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.

References and Notes

(1) (a) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 2161, 2171 (1965); *J. Org. Chem.*, **31**, 4167 (1966); (b) V. L. Heasley and S. K. Taylor, *ibid.*, **34**, 2779 (1969); V. L. Heasley, G. E. Heasley, S. K. Taylor, and C. L. Frye, *ibid.*, **35**, 2967 (1970); (c) D. F. Shellhamer, V. L. Heasley, G. E. Heasley, J. E. Foster, and J. K. Luttrull, *ibid.*, **42**, 2141 (1977); (d) K. W. Field and P. Kovicic, *ibid.*, **36**, 3566 (1971), and references cited therein; V. L. Heasley and G. E. Heasley, unpublished results; (e) D. Tanner and G. Gidley, *J. Org. Chem.*, **33**, 38 (1968); V. L. Heasley, G. E. Heasley, K. D. Rold, and D. B. McKee, *ibid.*, **41**, 1287 (1976).

(2) D. F. Shellhamer, D. B. McKee, and C. T. Leach, *J. Org. Chem.*, **41**, 1972 (1976).

(3) M. L. Poutsma and J. L. Kartch, *Tetrahedron*, **22**, 2167 (1966).

(4) J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970); R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).

(5) I. N. Nazarov and L. D. Bergel'son, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 887, 896 (1960); *Zh. Obshch. Khim.*, **37**, 1540 (1967).

(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).

(7) (a) A. Sherrod and R. G. Bergman, *J. Am. Chem. Soc.*, **93**, 1925 (1971); (b) L. R. Subramanian and M. Hanack, *J. Org. Chem.*, **42**, 174 (1977); *J. Chem. Educ.*, **52**, 80 (1975), and references cited therein.

(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).

(15) Ya. M. Slobodin and I. Z. Egenburg, *Zh. Org. Khim.*, **5**, 1315 (1969).

(16) W. Kirmse, B. G. Bulow, and H. Schepp, *Justus Liebigs Ann. Chem.*, **641**, 41 (1966).

(17) P. Kovacic and S. S. Chudary, "Organic Syntheses", Collect. Vol. 5, Wiley, New York, N.Y., 1973, p 35.

(18) H. J. Lucas and E. R. Kennedy, "Organic Syntheses", Collect. Vol. 3, Wiley, New York, N.Y., 1973, p 482.

(19) Control experiments were performed to show that rearrangement of the products did not occur. Pure compounds were reinjected into the VPC instrument and found to be stable under our analysis conditions. The appearance of the baseline between well-separated peaks of the isomers on our analytical column also ruled out on-column rearrangement. The area/weight response factors for our isomers were similar on the hydrogen flame chromatograph.[20] The value of the cyclobutyl product differed slightly because we could only obtain a small amount of this minor isomer.

(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

J. F. Harris, Jr.

Central Research and Development Department,[1] Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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$_3$SCl[2] and Cl$_3$CSCl[3] with alkanes contrast sharply: only chloroalkanes are derived from the alkane in the Cl$_3$CSCl reactions, while in the CF$_3$SCl 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).

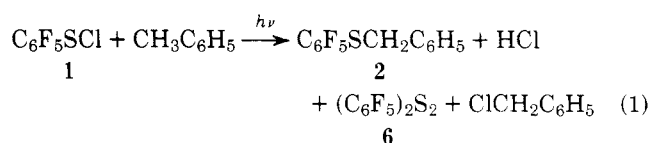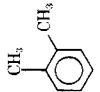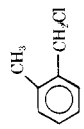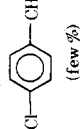$$C_6F_5SCl + CH_3C_6H_5 \xrightarrow{h\nu} C_6F_5SCH_2C_6H_5 + HCl$$

