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# Thiyl Radical Abstraction. A Mechanism for the Free Radical Substitution Reactions of Pentachlorobenzenesulfenyl Chloride

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The substitution reactions of pentachlorobenzenesulfenyl chloride with saturated alkanes were found to proceed by a free radical chain mechanism where the pentachlorobenzenethiyl radical is the predominant chain-carrying species. The selectivity of this radical could be determined by the investigation of the photoinitiated reactions of bispentachlorophenyl disulfide with a number of alkanes.

Il a été démontré que les réactions de substitution du chlorure de pentachlorobenzène-sulfényle avec des alcanes saturés se déroulent, selon un mécanisme radicalaire en chaîne où le radical pentachlorobenzène thiyle est l'agent principal de propagation de chaîne. La sélectivité de ce radical peut être déterminée par une étude des réactions de photoinitiées des bisulfures de bis-pentachlorophényle avec plusieurs alcanes. Can. J. Chem., 51, 1870 (1973)

Introduction

## Homolytic substitution reactions of a number of sulfenyl chlorides (1-5) have been proposed to take place by free radical chain mechanisms where the chain-carrying species could involve the chlorine atom, the thiyl radical, or a mixture of these processes. The choice of the abstracting radical for a particular reagent can be decided on the basis of results obtained from the comparison of the reaction of the reagent with those of the chlorine atom. Product isomer distributions, relative reactivities between substrates (including deuterium isotope effect) and primary: secondary: tertiary (P:S:T) hydrogen selectivities have been used in these comparisons. However, the usefulness of the methods described depends upon the irreversibility of the abstraction (product determining) reaction. The possibility of extensive reversal of thiols formed by thivl radical abstraction (eq. 1) makes the information obtained from the product studies of these reactions of limited use, since the reversibility of the reaction will mask any kinetically meaningful information that can be obtained.<sup>3</sup>

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<sup>2</sup>Taken in part from the M.Sc. dissertation in Chemistry of B. G. Brownlee, University of Alberta, Edmonton, Alberta, 1968.

<sup>3</sup>The kinetic distribution of the radicals initially formed is determined by the selectivity or reactivity of the abstracting radical; however, if a reversible abstraction process is involved in the reaction sequence the rates of reversal of the initially formed radicals will not be necessarily the same as their relative rates of formation. The analysis of the final product distribution of such a sequence of reactions will only give an apparent relative reactivity or selectivity for the abstraction species. For a more detailed discussion of the problem see ref. 6.

$$[1] \qquad RH + YS \rightleftharpoons R + YSH$$

If the reactivity of the reagent is different from that of molecular chlorine then one is most likely dealing with a thiyl radical or a mixed chain reaction. It is difficult, however, to determine the true selectivity of the thiyl radical using these methods since the production of thiol which is potentially capable of reversal cannot be ignored.

A typical sulfenyl chloride, pentachlorobenzenesulfenyl chloride (PBSC), was first prepared by Putnam and Sharkey (7). Kharasch and Ariyan found that the reagent underwent reaction with cyclohexane in diffuse sunlight to yield a mixture of products which were qualitatively identified as cyclohexyl chloride, cyclohexyl pentachlorophenyl sulfide, hydrogen chloride, and bispentachlorophenyl disulfide (8). The mechanism of the reaction can potentially yield products via thiyl radical or chlorine atom abstraction or, alternatively, by a mixed chain involving both of these reactive intermediates.

### Results

### The Photolysis of PBSC with Cyclohexane

The reaction of PBSC with cyclohexane was shown to be a moderately long-chain process since, although not inhibited by *sym*-trinitrobenzene or molecular oxygen, 90% of the material was consumed by initiation with 2 mol % of AIBN (Table 1).

The major products of the photoinitiated reaction of a carbon tetrachloride solution of cyclohexane and PBSC were those which were previously reported. In addition to these four products, hydrogen chloride, bispentachlorophenyl disulfide (1), cyclohexyl chloride (2), and

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TABLE 1. The effects of free radical initiators and inhibitors on the reaction between PBSC and cyclohexane<sup>a</sup>

Conditions	Time, (h)	% reaction
Degassed, 40°, hv	1.0	87
Degassed, 40°, hv plus sym-trinitrobenzene <sup>b</sup>	1.0	81 82
Not degassed, $40^\circ$ , $hv$	1.0	78 80
	2.0	91 93
Degassed, 40°, dark	333	4 6
Degassed, 40°, dark plus AIBN (10 mol %) <sup>c,d</sup>	98 333	86 98 98
Degassed, 71°, dark	25	5 4
Degassed, 71°, dark plus AIBN (2 mol %) <sup>4</sup>	25	90 89

\*Carbon tetrachloride solutions of PBSC (0.3 *M*), cyclohexane (3.7 *M*) run under the defined conditions. \*Saturated solution,  $\leq 5 \mod \%$  of PBSC. <At 40°, AIBN has a  $t_{1/2} > 800$  h and less than 3% of the AIBN had decomposed (16). \*Mole % of PBSC. \*Percent reaction of PBSC.

