadienyl radical species which loses chlorine to form product (Scheme III).

Three additional experiments were run to test this mechanism: (a) a solution of 2.18×10^{-2} M pentachlorobenzene in CH_3CN/H_2O (8:2) was irradiated in the presence of excess KBr at 254 nm for 5 min, a 44.5% yield of bromotetrachlorobenzenes was obtained; (b) in the irradiation of pentachlorobenzene with excess Et₃N and KBr in CH_3CN/H_2O (8:2), only tetrachlorobenzenes were produced, with no evidence of brominated products; (c) no bromotetrachlorobenzenes were formed as a consequence of the irradiation of 1 in CTAB solution in the presence of excess Et₃N. In experiment a the concentration of pentachlorobenzene is in the region where excimer for-mation is dominant.^{2c} The distribution of the three bromotetrachlorobenzene isomers (5:6:7 = 11.3:66.8:21.9%)is remarkably close to that observed in micellar media (Table III) and supports the notion that these two different reactions result in the trapping of the same intermediate: the triplet excimer. In experiment b, exciplex $ArCl^{-}Et_3N^{+}$ is dominant over excimer formation, and in c radical anion ArCl⁻⁻ is formed in the micellar interior, with separation

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from the radical cationic partner Et_3N^{*+} assured by the sphere of positively charged head groups which are interposed. In experiments b and c photochemical hydrodechlorination is achieved without the generation of excimer. It is only in experiment a and in the hydrodechlorination in micellar media without triethylamine that excimer and the accompanying radical cationic moiety are formed, and thus it is only in a that trapping with bromide occurs.

Support for this view of the trapping process can be found in the distribution of the bromotetrachlorobenzene isomers. The ability of chlorine to stabilize the pentadienyl radical can be estimated using the partial rate factors reported by Ito et al. for the phenylation of chlorobenzene $(f_o; f_m; f_p = 3.09:1.01:1.48)$.¹⁶ Using these factors the relative rates for reaction through radical intermediate 8, 9, and 10 in Scheme IV would be 2.09:3.07:1 which compares well with the observed relative rates for formation of bromides 7.6. and 5 (4.8:6.9:1). The 2-bromo product is predominant since it is only by attack at C-2 that an intermediate (9)can be generated that allows radical delocalization onto three carbons which contain chlorine. If trapping of excimer were to proceed by an S_NAr process generating intermediates such as 11, the regiochemistry should be in harmony with that predicted using partial rate factors derived from the research of Chambers et al. (ortho: meta:para = 12.1:4.85:1.00, calculated for ClC_6H_4F in $CH_3O^-/CH_3OH)^{2f,17}$ or Schmidt (ortho:meta:para = 4.20:4.29:1.00, from C_6HCl_5 in CH_3O^- , DMSO/CH₃OH).¹⁸ This mechanistic variation can be ruled out, since following either precedent, 7 is the expected major product rather than 6. Finally, an $S_{RN}1$ process can also be ruled out on a regiochemical basis, since the regiochemistry would be established by fragmentation of a free pentachlorobenzene radical anion which would clearly favor formation of 7 over $6.^3$ This is reinforced by the fact that no bromotetrachlorobenzenes are formed when free pentachlorobenzene radical anion is formed in the presence of bromide ion (experiments b and c above).

The photohydrodehalogenation reaction may very well provide an important basis for the development of an efficient method of toxic waste disposal. There are, however, two hurdles to overcome. In the present case the triplet state of pentachlorobenzene undergoes fission directly to product and is the gateway to excimer formation. Thus, in a system exposed to the air, oxygen would be expected to quench the triplet state and retard the reac-



Figure 3. Plot of the relative amounts of penta-, tetra-, tri-, and dichlorobenzene in CTAB solution versus irradiation time.

tion. Secondly, hydrogen abstraction to complete the reduction process could be derailed, since the O–H bond in water (119 kcal/mol) is too strong to donate hydrogen to an aryl radical, and, consequently, even more toxic dimers may be produced. However, these two problems might be solved quite nicely by carrying out the photohydrodehalogenation in micellar media. In a reasonably dilute micellar environment the odds that a substrate molecule and an oxygen molecule would occupy the same micelle are low. The phosphorescence of halonaphthalenes can be observed in aerated, aqueous CTAB solution at room temperature, for example.¹⁹ Hydrogen abstraction should no longer be a concern, since aryl radical abstraction from a CTAB alkyl tail provides an exothermic route to product (-15 kcal/mol).20