$$\quad \text{1} \qquad\qquad\qquad\qquad\qquad \text{2}$$

$$+ (C_6F_5)_2S_2 + ClCH_2C_6H_5 \quad (1)$$

$$\qquad\qquad \text{6}$$
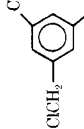
Table I. Photoreactions of C_6F_5SCl (1) with Hydrocarbons
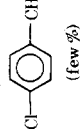
Hydrocarbon	Registry no.	C_6F_5SCl, g, (mol)	Hydrocarbon/C_6F_5SCl	Irradiation time, min	Yield of $(C_6F_5)_2S_2$, %	Sulfide (S) (yield)	Registry no.	Chloride (Cl) (yield)	S/Cl	Other products	Remarks
$C_6H_5CH_3$ 75 mL 65 g 0.705 mol	108-88-3	10.08 (0.0429)	16.4	30	~1	$C_6F_5SCH_2C_6H_5$ 2 (>95%)	33288-16-3	$C_6H_5CH_2Cl$ (trace)	>100:1	2 unknown traces	
(o-xylene, CH_3, CH_3) 100 mL 90 g 0.845 mol	95-47-6	16.31 (0.0695)	12.1	25	3–5	($C_6F_5SCH_2$–, CH_3) 3 (~95%)	65015-48-7	(–CH_3, –CH_2Cl) (trace)	100:1	2 unknown traces	Yield of distilled sulfide 3 = 82%
(p-chlorotoluene, CH_3, Cl) 60 mL 64 g 0.507 mol	106-43-4	4.0 (0.0171)	29.7	73	<10	(Cl–, –$CH_2SC_6F_5$) 4 (>90%)	65015-49-8	(Cl–, –CH_2Cl) (few %)		2 unknown traces	
(mesitylene, CH_3, CH_3, CH_3) 60 mL 52 g 0.431 mol	108-67-8	4.54 (0.0193)	22.3	30	<10	($C_6F_5SCH_2$–, CH_3, CH_3) 5 (>90%)	65015-50-1	(ClCH_2–, CH_3, CH_3) (few %)		Unknown trace	Sulfide 5 crystallized after excess mesitylene was distilled
$C_6H_5CH_2CH_3$ 67 mL 58.1 g 0.547 mol	100-41-4	9.70 (0.0413)	13.2	15	2–4	$C_6F_5SCH(CH_3)C_6H_5$ 7 (94–95%) $C_6F_5SCH_2CH_2C_6H_5$ 8 (~3%)	65015-51-2 65015-52-3	$C_6H_5CHClCH_3$ (1–2%) $C_6H_5CH_2CH$ (trace)	50–100:1	Unknown trace	Yield of distilled sulfides 7 and 8 > 80%
$C_6H_5CH(CH_3)_2$ 50 mL 43.2 g 0.359 mol	98-82-8	7.00 (0.0298)	12.0	17	1–2	$C_6F_5SC(CH_3)_2$-C_6H_5 9 (91%) $C_6F_5SCH_2CH(CH_3)C_6H_5$ 10 (8%)	65015-53-4 65015-54-5	$C_6H_5C(CH_3)_2$-Cl $C_6H_5CH(CH_3)$-CH_2Cl (1–2%)	~50:1	Traces of α-methylstyrene + several unknowns	Sulfide 9 crystallized after excess cumene was distilled
$C_6H_5C(CH_3)_3$ 60 mL 52.0 g 0.388 mol	98-06-6	10.00 (0.0426)	9.1	83	24	$C_6F_5SCH_2C$-$(CH_3)_2C_6H_5$ 11 (76%)	65036-37-5	$C_6H_5C(CH_3)_2$-CH_2Cl (8%)	9.5	Traces of C_6F_5Cl + several unknowns	Distillation yielded fraction boiling at 85–88 °C (0.5 mm) which solidified; recrystallization from CH_3OH gave 11 as needles
$(C_6H_5)_2CH_2$ 97 mL 97.1 g 0.577 mol	101-81-5	10.00 (0.0426)	13.5	161	10–20	C_6F_5SCH-$(C_6H_5)_2$ 12 (~70%)	65015-55-6	$ClCH(C_6H_5)_2$ (10–20%)			The sulfide 12, which crystallized after the excess diphenylmethane was distilled, was isolated in 50% yield
c-C_6H_{12} 75 mL 58.4 g 0.694 mol	110-82-7	9.96 (0.0425)	16.3	40	32.4	c-$C_6H_{11}SC_6F_5$ 13 (67.6%)	56717-64-7	c-$C_6H_{11}Cl$ (15.2%)	4.45		Distillation through a small spinning band still did not cleanly separate 13 from disulfide