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cyclohexyl pentachlorophenyl sulfide (3), traces of pentachlorothiophenol were found as well as a small amount of hexachlorobenzene. The yields of these materials for reactions run at 40 and 80° constitute a material balance for these reactions and are listed in Table 2. When the photolysis was carried out to 29-100% completion the ratio of the products formed remained unchanged (Table 2, runs 3-7 and 10-12). Reactions run with added pentachlorothiophenol (Table 2, runs 8-9) gave increased yields of 1 and decreased yields of 3.

The reaction of PBSC (0.32 M) with a 1:1 mixture of cyclohexane (1.8 M) and perdeuteriocyclohexane (1.8 M) was run to completion. The unreacted mixture of cyclohexane and perdeuteriocyclohexane was reisolated by g.l.p.c. and the mixture was subjected to mass spectral analysis. Neither incorporation (<1%) of deuterium into the cyclohexane nor incorporation of hydrogen into the perdeuteriocyclohexane could be observed.

## Photolysis of PBSC with n-Butane and Isobutane

The reactions of these isomeric butanes each gave mixtures of two chlorides and two aryl sulfides. A quantitative determination of the products from each of these reactions is listed in Table 3. Traces (<0.5%) of pentachlorothiophenol were produced in these reactions. From the combination of the yields of the corresponding chloride and sulfide for each of the reactions a relative selectivity/H could be calculated for the reagent of (P:S:T) 1:8:25 at 40°.

### The Selectivity of Complexed Molecular Chlorine

The possibility existed that the selectivity observed with the reagent was due to the abstraction reaction of chlorine atoms which had been stabilized by complex formation with PBSC or one of the products of the reaction.

Butane and isobutane were each separately photochlorinated with molecular chlorine at 40° in the presence of 0.1 M n-butyl pentachlorophenyl sulfide. The P:S:T selectivities calculated from the results of these photochlorinations were 1:2.7:3.5. The results were identical, within experimental error, to the value of 1:2.5:3.2 obtained for chlorination with molecular chlorine alone. Thus the presence of low concentrations of alkyl pentachlorophenyl sulfides did not enhance the selectivity of chlorine atoms. In these photochlorination reactions in the presence of added sulfide the yields of alkyl chlorides were in the order of 50-60% of that expected from the amount of chlorine present. Recovery of the sulfide and analysis by n.m.r. spectroscopy showed that the sulfide itself had undergone substantial chlorination, especially in the  $\alpha$ -position. Approximate values for the reactivity of *n*-butyl pentachlorophenyl sulfide relative to the reactivity of butane and isobutane toward chlorine atoms were 17:1 and 27:1 respectively.

PBSC itself was tested as a possible complexing agent by treating isobutane with approximately equimolar amounts of PBSC and molecular chlorine. Reaction conditions and analyses were the same as those used for the PBSC-isobutane reactions. Product yields are quoted in Table 4 along with the selectivities calculated from these yields. The selectivity of the PBSC-chlorine mixture was calculated from the combined yields of the primary chloride and sulfide compared to the yield of the corresponding tertiary substitution products. The values obtained, 1:11 (P:T), can be compared to those predicted, 1:15, for the reaction if the two halogenating reagents reacted independently. Therefore, PBSC could also be eliminated as a complexing agent.

## The Abstraction Reactions of Pentachlorophenyl Thiyl Radicals

The photoinitiated reactions of bispenta-

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TABLE 2. Product yields of the reactions of PBSC with cyclohexane

	Yield, mol/mol PBSC <sup>d</sup>					
Runª	HCI	ArSSAr (1)	C <sub>6</sub> H <sub>11</sub> Cl (2)	$\begin{array}{c} C_{6}H_{11}SAr \\ (3) \end{array}$	C <sub>6</sub> Cl <sub>6</sub>	
1–2	$0.74 \pm 0.01$			<u>_</u>		
3–7	-	$0.190 \pm 0.004$	$0.174 \pm 0.008$	$0.630 \pm 0.008$	0.030 + 0.002	
89 <sup>b</sup>		$0.30 \pm 0.00$	$0.16 \pm 0.00$	$0.525 \pm 0.005$	$0.02 \pm 0.00$	
10 <sup>c</sup>			0.19	0.61	0.01	
11			0.182	0.591		
12			0.178	0.501		

<sup>a</sup>All runs were at 40°, except runs 6 and 7 at 80°; all runs were 0.3 *M* in PBSC; runs 3-10 were 0.12 *M* in Freon 112. <sup>a</sup>Runs 8 and 9 were 0.04 *M* in pentachlorothiophenol. <sup>c</sup>Run 10 was carried to 75% completion, analyzed after iodometric titration, and the yields were corrected to 100% reaction. Run 11 was carried out to 29% and run 12 to 65% reaction. <sup>d</sup>The errors reported are average deviations from the mean.

