Table III. Titration of N-Methyl-p-chlorobenzenesulfonanilide with Sodium Anthracene in DME at 25 °C

Sodium anthracene, mmol	Yield of N-methylaniline,[a] mmol	Amine/electron-donor ratio
0.308	0.129	0.419
0.532	0.222	0.417
0.720	0.331	0.460
0.910	0.364	0.400
		(0.42 ± 0.01)[b]

[a] Each sample contained 1.23 mmol of sulfonamide in 10 mL of DME. [b] Average value of ratio.

0.6 g of ferric chloride in 17 mL of 1.7 M hydrochloric acid. Extraction with benzene, drying, and concentration yielded a brown material which was purified by liquid chromatography on silica gel (dichloromethane eluent). Recrystallization from ethanol yielded 3.3 g (0.012 mol, 50%) of tan crystals, mp 113–114 °C.

Sodium p-bromobenzenesulfinate was prepared from p-bromobenzenesulfonyl chloride after the manner of Whitmore and Hamilton.[24] A 62% yield of white crystals, mp 370 °C dec, was obtained by crystallization from water.

Tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) was prepared by a modification of the procedure reported by Ferguson.[25] To a stirred solution of 100 g of tetra-n-butylammonium iodide in 700 mL of acetone was slowly added a solution of 50 g of ammonium hexafluorophosphate in 175 mL of acetone. The resulting solution was filtered to remove some of the precipitated ammonium iodide, and then ca. 1 L of water was slowly added to precipitate the $TBAPF_6$. The resulting salt was collected on a filter funnel and washed several times with water. It was then redissolved in 250 mL of acetone along with 5 g of ammonium hexafluorophosphate and reprecipitated by the slow addition of ca. 150 mL of water. The material was collected by filtration and then recrystallized from ethanol–water. The white solid was dried under vacuum (0.5 mm) at 100 °C, affording 75 g (72%) of product, which was used without further treatment.

Competition experiments were carried out by dissolving a total of 0.4 mmol of an N-methylsulfonamide and the reference compound 12 in 2 mL of dry THF, which also contained 0.4 mmol of dry sodium perchlorate and ca. 0.02 mmol of n-decane, used as an internal standard. The reaction vial was then sealed with a septum and deoxygenated by alternately evacuating and filling with nitrogen. To the stirred solution, at 25 °C, was added slowly ca. 0.44 mL of 0.18 M sodium anthracene solution. After several minutes a few drops of water were added, and the mixture was analyzed by GC. All results are the average of two or more determinations; reproducibility was at least ±5%.

Titrations of sulfonamides with anion radical solutions were carried out in the manner described previously.[3] The data for a typical titration plot are given in Table III.

Electrochemical experiments were carried out as follows. A solution of 0.2 M $TBAPF_6$ in acetonitrile was prepared immediately before use. Using this solution, an amount of sulfonamide was added to give a concentration of 4×10^{-3} M. All measurements were carried out under a nitrogen atmosphere and are the average of three or more determinations. A reference voltammogram of anthracene was run at the start and finish of each series of measurements to ensure against any drift in potential. A scan rate of 200 mV/s was employed.

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Addition of Halogens to Cyclopropylacetylene

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The halogenation of cyclopropylacetylene (1) with chlorine, bromine, trichloramine (NCl_3), and iodobenzene dichloride (IBD) is reported. Chlorine reacts with 1 primarily by an ionic pathway, while bromine can react by either an ionic or radical methanism. IBD and NCl_3 were found to react only by a radical process. The reactivity of 1 with these halogenating reagents is used to make some statements about the relative energy of the transition states in these reactions.

Chlorine (Cl_2),[1a,c] bromine (Br_2),[1b,c] trichloramine (NCl_3),[1d,2] and iodobenzene dichloride ($C_6H_5ICl_2$) (IBD)[1e,2] are known to react with olefins and dienes by an ionic or radical process under the appropriate reaction conditions. The reactions of these halogenating reagents with acetylenes has not been studied extensively. Bromine reacts with acetylenes by an ionic mechanism in acetic acid as solvent.[4] Nazarov and Bergel'son examined the stereochemistry of the radical addition of bromine to a variety of substituted acetylenes.[5] They found that the cis isomers were favored due to the preference of a trans relationship of the bulky substituents in the intermediate **3a**.[6] Poutsma reported that chlorine reacts only by