Olefin	Registry no.	C6F5SCl, g (mol)	Olefin amount		Irradiation time, min		Products (yield)	Registry no.	Products (yield)		Remarks
n-C4H10	106-97-8	20.00 (0.0852)	75 mL / 60 g / 1.03 mol	12.1	400	38.6	n-C4H9SC6F5 15 (15.9%) / C6F5SCH(CH3)C2H5 16 (45.6%)	33288-22-1	n-C4H9Cl (2.8%) / CH3CHClC2H5 (5.8%)	5.63 / 7.92	Traces of C6F5Cl and two pentafluorophenyl chlorobutyl sulfides
(CH3)3CH	75-28-5	1.00 mL / 1.68 (0.00716) mol	24 mL / 19.2 g / 0.33 mol	46.1	70	40.4	C6F5SCH2CH-(CH3)2 17 (20.2%) / C6F5SC(CH3)3 18 (39.3%)	65015-57-8 / 65015-58-9	ClCH2CH-(CH3)2 (0.4%) / ClC(CH3)3 (6.1%)	47.05 / 6.49	Isobutylene and small quantity of a pentafluorophenyl chlorobutyl sulfide
(CH3)2CH-CH(CH3)2	79-29-8	10.0 (0.0426)	65 mL / 43 g / 0.50 mol	11.7	75	54.5	C6F5SC(CH3)2-CH(CH3)2 19 (45.4%) / C6F5SCH2CH-(CH3)CH-(CH3)2 20 (trace)	65015-59-0 / 65015-60-3	(CH3)2CClCH-(CH3)2 (20%)	2.27	C6F5Cl (trace), detected by MS-GC

a Registry no.: C6F5SCl (1), 27918-31-6.

Table II. Free-Radical Additions of C6F5SH[a] to Olefins: C6F5SH + C=C $\xrightarrow{h\nu}$ C6F5SCCH

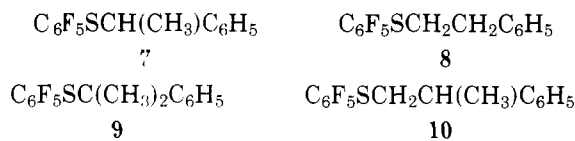| Olefin	Registry no.	C6F5SH, g (mol)	Olefin/ C6F5SH	Irradiation time, min	Products (yield)	Remarks
C6H5CH=CH2	100-42-5	12 mL / 10.91 g / 0.105 mol	10.00 (0.050)	2.1	195	C6F5SCH2CH2C6H5 8 (80%)	
C6H5C(CH3)=CH2	98-83-9	15 mL / 13.7 g / 0.116 mol	10.00 (0.050)	2.32	230	C6F5SCH2CH(CH3)C6H5 10 (80%)	
⬡	110-83-8	35 mL / 28.4 g / 0.343 mol	8.00 (0.040)	8.6	390	c-C6H11SC6F5 13 (60%) + C6F5SSC6F5 (few %)	
CH2=CHCH2CH3	106-98-9	30 mL / 24 g / 0.428 mol	10.00 (0.050)	8.6	320	C6F5SCH2CH2CH2CH3 15 + C6F5SSC6F5	sulfide/disulfide ratio 3:1
CH3CH=CHCH3 (cis)	590-18-1	25 mL / 20 g / 0.357 mol	10.00 (0.050)	7.1	825	C6F5SCH(CH3)CH2CH3 16 + C6F5SSC6F5	sulfide/disulfide ratio 3:1
CH2=C(CH3)2	115-11-7	30 mL / 19.8 g / 0.353 mol	8.00 (0.04)	8.8	293	C6F5SCH2CH(CH3)2 17 (85–90%) + C6F5SSC6F5 (5–7%)	
CH2=C(CH3)CH(CH3)2	563-78-0	20 mL / 13.6 g / 0.16 mol	10.00 (0.05)	3.2	127	C6F5SCH2CH(CH3)CH(CH3)2 20 (>90%) + C6F5SSC6F5 (few %)	

a Registry no.: C6F5SH, 771-62-0.