To test these ideas, the photolysis of pentachlorobenzene in a CTAB aqueous micellar solution exposed to air was carried out. A sun lamp was used in the irradiation of 3.91 $\times 10^{-3}$ M pentachlorobenzene in aqueous 0.20 M CTAB solution, and the results are illustrated in Figure 3. Pentachlorobenzene disappears after 24 h, and tetrachlorobenzene is produced rapidly and is then subsequently converted to trichlorobenzene completely within 72 h. Trichlorobenzene is dechlorinated after 48 h and is expected to be converted to dichlorobenzene completely. Dichlorobenzene did not yield monochlorobenzene at all since dichlorobenzene does not absorb in the sun lamp spectral range (Figure 3).

Conclusions

In the photohydrodechlorination of pentachlorobenzene carried out in aqueous micellar CTAB solution, products are formed in a competition between fission of triplet state and conversion of triplet state to excimer followed by fragmentation. The bimolecular pathway to products generates triplet excimer which has a long enough lifetime to be trapped by bromide ion. The orientation of the trapping process suggests that a radical cationic moiety of the triple excimer is the target of the nucleophilic trapping agent. In the present study, a plot of $1/\phi$ versus the reciprocal of the bulk concentration of 1 allows us to calculate that $k_2/k_{td} = 1.89 \times 10^3 \text{ M}^{-1}$ as compared to that in acetonitrile $(k_2/k_{td} = 1.81 \times 10^1 \text{ M}^{-1})$ under similar conditions.^{2c} Thus excimer formation is enhanced at least 100-fold and perhaps more, since k_{td} may be increased in aqueous CTAB solution relative to acetonitrile solution as

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a result of heavy atom catalysis of intersystem crossing. Finally, the photohydrodechlorination reaction of pentachlorobenzene can be carried out successfully in an aerated aqueous micellar solution of CTAB in the sunlight wavelength range, which augers well for use of the photohydrodehalogenation process as a basis for toxic waste disposal systems.

Experimental Section

Materials. Pentachlorobenzene (Aldrich) was recrystallized twice from ethanol. The purity was checked by gas chromatography and was greater than 99.9%. Hexadecyltrimethylammonium bromide (CTAB) (Aldrich) was washed with pentane twice and recrystallized from ethanol. Deionized water was distilled from potassium permanganate.

General Procedure for Photolysis and Analysis, Samples (1.0 mL) were placed in quartz tubes (Ace Glass, $170 \times 15 \text{ mm}$) and degassed twice by using freeze-pump-thaw cycles. The samples were sealed under vacuum using resealable nylon/glass stopper valves. The photolyses of the samples were carried out in a Rayonet merry-go-round reactor (The Southern New England Co.) equipped with eight 2537-Å Rull lamps. The temperature in the reactor was 50 °C and constant under a stream of air. After photolysis of 2 min, the samples were extracted several times with pentane. The efficiency of extraction with pentane was greater than 90%. Dodecane as an internal standard was added to the extracts, and most of the pentane was removed by using a rotary evaporator to get more concentrated reaction mixtures. The photolysis mixtures were analyzed by GLC on a Varian 3300 capillary gas chromatograph equipped with an FID and Varian 4290 integrator. A 30-m \times 0.25-mm DB-225 capillary column (J and W Scientific Inc.) was used. The temperature of the column was held at 60 °C for 5 min and increased to 180 °C at a rate of 5 °C/min. The carrier gas was helium, and the flow rate was 30 mL/min. Azoxybenzene was used as an actinometer according to the procedure of Bunce et al.⁷ A Finnigan 4023 mass spectrometer equipped with a Finnigan 9610 gas chromatograph was

also used to identify the reaction mixtures. Byproduct, bromotetrachlorobenzene, was analyzed by GC-MS using a 15-m × 0.20-mm OV-225 capillary column (temperature programming: 60-150 °C, 5 °C/min, 150-180 °C, 2 °C/min).