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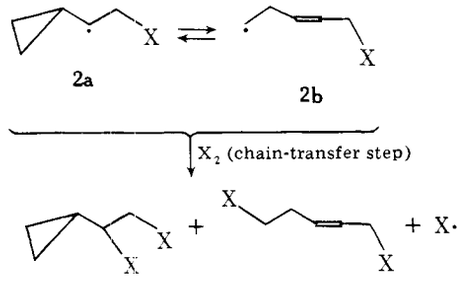
Table I. Halogenation of Cyclopropylacetylene (1)

Entry	Solvent	Mol fraction of 1[a]	Reaction conditions[b]	Halogenating reagent[c]	Percent composition,[d] % 5a or 5b	6a or 6b	7a or 7b	8a or 8b
1	CCl_4	0.02	O_2, dark	Br_2	65	10	4	21
2	CCl_4	0.02	Inhibitor,[e] dark	Br_2	64	12	3	21
3	CH_2Cl_2	0.02	O_2, dark	Br_2	43	19	4	34
4	CCl_4	0.50	N_2, UV	Br_2	44	43	10	3
5	CCl_4	0.05	N_2, UV	Br_2	61	32	7	0
6		Neat	N_2, UV	Cl_2	50	36	6	8
7	CCl_4	0.05	N_2, UV	Cl_2	42	43	3	12
8	CCl_4	0.005	N_2, UV	Cl_2	41	44	5	10
9	c-C_6H_{12}	0.10	N_2, dark	Cl_2[f]	39	48	1	12
10	c-C_6H_{12}	0.02	N_2, dark	Cl_2[f]	35	51	3	11
11	CCl_4	0.02	O_2, dark	Cl_2	37	40	8	15
12	CCl_4	0.05	N_2, UV	IBD	91	2	1	6
13	CCl_4	0.005	N_2, UV	IBD	85	2	3	10
14	CCl_4	0.05	Inhibitor,[e] dark	IBD	*g*	*g*	*g*	*g*
15		Neat	N_2, UV	NCl_3	72	14	5	9
16	CCl_4	0.05	N_2, UV	NCl_3	73	14	4	9
17	CCl_4	0.005	N_2, UV	NCl_3	69	19	8	4
18	CCl_4	0.05	Inhibitor,[e] dark	NCl_3	*g*	*g*	*g*	*g*

[a] Mole fraction of 1 in solvent before the addition of halogenating reagent. [b] The temperature of the reaction mixture was −10 to −5 °C, except for IBD, which was done at 25 °C. The UV light was from a 275-W General Electric sunlamp. [c] Bromine was added neat; chlorine and NCl_3 were added in a CCl_4 or CH_2Cl_2 solutions of known molarity; IBD was added as a solid. [d] Product compositions were determined by VPC analysis on at least two separate runs. [e] The organic inhibitor was 1.0 M 2,6-di-*tert*-butyl-4-methylphenol. [f] Yields of 9.0 and 0.5% of chlorocyclohexane were obtained at 0.10 and 0.02 mol fractions, respectively. Control experiments showed that chlorocyclohexane was not formed by direct chlorination of the solvent. [g] Did not react.

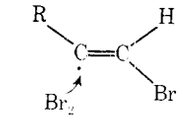
a radical mechanism with 1-butyne to give *trans*-1,2-dichloro-1-butene as the major product[3] (85–90%).

In a recent study of ours[2] on the reaction of various halogenating reagents with vinylcyclopropanes, we reported that 2-cyclopropylpropene reacts with chlorine, bromine, and trichloramine only by an ionic process, whereas IBD reacts primarily by a radical process. Apparently these reagents prefer to react by an ionic process because a very stable cyclopropylcarbinyl cation intermediate can be formed. The

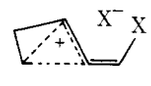


radical process was indicated by an increase in the ring-opened products when the concentration of the radical addend was decreased. This dilution effect was observed because the equilibrium between the classical cyclopropylcarbinyl (**2a**) and homoallyl (**2b**) intermediates was competitive with the chain-transfer step.