Table III. Ratio of Pentafluorophenyl Cyclohexyl Sulfide (S) and Chlorocyclohexane (Cl) Formed at Various Conversions in the Photoreaction of 1 with Cyclohexane: Analysis by Gas Chromatography

Sample no.	Time,[a] min	Conversion,[b] %	S/Cl[c]	S/Cl[d]
2	2	31	6.68	5.84
3	5	52	7.08	5.94
4	7.75	83	6.45	5.93
5	11	>95	6.83	6.62
6	16	100	6.97	6.44

[a] Time elapsed after light was turned on. [b] Conversion was estimated from the area of the peak for the product (14) of the dark reaction of excess 1 and p-methylacetophenone. [c] These ratios were determined from peak areas calculated from the product of the peak heights and the widths at half-height. [d] These ratios were determined by weighing the cut-out peaks traced onto thick, translucent paper.

With alkylbenzenes containing hydrogens on carbons both α and β to the benzene ring, both possible sulfides were obtained, with that derived by substitution on the α-carbon predominating. Thus, from ethylbenzene, 7 and 8 in a ratio of 30:1 were the major products. With cumene, again the major products were sulfides 9 and 10 in a ratio of 10:1. Low yields of 6, α- and β-chlorocumene, and α-methylstyrene were also obtained.[7] Both of these were long chain reactions.

$$C_6F_5SCH(CH_3)C_6H_5 \qquad C_6F_5SCH_2CH_2C_6H_5$$
$$7 \qquad\qquad\qquad 8$$
$$C_6F_5SC(CH_3)_2C_6H_5 \qquad C_6F_5SCH_2CH(CH_3)C_6H_5$$
$$9 \qquad\qquad\qquad 10$$

The reactions with tert-butylbenzene, the only case examined of an alkylbenzene with no benzylic hydrogens, and diphenylmethane appeared to be slower than the reactions just discussed. The respective sulfides (11 and 12) were the major products, but much higher yields of 6 and the chlorides were obtained than were seen in the reactions discussed above.
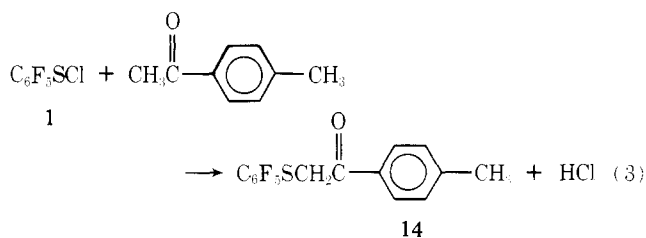
$$C_6F_5SCH_2C(CH_3)_2C_6H_5 \qquad (C_6H_5)_2CHSC_6F_5$$
$$11 \qquad\qquad\qquad 12$$
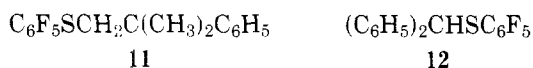
Alkanes. Light-induced reactions of 1 with excess cyclohexane, n-butane, isobutane, and 2,3-dimethylbutane did not appear to be as rapid as the reactions with methylbenzenes. In all cases but one, the highest yield products were pentafluorophenyl alkyl sulfides, but the yields of 6 and chlorohydrocarbons were much higher than in the methylbenzene reactions (Table I). The distributions of products in the cyclohexane, n-butane, and isobutane reactions were similar to those reported previously for the analogous reactions of pentachlorobenzenesulfenyl chloride,[5] except that in the reactions of 1 with n-butane and isobutane, chlorobutyl sulfides were also obtained, and in the isobutane reaction, isobutylene[10] was formed, all in very small yields.