TABLE 3. Product yields in the photoinitiated reaction of PBSC with normal butane and with isobutane at 40°

Mol product/mol of PBSC					
	Butane		Isob	utane	
	Run 13	Run 14	Run 15	Run 16	
$n-C_4H_9Cl$	0.003	0.003	0.01	0.01	iso-C₄H₀Cl
sec-C <sub>4</sub> H <sub>9</sub> Cl	0.10	0.10	0.15	0.16	t-C <sub>4</sub> H <sub>9</sub> Cl
$n-C_4H_9SC_6Cl_5$ (7)	0.13	0.13	0.19	0.18	$iso-C_4H_9SC_6Cl_5$ (5)
$sec-C_4H_9SC_6Cl_5(6)$	0.58	0.58	0.39	0.39	$t-C_4H_9SC_6Cl_5$ (4)
$C_6Cl_6$	0.03	0.03	0.04	0.03	$C_6Cl_6$
$(C_6C_1S)_2$	0.15	0.16	0.20	0.20	$(C_6C_5S)_2$
Primary:secondary selectivity	1:7.7	1:7.7	1:24.3	1:26.1	Primary: tertiary selectivity

### TABLE 4. Product yields in the photoinitiated reaction of isobutane with mixtures of PBSC and molecular chlorine at 40°a

Mol/mol PBSC + Cl <sub>2</sub>					
	Run 17 <sup>b</sup>	Run 18 <sup>b</sup>			
iso-C <sub>4</sub> H <sub>9</sub> Cl	0.22	0.21			
t-C₄H₀Cl	0.22	0.22			
5	0.16	0.16			
4	0.23	0.22			
C <sub>6</sub> Cl <sub>6</sub>	0.02	0.02			
$(C_6Cl_5S)_2$	0.07	0.07			
Primary:tertiary selectivity	1:10.6	1:10.7			

<sup>a</sup>Reaction mixtures contained 50 mmol of isobutane in 10 ml of carbon tetrachloride and 1.00 mmol of Freon 112 as internal standard, <sup>b</sup>Run 17 was with 1.69 mmol (55 mol %) of PBSC and 1.37 mmol (45 mol %) of chlorine. Run 18 was with 1.60 mmol (54 mol %) of PBSC and 1.37 mmol (46 mol %) of chlorine.

chlorophenyl disulfide were carried out with butane and with isobutane and yielded a mixture of the corresponding primary and secondary, or primary and tertiary aryl alkyl sulfides and pentachlorothiophenol. The reaction of the disulfide with isobutane (80°, 50 h with incandescent light, 2  $\times$  200 W) yielded pentachlorothiophenol (80%), t-butyl pentachlorophenyl sulfide (4) (90%), and iso-butyl pentachlorophenyl sulfide (5) (2-2.5%). The photoinitiated reaction of butane with bispentachlorophenyl disulfide yielded only pentachlorothiophenol, sec-butyl pentachlorophenyl sulfide (6), and *n*-butyl pentachlorophenyl sulfide (7).

Only apparent selectivities (P:S:T) could be calculated from product ratios obtained in this manner since abstraction reactions which take place in the presence of high concentrations of thiophenols lead to reversal of the abstraction processes. At low conversion of the reactants to products when [ArSH] approaches zero the true selectivities could be estimated. Plots of the ratio of products obtained vs. the percentage conversion for the reaction of isobutane and butane are given in Figs. 1 and 2.

When small amounts of pentachlorothiophenol (12 mol %) were added to the mixture of the disulfide and the hydrocarbon, the photolysis, even at low percentage reactions, gave high ratios of secondary/primary (butane) product, 93/7, and tertiary/primary (isobutane) product, 97/3.

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FIG. 1. The ratio of tertiary to primary sulfide formed in the reaction of bispentachlorophenyl disulfide with isobutane vs. the % conversion.

### The Photolysis of PBSC

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The photolysis of PBSC was reported to give bispentachlorophenyl disulfide (8); however, under our reaction conditions (24 h irradiation in carbon tetrachloride) 17% of hexachlorobenzene is obtained (68% of the active halogen, determined by iodometric titration, remained as volatile and nonvolatile products).