Ionic additions to cyclopropylacetylene (**1**) would give a vinylcyclopropylcarbinyl cation intermediate (**4**). This ion should be nonclassical since a nonclassical vinylcyclopropylcarbinyl cation has been reported in solvolysis reactions of 1-cyclopropyl-1-iodoethylene[7a] and similar substrates.[7b] As far as we can determine, the cation intermediate (**4**) has not been formed by the addition of electrophiles to cyclopropylacetylene. Also, we were unable to find a report in the literature of a vinyl radical α to a cyclopropane ring (**3b**).



3a, R = alkyl
b, R = cyclopropyl



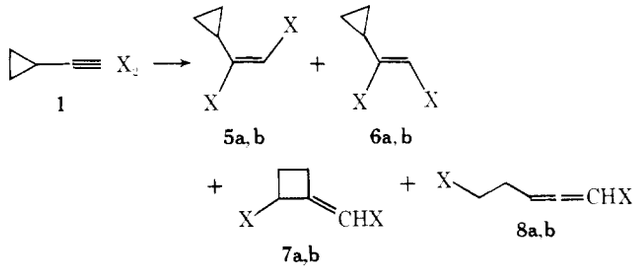
4, X = Br, Cl

In this paper we investigated the halogenation of cyclopropylacetylene (**1**) with Cl_2, Br_2, NCl_3, and IBD.[8] Our purpose was to (1) identify the products obtained from the addition of electrophiles to **1**, and (2) to determine whether these reagents react by an ionic and/or a radical process. We felt that a comparison of these data with that reported earlier for vinylcyclopropanes[2] might allow us to make a statement about the relative energy of the transition states derived from vinylcyclopropanes and cyclopropylacetylene with these reagents.

Results and Discussion

Bromination of **1** under ionic conditions gives 1,2 addition (**5a** and **6a**) and ring-opened products (**7a** and **8a**). The data in Table I show that the 1,2 products are favored by ca. 60–75% (entries 1–3).[9] Addition of bromine to **1** under radical conditions (entries 4 and 5) gives less ring-opened products than bromination under ionic conditions.[10] The increase in *cis*-dibromide **6a** relative to *trans*-dibromide **5a** is typical of radical brominations of acetylenes[5] and is evidence for a radical intermediate in this reaction (compare entries 4 and 5 with 1–3). Molecular chlorine appears to react with **1** predominately by an ionic process since oxygen[11] does not inhibit the reaction or change the product composition significantly (compare entry 11 to 7 and 8).[9,12]

We propose that the chlorinations of **1** with IBD (entries



a, X = Br; b, X = Cl

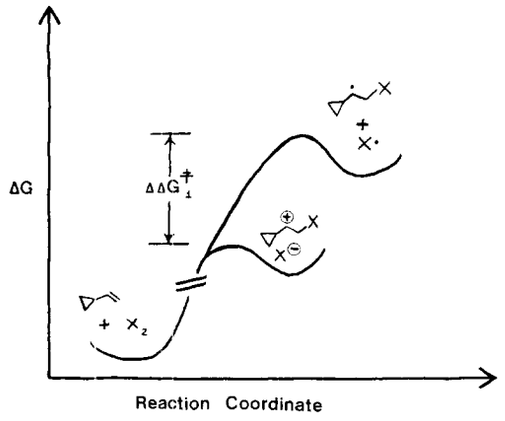


Figure 1. ΔG vs. reaction coordinates for the formation of a cyclopropylcarbinyl radical and cation. $\Delta\Delta G^{\ddagger}_1$ is the energy difference.

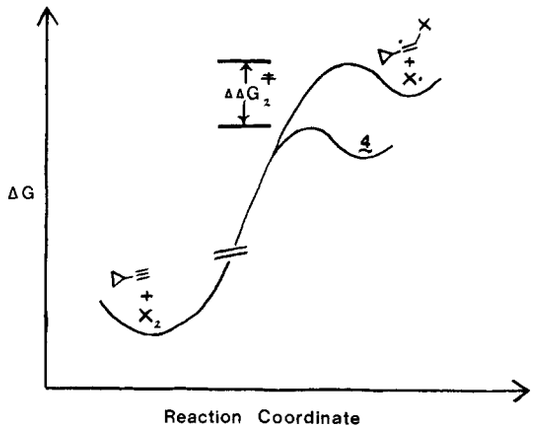
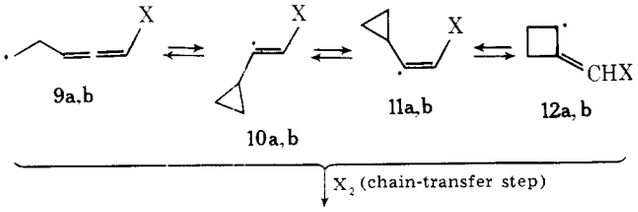


Figure 2. ΔG vs. reaction coordinates for the formation of a vinylcyclopropylcarbinyl radical and cation. $\Delta\Delta G^{\ddagger}_2$ is the energy difference.