In one experiment, a cyclohexane reaction (eq 2) was sampled periodically to detect any variation in the relative

$$c\text{-}C_6H_{12} + C_6F_5SCl \xrightarrow{h\nu} c\text{-}C_6H_{11}SC_6F_5 + c\text{-}C_6H_{11}Cl$$
$$1 \qquad\qquad\qquad 13$$
$$+ (C_6F_5)_2S_2 + HCl \quad (2)$$

amounts of the sulfide 13 and chlorocyclohexane during the course of the reaction. Each withdrawn aliquot was treated with excess p-methylacetophenone in order to convert unreacted 1 to a material (14) which gave a reproducible gas chromatography (GC) peak (eq 3). The GC analysis showed a small increase in the ratio of 13 to chlorocyclohexane be-

$$C_6F_5SCl + CH_3\overset{O}{\underset{\|}{C}}\!\!-\!\!\bigcirc\!\!-\!\!CH_3$$
$$1$$
$$\rightarrow C_6F_5SCH_2\overset{O}{\underset{\|}{C}}\!\!-\!\!\bigcirc\!\!-\!\!CH_3 + HCl \quad (3)$$
$$14$$

tween 30 and 100% conversion of 1 (Table III). In another cyclohexane experiment in which a 1:1 molar mixture of 1 and 6 in an excess of cyclohexane was irradiated until 1 was consumed, the GC ratio of 13 to chlorocyclohexane at the end of the experiment was 7.38, compared to 6.31 for an analogous experiment with no added 6.

From the reaction with 2,3-dimethylbutane, the main products were pentafluorophenyl 1,1,2-trimethylpropyl sulfide (19), 2-chloro-2,3-dimethylbutane, and 6. A trace amount of the other possible sulfide (20) was also obtained, but none of the corresponding chloroalkane, i.e., 1-chloro-2,3-dimethylbutane, was detected.
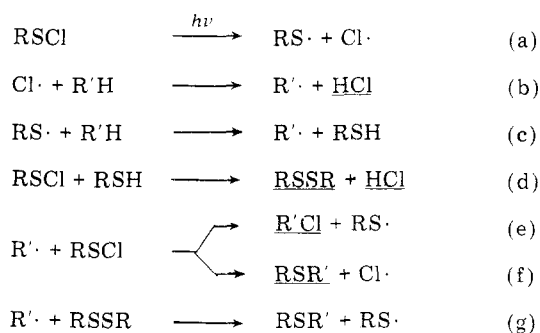
$$C_6F_5SC(CH_3)_2CH(CH_3)_2 \qquad C_6F_5SCH_2CH(CH_3)CH(CH_3)_2$$
$$19 \qquad\qquad\qquad 20$$
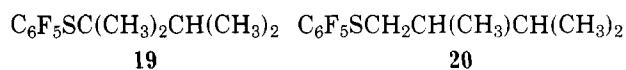
Discussion

In free-radical reactions of S–Cl compounds with hydrocarbons studied to date, the fate of the chain-carrying alkyl radicals has varied from exclusive C–S bond formation, e.g., in the reaction of SCl_2 with cyclohexane,[12] to exclusive C–Cl bond formation in the trichloromethanesulfenyl chloride reactions referred to above.[3] All other cases so far studied, including the reactions of 1, fall between these two extremes, giving both chloride and sulfide from the alkyl radical.

The steps in Scheme I have been proposed as the principal sources of the major products of sulfenyl halide–hydrocarbon free-radical reactions.[2,4,5] There is agreement that step e is the primary source of chlorohydrocarbon, but both steps f and g have been proposed to account for sulfide formation. If step f was the sole pathway for forming sulfide, then the ratio of sulfide to chlorohydrocarbon should remain constant throughout the reaction since both products would derive from a single substrate. It is apparent in the cyclohexane reaction examined in this study that some sulfide is being formed by a process other than step f (presumably step g) since the sulfide/chloride ratio increases somewhat as the reaction goes on (Table III). But since the increase is small, it is concluded that step g does not contribute importantly to sulfide formation. The same conclusion is drawn from the cyclohexane experiment done in the presence of a molar equivalent of 6; the moderately higher sulfide/chloride ratio observed at the end of the reaction suggests relatively small involvement of step g.