### Discussion

Several mechanistic schemes can be proposed to rationalize the formation of the products produced in the initiated substitution reactions of PBSC. The observation that the reaction was initiated by small amounts (2%) of AIBN implies a radical chain substitution process of a moderately long chain length (22–45). Following the initiation step in the lightcatalyzed reaction (eq. 2), the chain may be propagated by two distinct and distinguishable sequences of ractions involving abstraction by chlorine atoms or thiyl radicals.

$$[2] \qquad \qquad \operatorname{ArSCl} \xrightarrow{nv} \operatorname{ArS} + \operatorname{Cl}$$

In order to determine the abstracting species in the chain sequence several control experiments were carried out. If thiyl radical abstraction is proposed as the chain-carrying step in the substitution reaction, and if thiol is only found in trace amounts at the end of the reaction, an efficient reaction is necessary to remove thiol as a reaction product and to produce disulfide in its stead. The reaction of pentachlorothiophenol and PBSC was shown to meet these requirements, eq. 3, since a mixture of these reagents resulted in a very rapid reaction  $(k_2 \simeq 2 \times 10^{-2} 1 \text{ mol}^{-1} \text{ s}^{-1})$  and gave a quantitative yield of bisaryl disulfide. A mixture of hydrogen chloride and

$$[3] \qquad \text{ArSH} + \text{ArSCl} \xrightarrow{k_2} \text{ArSSAr} + \text{HCl}$$

PBSC was not reactive under the reaction conditions. The third control experiment that allows a determination of the abstracting species in the substitution reaction was one which demonstrates that a reversible abstraction reaction was not involved in the formation of the products. If thiyl radical abstraction is involved in the chain propagation step then the formation of the transfer reagent, ArSH, could lead to reversible abstraction (eq. 4) and to observed radical selectivities which were not the results of the



FIG. 2. The ratio of secondary to primary sulfide formed in the reaction of bispentachlorophenyl disulfide with butane vs. the % conversion.

kinetically determined distribution of the radicals involved.

$$[4] \qquad ArS \cdot + RH \rightleftharpoons ArSH + R \cdot$$

The failure to observe any detectable scrambling of protium and deuterium during the reactions of cyclohexane and perdeuteriocyclohexane with PBSC eliminates the possibility that the observed selectivity of the reagent was only an artifact of a combination of abstraction and reversal steps (eq. 4). The absence of this reversal reaction, eq. -4, does not, however, eliminate the possibility that thiol is present during the reaction (traces of this product are found at the completion of the reaction), since the rapid reaction of PBSC with thiol  $(k_2 \simeq 2 \times 2)$  $10^{-2}$  l mol<sup>-1</sup> s<sup>-1</sup>, a rate constant which is not incompatible with this suggestion under the concentration conditions of the reaction) could make transfer of an alkyl radical with this reagent a noncompetitive process. The two processes, thiyl radical abstraction and chlorine atom abstraction, are presented in Schemes 1a or band 2.

	<i>(a)</i>
[4]	$ArS \cdot + RH \rightarrow ArSH + R \cdot$
[5]	$R \cdot + ArSCl \rightarrow RCl + ArS \cdot$
[6]	$R \cdot + ArSSAr \rightarrow ArSR + ArS \cdot$
[3]	$ArSH + ArSCl \rightarrow HCl + ArSSAr$
	AND/OR
	(b)
[7]	$R \cdot + ArSCl \rightarrow RSAr + Cl$

[8] 
$$Cl + ArSSAr \rightarrow ArSCl + ArScl$$

Scheme 1

[9]	$Cl \cdot + RH \rightarrow HCl + R \cdot$
[5]	$R \cdot + ArSCl \rightarrow RCl + ArS \cdot$
[7]	$R\cdot \ + \ ArSCl \rightarrow ArSR \ + \ Cl\cdot$
[6]	$R \cdot + ArSSAr \rightarrow ArSR + ArS \cdot$
[9]	$ArS \cdot + ArSCI \rightarrow ArSSAr + CI$

### Scheme 2

The reagent, PBSC, demonstrated a primary: secondary:tertiary selectivity/H of 1:8:25 at 40°. Since the selectivity/H of chlorine atoms, under the reaction conditions, was found to be 1:2.7:3.5the process depicted by Scheme 2 could not be the sole mechanistic pathway for the formation of the reaction products. The chain process depicted by Scheme 1a and b or a mixture of the chain reactions, Schemes 1 and 2, could determine the mechanistic course of the reaction. A choice between these two alternatives could be made if the selectivity of the thiyl radical were known. The selectivity of the pentachlorophenylthiyl radicals can be estimated from the plots of the isomer distribution of products vs. the percent conversion for the photoinitiated substitution reaction of the aryldisulfide with butane and isobutane (Scheme 3).

$$Ar - S - S - Ar \rightleftharpoons 2ArS$$

$$ArS + RH \rightleftharpoons R + ArSH$$

$$R + Ar - S - S - Ar \rightleftharpoons R - S - Ar + ArS$$

$$R + ArS \rightarrow R - S - Ar$$

$$ArS = C_6 Cl_5 S$$

$$SCHEME 3$$

The true selectivity of the thiyl radical will be its selectivity in the absence of reversible abstraction, *i.e.* the selectivity obtained at 0% reaction. The extrapolated values of the selectivity obtained for the thiyl radical in the absence of thiol, 0% reaction, were estimated to be 1:8.5:31. These values are not significantly different from the values (1:8:25) obtained from the reaction of PBSC with the same substrates. An interpretation of this observation infers that the radical chain substitution processes of PBSC proceed via a mechanism involving thiyl radical abstraction as the dominant chain carrying step (Scheme 1).