12–14) and NCl_3 (entries 15–18) occur by a radical pathway since there is no reaction when an inhibitor is added to the reaction mixture.[13] The smaller amount of *cis*-dichloride **6b** with NCl_3 and IBD compared to *cis*-dibromide **6a** under radical conditions (compare entires 12–18 with 4 and 5) is probably due to a larger steric effect in **10b** than **11b** when these intermediates react in the chain-transfer step.[14]

There is no significant dilution effect when Br_2, NCl_3, or IBD is added to cyclopropylacetylene (**1**) like that observed for the addition of radical halogenating reagents to vinylcyclopropanes.[2] Possibly equilibration of the radical intermediates derived from **1** is faster than the chain-transfer step. Thus, product ratios from these radical reactions are a function of the reactivity of each intermediate (**9a,b–12a,b**) and



5a,b + 6a,b + 7a,b + 8a,b + X·

a, X = Br; b, X = Cl

not the equilibrium concentration as we observed for the intermediates from vinylcyclopropanes.[2]

Trichloramine and iodobenzene dichloride readily react by a radical pathway with **1**, while molecular bromine can react by an ionic or radical mechanism under the appropriate reaction conditions. Our previous work showed that only IBD could be forced to react with a vinylcyclopropane by a radical process.[2] This comparison shows that the energy difference between the formation of a vinylcyclopropylcarbinyl radical and cation ($\Delta\Delta G^{\ddagger}_2$, see Figure 2) is not as large as the energy difference between the formation of a cyclopropylcarbinyl radical and cation ($\Delta\Delta G^{\ddagger}_1$, see Figure 1). Conceivably, $\Delta\Delta G^{\ddagger}_1$ is greater than $\Delta\Delta G^{\ddagger}_2$ due to the unusual stability of a nonclassical cyclopropylcarbinyl cation intermediate.

Experimental Section

General. Cyclopropylacetylene (**1**) was prepared from the dibromide of vinylcyclopropane as reported by Slobodin.[15] Vinylcyclopropane was prepared from the tosylhydrazone of methylcyclopropyl ketone.[16] Trichloroamine[17] and iodobenzene dichloride[18] were prepared as described in the literature. All other reagents and solvents were obtained commercially. Ionic conditions were low mole fractions of olefin, the absence of light, and added inhibitor.[11] Radical conditions were high mole fractions of olefin, the removal of oxygen by nitrogen gas, and ultraviolet light. The light was from a 275-W General Electric lamp. When the reaction was complete, the mixture was concentrated to about 0.3 mL at 25 °C on a rotary evaporator. The crude product mixture was transferred to an NMR tube, and 20–30 μL of a 1.0 M solution of benzene in carbon tetrachloride was added as a standard. Reaction yields were determined by NMR integration. Product ratios were determined by VPC analysis with a Hewlett-Packard 5730 flame ionization chromatograph on a 10 ft × 0.25 in stainless steel column of 5% SE-30 on 80–100 Chromosorb W.[19] Collection of products by VPC was accomplished with a Varian aerograph on a similar column except 12 ft × 0.25 in. NMR spectra were obtained on a Varian T-60A spectrometer.

Reaction of Bromine with 1. To 66 mg (1.0 mmol) of **1** in a weighted amount of solvent so as to obtain the mole fraction listed in Table I at −10 to −5 °C was added 100 mg of neat bromine. The yield by NMR analysis was ca. 50 and 80% under radical and ionic conditions, respectively. Product ratios by VPC are reported in Table I. The products were collected by preparative VPC and had the following retention times on the analytical column: $t_R^{76°C}$ = 16, 21, 24, and 35 min for **5a, 6a, 7a,** and **8a,** respectively. The products had the following NMR spectra: **5a** (CCl_4), δ 0.92 (m, 4 H), 2.05 (m, 1 H), 6.43 (s, 1 H); **6a** (CCl_4), δ 0.75 (m, 4 H), 2.63 (m, 1 H), 6.65 (d, J = 1.0 Hz, 1 H); **7a** (CCl_4), δ 2.37–3.07 (m, 4 H), 4.87 (m, 1 H), 6.08 (m, 1 H); **8a** (CCl_4), δ 2.72 (m with apparent q of d, J = 6.0, 2.5 Hz, 2 H), 3.37 (t, J = 6.0 Hz, 2 H), 5.37 (apparent q, J = 6.0 Hz, 1 H), 5.95 (m, 1 H).