Results of a previous study of free-radical reactions of

Scheme I

$$RSCl \xrightarrow{h\nu} RS\cdot + Cl\cdot \qquad (a)$$
$$Cl\cdot + R'H \longrightarrow R'\cdot + \underline{HCl} \qquad (b)$$
$$RS\cdot + R'H \longrightarrow R'\cdot + RSH \qquad (c)$$
$$RSCl + RSH \longrightarrow \underline{RSSR} + \underline{HCl} \qquad (d)$$
$$R'\cdot + RSCl \nearrow \underline{R'Cl} + RS\cdot \qquad (e)$$
$$\qquad\qquad\qquad \searrow \underline{RSR'} + Cl\cdot \qquad (f)$$
$$R'\cdot + RSSR \longrightarrow RSR' + RS\cdot \qquad (g)$$

CF_3SCl with a group of alkanes show that the preference of attack by various alkyl radicals on sulfur vs. chlorine is best ordered on a steric basis, assuming that alkyl radicals intrinsically prefer to attack sulfur, but increasingly settle for attack on the more accessible chlorine as they become more bulky.[2] The same trend is evident in the reactions of 1 with alkyl radicals (Table I), but the shift to preference for chlorine by the more bulky radicals appears to be less pronounced than in the CF_3SCl reactions. The extremely high preference for attack on sulfur by benzylic radicals suggests that factors other than steric, e.g., reactivity of the radical, can be important in determining the pattern of attack by hydrocarbon radicals upon sulfenyl chlorides.

Experimental Section

I. Free-Radical Reactions of 1 with Hydrocarbons. A stirred solution of 1 dissolved in excess hydrocarbon contained in a quartz tube (7 × 1.5 in.) was irradiated under nitrogen with a sunlamp until the characteristic color of 1 was gone and the evolution of gas ceased. The reaction mixture was analyzed quantitatively by gas chromatography, and the principal products were identified by (1) comparison of retention times with materials of known structure, (2) mass spectroscopic examination of peaks in the gas chromatogram, or (3) isolation by distillation followed by elemental and proton NMR analyses. Details of the experiment are tabulated in Table I. Characterization of all new compounds is given in Tables IV and V.[6]

II. Free-Radical Reactions of Pentafluorobenzenethiol with Olefins. A stirred solution of the thiol and olefin contained in a quartz tube (7 × 1.5 in) fitted with a dry ice condenser and a magnetic stirrer was irradiated under nitrogen with a spiral-shaped, low-pressure mercury resonance lamp fitted around the reactor. The adducts were isolated by distillation, and structures were established by ^{1}H NMR spectroscopy. The details of these reactions are tabulated in Table II.

III. Determination of the Ratio of Pentafluorophenyl Cyclohexyl Sulfide (13) to Chlorocyclohexane at Various Conversions in the Photoreaction of 1 with Cyclohexane. A solution of 2.0 mL of 1 and 30 mL of cyclohexane (both freshly distilled) was placed in a small Pyrex flask fitted with a magnetic stirrer, a reflux condenser, and a syringe adapter. The mixture was irradiated with a sunlamp placed 5–6 in from the reactor. Samples (0.5 mL) were withdrawn periodically via syringe. Each sample was placed in a test tube containing 0.2 mL of *p*-methylacetophenone and shaken until colorless. A 5-µL sample was then examined by GC. The results of the measurements are given in Table III.