The absence of appreciable numbers of chlorine atoms during the PBSC reaction was attested to by the absence in the reaction mixture of the chlorination products of arylalkyl sulfides. It would be expected that chlorine atoms would favor abstraction from the sulfides rather than the hydrocarbons since the relative reactivity of the sulfides to the hydrocarbons butane and isobutane was found to be from 20–30 in the photochlorination reactions of these substrates with molecular chlorine.

The mechanism of formation of the major substitution product, the sulfide, has been the subject of some speculation for the reaction of a number of sulfenyl chlorides (1-5). A choice between a displacement on the sulfur of the

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secondary product, disulfide, or on the sulfenyl chloride itself should, in principle, be able to be made. Since reaction 7 produces a

$$[6] \qquad \mathbf{R} \cdot + \mathbf{ArSSAr} \to \mathbf{ArSR} + \mathbf{ArS} \cdot$$

[7] 
$$\mathbf{R} \cdot + \mathbf{ArSCl} \rightarrow \mathbf{ArSR} + \mathbf{Cl} \cdot$$

chlorine atom, it would be inconsistent with both the selectivity observed with the reagent and with the absence, as secondary products, of chlorinated arylalkyl sulfide, unless a chlorine destroying process, [8], were also involved. An attempt was made to ascertain the importance of [7] as a major path for the production of sulfide by comparing the ratios of [RCl]/[RSAr] at various percentages of conversion (see Table 2, runs 3-7, 10-12). As the reaction proceeds the sulfenyl chloride to disulfide ratio decreases, and if reactions 7 and 5 are the important product-forming reactions the ratio of [RCl]/ [RSAr] should be independent of the percentage of reaction, while if reactions 5 and 6 were the major paths the ratio of products should decrease. The product ratio was found to be, within experimental error, constant; however, it was also observed that at concentrations equivalent to approximately 50% reaction the disulfide began to precipitate from solution. Since the ratio of [ArSCl]/[ArSSAr] would not change as fast under these conditions, no clear choice of reactions could be made for the sulfide-forming reaction.

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Hexachlorobenzene was observed as a minor reaction product (1-4% based on PBSC) in all of the reactions run with PBSC. One explanation considered for this was a displacement reaction analogous to that observed by Miller and Walling for displacement of bromine atoms from bromobenzene by chlorine atoms (9), and by Tanner and Van Bostelen for displacement of iodine from iodobenzene by chlorine atoms (10). The yield of hexachlorobenzene did not increase in the reactions using mixtures of chlorine and PBSC, thus discounting the feasibility of proposing a displacement reaction on PBSC by chlorine atoms. A precedent for obtaining hexachlorobenzene as a product during free radical reactions of PBSC was that thermolysis of benzenesulfenyl chloride gave chlorobenzene (60%) plus diphenyl disulfide and sulfur monochloride (11). By analogy a similar mechanism can be suggested for the formation of hexachlorobenzene from the photoinitiated decomposition reaction of PBSC (Scheme 4).

$$\begin{array}{l} hv \\ ArSCl \rightarrow ArS \cdot + Cl \cdot \\ ArS \cdot \rightarrow Ar \cdot + S \\ Ar \cdot + ArSCl \rightarrow ArCl + ArS \cdot \\ SCHEME 4 \end{array}$$

### Experimental

Materials

Pentachlorobenzenesulfenyl chloride was prepared by the method of Putnam and Sharkey (7), m.p.  $103-104^{\circ}$  (lit. (7) m.p.  $103-104^{\circ}$ ).

Anal. Calcd. for  $C_6Cl_6S$ : Cl, 67.14. Found: Cl, 67.55. Iodometric titration showed the material to contain

 $99.1 \pm 0.4\%$  of the theoretically calculated active halogen. Cyclohexane, butane, and isobutane were Phillips research grade materials and were used without further purification.

Pentachlorothiophenol (Aldrich Chemical Co., technical grade) was purified by crystallization from benzene – carbon tetrachloride, m.p. 238–240° (sealed tube), lit. (12) m.p. 243°.

Fisher spectranalyzed reagent grade carbon tetrachloride was checked for purity by g.l.p.c. prior to use; purified benzene was prepared for analytical work by twice crystallizing reagent grade material and was free from impurities by g.l.p.c. and n.m.r.