Reaction of Chlorine with 1. To 66 mg (1.0 mmol) of **1** in a weighed amount of solvent (Table I) at −10 to −5 °C was added a 1.8-mL solution of 0.39 M chlorine in carbon tetrachloride. The yields determined by NMR analysis varied from 50 to 80%. Product ratios were determined by VPC on the analytical column with the following retention times: $t_R^{52°C}$ = 8.5, 11.5, 12, and 18 min for **5b, 6b, 7b,** and **8b,** respectively. The products gave the following NMR spectra: **5b** (CCl_4), δ 0.92 (m, 4 H), 2.55 (m, 1 H), 6.18 (s, 1 H); **6b** (CCl_4), δ 0.80 (m, 4 H), 2.2–2.8 (m, 1 H), 6.17 (d, J = 1.0 Hz, 1 H); **7b** (CCl_4), δ 2.1–2.9 (m, 4 H), 4.8 (m, 1 H), 6.20 (m, 1 H); **8b,** δ 2.62 (m with apparent q of d, J = 6.0, 2.5 Hz, 2 H), 3.60 (t, J = 6.0 Hz, 2 H), 5.70 (apparent q, J = 6.0 Hz, 1 H), 6.10 (m, 1 H).

Small amounts of chlorocyclohexane (0.5 and 9.0% at 0.02 and 0.10 mol fractions, respectively) were obtained when the chlorination was carried out in cyclohexane as solvent. Control experiments showed that molecular chlorine does not chlorinate cyclohexane under the conditions of this reaction (under nitrogen and the absence of light).

Reaction of Trichloramine with 1. The reaction was carried out as described above for the chlorination of **1**. Trichloramine[17] was added as a 0.60-M solution in carbon tetrachloride. The reaction mixture was stirred for 10 min at −10 to −5 °C and then concentrated and analyzed as described above. Analysis by NMR showed yields of about 60%. The product ratios are listed in Table I.

Reaction of Iodobenzene Dichloride with 1. To 66 mg (1.0 mmol) of **1** in a weighed amount of carbon tetrachloride (Table I) at 25 °C with stirring was added 190 mg (0.69 mmol) of IBD. The reaction mixture was stirred for 15 min and then concentrated and analyzed as described above. Product ratios are listed in Table I.

Acknowledgment. Support for this work was provided by Research Associates of Point Loma College.

Registry No.—**1,** 6746-94-7; **5a,** 64871-18-7; **5b,** 64871-19-8; **6a,** 64871-20-1; **6b,** 64871-21-2; **7a,** 64871-22-3; **7b,** 64871-23-4; **8a,**

64871-24-5; **8b**, 64871-25-6; Br_2, 7726-95-6; Cl_2, 7782-50-5; IBD, 932-72-9; NCl_3, 10025-85-1.

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(6) The radical addition of trichlorosilane, chloroform, and thioacetic acid to terminal acetylenes gives predominantly the cis product. For thioacetic acid, see J. A. Kampmeir and G. Chen, *J. Am. Chem. Soc.*, **87**, 2608 (1965); for chloroform, see R. M. Kochik and J. A. Kampmeir, *ibid.*, **90**, 6733 (1968); for trichlorosilane, see R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Sivisher, *ibid.*, **83**, 4385 (1961), and R. A. Benkeser and R. A. Kichner, *ibid.*, **80**, 5298 (1958).

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(8) Our investigation of the halogenation of vinylcyclopropane (ref 2) included a study of methyl hypochlorite. We were unable to isolate any addition products or a propargyl chloride product when cyclopropylacetylene was treated with methyl hypochlorite in a nonpolar solvent.

(9) Cyclobutyl and allenic products are also formed in the solvolysis of 1-cyclopropyl-1-iodoethylene in acetic acid at 25 °C. Cyclopropyl products are also the major components (97%) of the solvolysis reaction (see ref 7a).