IV. Reaction of 1 with *p*-Methylacetophenone. A 5-mL amount of 1 was added in small portions to 80 mL of freshly distilled *p*-methylacetophenone with stirring. The color of 1 faded quickly after each addition. GC analysis showed the presence of one product. Distillation through a small Vigreux still gave 8.40 g (70%) of pentafluorophenyl *p*-methylphenacyl sulfide (14), distilling at 116–122 °C (0.20 mm). Elemental analysis and a ^{1}H nmr spectrum data are given in Tables IV and V.[6]

V. Reaction of 1 with Cyclohexane in the Presence of 6. A mixture of 0.2 mL (0.31 g, 0.00132 mol) of 1, 0.53 g (0.00133 mol) of 6, and 3 mL of cyclohexane was irradiated as described above for 21 min. The color of the reaction mixture remained pale yellow during the last 5 min of the irradiation period. The mixture was analyzed by GC, and the ratio of the peak areas corresponding to 13 and chlorocyclohexane was found to be 7.38 (average of two determinations).

For comparison, a mixture of 0.2 mL of 1 and 3 mL of cyclohexane was similarly irradiated for 13 min, after which the mixture was essentially colorless. The peak area ratio of 13 to chlorocyclohexane was found to be 6.31.

VI. Preparation of 1. Compound 1 was prepared by the chlorination of pentafluorobenzenethiol (Peninsular Chem. Research) in carbon tetrachloride as described by Sheppard and Foster.[13]

VII. Gas Chromatography. The GC analyses were done primarily with a 6 ft × 0.25 in column packed with 20% SE-30 on 60–80 mesh WAWDMCS. Temperatures varied from 50 to 200 °C. The helium flow rate was about 100 mL/min.

VIII. Mass Spectroscopy/Gas Chromatography. A Du Pont Model 21-490 mass spectrometer interfaced to a Varian Model 1440 gas chromatograph and a VG 2040 data system was used.

Registry No.—14, 65015-61-4; *p*-methylacetophenone, 122-00-9.

Supplementary Material Available: Tables IV and V of elemental analyses and ^{1}H NMR spectral data for the new pentafluorophenyl alkyl and aralkyl sulfides (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Contribution No. 2451.
(2) J. F. Harris, Jr., *J. Org. Chem.*, **31**, 931 (1966).
(3) H. Kloosterziel, *Recl. Trav. Chim. Pays–Bas*, **82**, 497, 508 (1963).
(4) N. Kharasch and Z. S. Ariyan, *Chem. Ind. (London)*, 929 (1964).
(5) D. D. Tanner, N. Wada, and B. G. Brownlee, *Can. J. Chem.*, **51**, 1870 (1973).
(6) See paragraph at the end of paper about supplementary material.
(7) The α-methylstyrene detected probably arose from the thermally induced loss of HCl from α-chlorocumene during the GC analysis.[8,9]
(8) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142 (1939).
(9) E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1949 (1946).
(10) The isobutylene no doubt arose from disproportionation of the *tert*-butyl radical.[11]
(11) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964).
(12) E. Müller and E. W. Schmidt, *Chem. Ber.*, **96**, 3050 (1963).
(13) W. A. Sheppard and S. S. Foster, *J. Fluorine Chem.*, **2**, 53 (1972).

Peracid Oxidations of Cyclopropenes and Cyclopropenones[1a]

Jack K. Crandall* and Woodrow W. Conover II[1b]

Contribution No. 3045 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401

The reactions of cyclopropenes 1a–c with peracid yield isomeric conjugated ketones 2a–c and 3a,b. These conversions are interpreted in terms of an oxabicyclobutane intermediate. The peracid oxidation of cyclopropenones 11 and 21 were shown to initially produce CO_2 and an acetylene. The latter is converted to other products under the reaction conditions.

Considerable recent effort has been directed toward the synthesis and chemical characterization of novel small-ring heterocyclic systems. 2-Oxabicyclo[1.1.0]butane is the parent of one such class of highly strained heterocycles. Although no authentic example of this elusive structure has yet been described in the literature, species of this type have been considered as reactive intermediates in photochemical isomer-izations of conjugated carbonyl compounds[2] and from peracid oxidations of cyclopropenes.[3–8] In this report, we detail our results concerning potential approaches to oxabicyclobu-tanes.

Concurrently with published studies, we too have explored the peracid oxidation of cyclopropenes. Thus, oxidation of 1,2-diethyl-3-carbethoxycyclopropene (1a) with an excess of