Freon 112 (1,2-diffuoro-1,1,2,2-tetrachloroethane) was distilled through a 3 ft helices-packed column and had b.p.  $89.5-90.0^{\circ}$  (700 mm). No impurities were detected by g.l.p.c.

Perdeuteriocyclohexane (99%) was obtained from Merck, Sharp and Dohme (Canada) Ltd.

Bispentachlorophenyl disulfide was prepared by the reaction (80°, 15 min) of a carbon tetrachloride mixture of pentachlorothiophenol (0.25 M) and PBSC (0.25 M). The disulfide was recrystallized from benzene several times, m.p. 235.5-237° (lit. (8) m.p. 235-236°).

#### G.l.p.c. Analysis

Analyses were carried out in triplicate. Peak areas were measured by multiplying peak height times peak width at one-half peak height. Calibration curves were used to convert the area ratios of the alkyl chlorides relative to Freon 112 as internal standard or area ratios of the alkyl sulfides relative to added hexachlorobenzene, into molar ratios. Precision of g.l.p.c. analyses was generally  $1\sim 3\%$ . Where quoted, the experimental uncertainties are standard deviations from the mean. Retention time comparison and peak enhancement refer to addition of authentic material to a portion of the sample and reanalysis by g.l.p.c.

# Initiation and Inhibition Reactions of PBSC

with Cyclohexane

Carbon tetrachloride solutions 0.3 M in PBSC and 3.7 M in hydrocarbon were allowed to react under the conditions indicated in Table 1. The photochemical and AIBN-initiated reactions did not differ in product composition.

#### Reaction of PBSC with Cyclohexane (Reactions 1–12)

Between 0.47 and 0.50 g of PBSC (1.48-1.56 mmol) was accurately weighed into an ampoule containing

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3.00 ml of carbon tetrachloride (0.200 *M* in Freon 112 for runs 3–12) and 2.00 ml of cyclohexane. Runs 8 and 9 contained 0.060 g (0.21 mmol) of pentachlorothiophenol. The ampoules were degassed in the absence of light, sealed under vacuum, wrapped in aluminum foil and equilibrated in a water bath at the desired temperature. The foil was then removed and the ampoules irradiated with  $2 \times 200$  W incandescent lamps. At first the reaction mixtures were orange in color. After about 1 h the color had faded to a light yellow and orange solid (1) began to crystallize out (except for the 80° runs). After 5–10 h, the reaction mixtures were colorless and crystallization of the solid had apparently been completed. In the reactions containing added pentachlorothiophenol, solid began to crystallize out after 10–15 min.

For the determination of hydrogen chloride (runs 1-2) the ampoules were frozen in liquid nitrogen and broken open under 50–100 ml of water in a stoppered flask. The flask was shaken for 10–15 min. The hydrogen chloride was titrated as iodine liberated after addition of excess potassium iodate and potassium iodide (13).

For the determination of the organic products, the reaction mixtures were first analyzed by g.l.p.c. for cyclohexyl chloride using a 10 ft  $\times$  1/4 in. SF-96 column programmed from 75-150°. The material was identified by its isolation and the comparison of retention time and i.r. spectrum with that of an authentic sample. After g.l.p.c. analysis of the supernatant solutions the solid precipitate of orange crystals, bispentachlorophenyl disulfide, was collected by filtration and weighed, m.p. 235-237°. A mixture melting point and i.r. spectrum (Nujol) were identical with those of an authentic sample. The filtrate was evaporated and gave a white solid, m.p. 109.5-112°. The weighed solid was analyzed by g.l.p.c. (5 ft  $\times$  1/4 in. SE-30, 15% on 60/80 Chromosorb W at 240°) and showed two components in the ratio 3:97 by area. The first was identical to hexachlorobenzene in retention time, and the mass spectrum of a collected sample was identical to the mass spectrum of an authentic sample of hexachlorobenzene (parent ions at m/e 282, 284, 286, and 288 were present with the intensities expected for a molecule containing six chlorine atoms, and were the most intense peaks in the spectrum).

The second component of the mixture was isolated and identified by dissolving the mixture in acetone, filtering the insoluble traces of disulfide and hexachlorobenzene, and crystallizing the soluble portion of the product which consisted of pure cyclohexyl pentachlorophenyl sulfide, m.p. 115–116°, (lit. (8) m.p. 116°); n.m.r. (CCl<sub>4</sub>)  $\tau$  6.4–7.0 (m, 1H), 7.8–9.0 (m, 10H); i.r. (CS<sub>2</sub>) 2935, 2855 (C—H); 1331, 1327, 1309, 1303 (aromatic C=–C) and 687 cm<sup>-1</sup> (C—Cl). The molar amounts of the sulfide and the hexachlorobenzene determined by isolation were confirmed by the addition of a standard to the admixed material and analysis by g.l.p.c.