Photolysis of Pentachlorobenzene in the Presence of KBr. (a) Pentachlorobenzene $(2.18 \times 10^{-2} \text{ M})$ in CH₃CN/H₂O (8:2) with 0.100 M KBr was degassed and irradiated at 254 nm for 5 min in a quartz tube under the conditions described in the general procedure for photolysis. After photolysis, the reaction mixture was analyzed by GLC: C₆HBrCl₄; 44.5% (5:6:7 = 11.3:66.8:21.9%), $C_6H_2Cl_4$; 55.5% (2:3:4 = 48.4:40.6:11.0%). (b) Pentachlorobenzene $(4.70 \times 10^{-3} \text{ M})$ in CH₃CN/H₂O (8:2) with 0.104 M KBr was degassed and irradiated in the presence of 0.526 M of Et₃N at 254 nm for 5 min. No bromotetrachlorobenzene was observed. Only tetrachlorobenzene was produced (2:3:4 + 25.9:69.5:4.7%). (c) Pentachlorobenzene $(3.91 \times 10^{-3} \text{ M})$ was dissolved in aqueous CTAB solution (0.200 M) with 8.16×10^{-2} M Et₃N and degassed. After irradiation for 30 min at 300 nm, the reaction mixture was extracted with pentane and analyzed by GLC. Only tetrachlorobenzene was observed (2:3:4 = 43.7:43.2:13.0%).

Photolysis of an Aerated Sample of Pentachlorobenzene. Pentachlorobenzene $(3.91 \times 10^{-3} \text{ M})$ was dissolved in 0.200 M aqueous CTAB medium, and 1 mL of the solution was transferred into each Pyrex tube. The Pyrex tube was not sealed and was open to the atmosphere. The temperature of the reaction mixture was kept constant by providing a stream of fresh air. The sample was irradiated with a 275-W Westinghouse sun lamp held at approximately 10 cm from the sample tube. After photolysis for a certain period, the reaction mixture was extracted with pentane and analyzed by GLC. Dodecane was used as an internal standard.

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Registry No. 1, 608-93-5; 2, 634-90-2; 3, 95-94-3; 4, 634-66-2; 5, 1125-52-6; 6, 139606-99-8; 7, 81067-39-2; CTAB, 57-09-0; KBr, 7758-02-3; tetrachlorobenzene, 12408-10-5; trichlorobenzene, 12002-48-1; dichlorobenzene, 25321-22-6.

Synthesis of Bridgehead Fluorides by Fluorodeiodination

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Fluorodeiodination is found to be an attractive procedure for the synthesis of bridgehead fluorides. Thus, treatment of the corresponding iodide with xenon diffuoride in dichloromethane at ambient temperature generally leads to high yields of the fluoride. Evidence suggests the intermediacy of the bridgehead cation in this reaction, and accordingly the substrates which are unfavorably disposed to fluorodeiodination are the bicyclo[n.1.1]alkyl iodides. In this context the isolation of a small quantity of methyl 4-fluorobicyclo[2.1.1]hexane-1-carboxylate (46, R = COOMe) is significant because it represents the first occasion on which the elusive 1-bicyclo[2.1.1]hexyl cation has been trapped. We have also demonstrated that synthesis of the iodides themselves can be accomplished efficiently both by Barton halodecarboxylation and by treatment of the carboxylic acid with lead tetraacetate and iodine.

Introduction

An important feature of our studies into the chemistry of strained bicycloalkanes and polycycloalkanes has been to develop convenient procedures for the synthesis of their bridgehead halide derivatives. Thus, we have shown that Barton halodecarboxylation methodology¹ involving radical decomposition of thiohydroxamic esters in the presence of the appropriate halogen donor represents a broadlybased high-yielding route to bridgehead chlorides and bromides² of the range of systems depicted in Chart I. Synthesis of the corresponding iodides has also been accomplished by *tert*-butyl hypoiodite-mediated iododecarboxylation.³

The analogous conversion of bridgehead acids into the corresponding fluorides has not been described, however.

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⁽²⁾ Della, E. W.; Tsanaktsidis, J. Aust. J. Chem. 1989, 42, 61.
(3) Abeywickrema, R. S.; Della, E. W. J. Org. Chem. 1980, 45, 4226.