(10) Products derived from **11a,b** are interesting since the saturated intermediates (**2a,b**) do not rearrange to the the cyclobutyl intermediate (see ref 2).

(11) Oxygen is known to be a very effective inhibitor of the radical reaction with molecular chlorine (see ref 1a).

(12) There is a minor radical component participating in this reaction since small amounts of chlorocyclohexane were obtained when cyclohexane was used as the solvent under reaction conditions which do not chlorinate cyclohexane (see the Experimental Section).

(13) The observation that 2,6-di-*tert*-butyl-4-methylphenol inhibits the reaction of trichloramine with **1** is curious since Kovacic[1d] was unable to inhibit the radical reaction of trichloramine with alkenes. It appears that the chain-transfer step is slower with alkynes than with alkenes. The discussion above on the dilution study also gives support for a slow chain-transfer step with **1**.

(14) A similar steric effect for IBD and NCl_3 was observed when cyclopentadiene was treated with these radical halogenating reagents: see V. L. Heasley, G. E. Heasley, K. D. Rold, and D. B. McKee, *J. Org. Chem.*, **41**, 1287 (1976).

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(20) Previous work from these laboratories has shown that flame ionization detector response values are similar from structural isomers if their retention times do not differ greatly: see G. E. Heasley, V. L. Heasley, S. L. Manatt, H. A. Day, R. V. Hodges, P. A. Kroon, D. A. Redfield, T. L. Rold, and D. E. Williamson, *J. Org. Chem.*, **38**, 4109 (1973).

Free-Radical Reactions of Pentafluorobenzenesulfenyl Chloride with Alkanes and Alkylbenzenes

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Light-induced, free-radical reactions of pentafluorobenzenesulfenyl chloride with methylbenzenes give very high yields of pentafluorophenyl benzyl sulfides. With other alkylbenzenes which contain benzylic hydrogens, high yields of benzylic sulfides are also obtained along with small quantities of nonbenzylic pentafluorophenyl aralkyl sulfides. In all of these reactions, minor amounts of chloroalkylbenzenes and bis(pentafluorophenyl) disulfide are also obtained. In reactions with several alkanes, the major products are usually pentafluorophenyl alkyl sulfides, but substantial yields of chloroalkanes and bis(pentafluorophenyl) disulfide are also obtained.

In the past few years, sporadic reports of free-radical reactions of sulfenyl halides with hydrocarbons have been published. The studies to date, which primarily involve reactions of highly halogenated alkanesulfenyl chlorides[2,3] and pentachlorobenzenesulfenyl chloride,[4,5] show that the course of these reactions is highly sensitive to the nature of the organic group of the sulfenyl chloride. For example, the reactions of CF_3SCl[2] and Cl_3CSCl[3] with alkanes contrast sharply: only chloroalkanes are derived from the alkane in the Cl_3CSCl reactions, while in the CF_3SCl reactions trifluoromethyl alkyl sulfides are often the major products. In the few reactions of pentachlorobenzenesulfenyl chloride examined, sulfides were also major products.[4,5] This paper summarizes a study of the free-radical substitution reactions of pentafluorobenzenesulfenyl chloride (**1**) with alkylbenzenes and alkanes.

Results

The results of the experiments are summarized below and are tabulated in Table I. Authentic samples of several of the sulfide products were prepared by the UV-initiated addition of pentafluorobenzenethiol to appropriate olefins (Table II). Characterization of new compounds is given in Tables IV and V.[6]

Alkylbenzenes. The light-induced reactions of **1** with excess methylbenzenes, e.g., toluene, *o*-xylene, *p*-chlorotoluene, and mesitylene, are long chain free-radical reactions which give very high yields of pentafluorophenyl benzyl sulfides (**2–5**, Table I) and HCl, along with very low yields of bis(pentafluorophenyl) disulfide (**6**) and α-chlorotoluenes. For example, the reaction with toluene gave pentafluorophenyl benzyl sulfide (**2**) in over 95% yield (eq 1).

$$\underset{\mathbf{1}}{C_6F_5SCl} + CH_3C_6H_5 \xrightarrow{h\nu} \underset{\mathbf{2}}{C_6F_5SCH_2C_6H_5} + HCl + \underset{\mathbf{6}}{(C_6F_5)_2S_2} + ClCH_2C_6H_5 \quad (1)$$

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