The analysis for trace amounts of pentachlorothiophenol was made by acetylation of a portion of the crude reaction mixture, after filtration. The analysis by g.l.p.c. of pentachlorophenyl thiolacetate formed was compared to the amount of hexachlorobenzene (independently calibrated) in the solution. By addition of known amounts of the thiol to the reaction mixture and carrying out the acetylation and analysis an upper limit of 0.2% could be placed on the amount of thiol present in the reaction.

### Pentachlorophenyl Thiolacetate

The acetylation was carried out by heating to reflux a carbon tetrachloride solution of the pentachlorothiophenol (0.001–1.0 mmol) with excess acetyl chloride (500 mg, 6.4 mmol). Pyridine (0.5 ml, 6.3 mmol) in 5 ml of carbon tetrachloride was added in small portions through the reflux condenser. After 0.5 h the reaction mixture was cooled and poured onto ice. The carbon tetrachloride layer was separated and washed with ice-cold 3 *N* hydrochloric acid (2 × 30 ml). After drying over anhydrous calcium chloride the solvent was removed to give a >94% yield of pentachlorophenyl thiolacetate, m.p. 116–118° (lit. (14) m.p. 118–119°); i.r. (CS<sub>2</sub>) 1722, 1708 (thiolester carbonyl), and 690 cm<sup>-1</sup> (C—Cl).

### The Reaction of PBSC with Cyclohexane and Perdenteriocyclohexane

A mixture of pentachlorobenzenesulfenyl chloride  $(0.25 \text{ g}, 7.9 \times 10^{-4} \text{ mol})$ , cyclohexane  $(0.39 \text{ g}, 4.5 \times 10^{-3} \text{ mol})$ , perdeuteriocyclohexane  $(0.44 \text{ g}, 4.6 \times 10^{-3} \text{ mol})$ , and carbon tetrachloride (2.4 g) was degassed and sealed in a Pyrex ampoule. The ampoule was irradiated with 2 × 200 W tungsten lamps at 40° for 20 h. Iodometric titration carried out after the irradiation showed the absence of any active halogen. Product analysis carried out in the previously described manner showed the presence of the following: H(D)Cl (74%), chlorocyclohexane (22%), bispentachlorophenyl sulfide (49%), hexachlorobenzene (2%), and pentachlorobenzenethiol (trace).

Mass-spectral analysis of the recovered cyclohexane and perdeuteriocyclohexane was undertaken to compare the ratios of the m/e 85 (C<sub>6</sub>H<sub>11</sub>D) to 84 (C<sub>6</sub>H<sub>12</sub>), and 95 (C<sub>6</sub>HD<sub>11</sub>) to 96 (C<sub>6</sub>D<sub>12</sub>) intensities with those of the starting mixture of cyclohexane and perdeuteriocyclohexane. The intensity ratios of the m/e 85/84 and 95/96 peaks obtained from the analysis were the same, within experimental error  $< \pm 1\%$ , as those observed from the starting mixture.

A similar experiment without solvent carbon tetrachloride gave the same results.

## Synthesis of the Isomeric Butyl Pentachlorophenyl

Sulfides, 4-7

The sulfides were prepared by alkylating the sodium salt of pentachlorothiophenol with the appropriate alkyl halide in boiling ethanol (25 ml, 1 h). Compounds 4-7 were isolated by pouring the reaction mixtures onto 100 g of ice. Sulfides 7 and 5 were collected as solids which were crystallized from acetone-ethanol; m.p. of 7 was 38° from methanol-ethanol (lit. (15) m.p. 39-40°). Compound 6 was obtained as a colorless oil which was extracted into benzene. To obtain the t-butyl isomer (4) free from starting material, the solvent was evaporated and the residue treated with excess 5% sodium hydroxide. The solid remaining was filtered off and crystallized from acetoneethanol. Analytical samples of 5 and 4 were prepared by sublimation at 110-120° (0.01 mm); m.p. of 5 was 37.5-38°, m.p. of 4 was 122.5-123°. The entire crude yield of 6 was distilled, b.p. 135–145° (0.01 mm),  $n_{D}^{20}$  1.6124. The analysis was obtained on this material. Table 5 summarizes the details.

The i.r. spectra (CS<sub>2</sub>) of all four isomers contained bands for C—H stretching between 2860 and 2980 cm<sup>-1</sup>. The aromatic C=C stretching appeared as two strong

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 TABLE 5.
 The isomeric butyl pentachlorophenyl sulfides 4–7

C₅Cl₅SH NaOH (mmol) (mmol		Alkylating agent (mmol)	Yield (%)		Analysis		
	NaOH (mmol)			C	Н	Cl	
10	20	t-C4H9Cl (20)	9	35.83	2.87	52.57	
10	12	$iso-C_4H_9Br$ (20)	60	35.45	2.79	52.36	
10	20	sec- $C_4H_9Br$ (20)	83	35.54	2.61	52.17	
10	12	$n-C_4H_9Br(20)$	80		_		
		Calcd	. for C10H9Cl5	S: 35.48	2.70	52.37	
	C <sub>6</sub> Cl₅SH (mmol) 10 10 10 10 10	C <sub>6</sub> Cl <sub>5</sub> SH (mmol)         NaOH (mmol)           10         20           10         12           10         20           10         12           10         20           10         12           10         12	$\begin{array}{c c} C_6 Cl_5 SH \\ (mmol) \\ \hline 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ $	$\begin{array}{c c} C_6 Cl_5 SH \\ (mmol) \\ (mmol) \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 1$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	

TABLE 6. Nuclear magnetic resonance data of the isomeric butyl pentachlorophenyl sulfides (CCl<sub>4</sub>)

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5 6 7

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	Group assignment	τ value (multiplicity <sup>a</sup> , J Hz)
7	ArSCH <sub>2</sub> <sup>b</sup>	7.12 (t, 6.5)
	CH <sub>2</sub> CH <sub>2</sub>	8.5 (m,)
	CH <sub>3</sub>	9.1 (m,)
6	ArSCH	6.66 (m, —)
		8.45 (m, —)
	ArS-C-CH3	8.77 (d, 6.5)
	-CH <sub>3</sub>	8.97 (t, 7)
5	ArSCH2	7.26 (d, 6.5)
	—С—Н	8.32 (m,)
	СН <sub>3</sub>   Н <sub>3</sub> С—С— 	8.99 (d, 6)
4	CH <sub>3</sub>   ArS-CCH <sub>3</sub>	8.61 (s,)
	CH <sub>3</sub>	

<sup>a</sup>s, singlet; d, doublet; t, triplet; m, multiplet. <sup>b</sup>Ar =  $C_6Cl_5$  group.

bands (split in 7 and 5) at 1300-1305 and 1325-1335 cm<sup>-1</sup>. The C-Cl stretching bands for all four isomers was a strong band between 683 and 686 cm<sup>-1</sup>.

The n.m.r. data of the four isomers are shown in Table 6.

Reaction of PBSC with Normal Butane (Runs 13 and 14) and Isobutane (Runs 15 and 16)

The reaction mixtures consisted of *ca.* 3 mmol of PBSC (0.95–1.0 g), *ca.* 50 mmol of hydrocarbon (5 ml at  $-80^{\circ}$ ), 2.00 mmol of Freon 112, and 10 ml of carbon tetrachloride.

The reaction mixtures were degassed and irradiated at  $40^{\circ}$  in the same way as the cyclohexane reactions (runs 1–12). Irradiation times of 7–10 h were required for complete reaction as shown by complete disappearance of

the orange color of PBSC, and crystallization of the disulfide.

The ampoules were frozen in liquid nitrogen, broken open, and analyzed for alkyl chlorides by g.l.p.c. (20 ft  $\times$ 1/8 in. SF-96 column 5% on 80/100 Chromosorb W, AW-DMCS at 50°). The chlorides were identified by a comparison of their retention times on two columns with those of authentic samples (20 ft SF-96 and 25 ft  $\times$  1/8 in. UCON POLAR, 5% on 80/100 Chromosorb W at 50°).

The disulfide was collected by filtration and was found to be identical with authentic material in mixture m.p. The yield and m.p. of the disulfide obtained in these four runs were: run 13, 0.257 g, m.p. 234–236°; run 14, 0.268 g, m.p. 232–235°; run 15, 0.341 g; run 16, 0.352 g, m.p. 234–236°.

Evaporation of the filtrates gave the crude sulfides. Run 13, 0.775 g; run 14, 0.751 g; run 15, 0.640 g; run 16, 0.664 g.

The isomer ratios were determined by n.m.r. By comparing the ArS—C—H signal of 6 ( $\tau$  6.65 multiplet) to the ArS—CH<sub>2</sub>— signal of 7 ( $\tau$  7.12, triplet) in CCl<sub>4</sub> solvent, the ratio of 6/7 was found to be 4.5 for run 13 and 4.1 for run 14. Similarly by comparing the *t*-butyl singlet of 4 ( $\tau$  8.82) to the gem-dimethyl doublet of 5 ( $\tau$  9.14) in benzene solvent, the ratio of 4/5 was found to be 2.1 for run 15 and 2.2 for run 16.

The product butyl pentachlorophenyl sulfide had an identical n.m.r. spectrum to that of an authentic sample. Further identification was accomplished by g.l.p.c. retention time comparison with authentic samples of 4, 5, 6, and 7 (5 ft × 1/4 in. SE-30 column at 220–240°). The area ratios were in agreement with the ratios determined from the n.m.r. spectra. Samples were collected by preparative g.l.p.c. for comparison of i.r. spectra and were found to be identical to authentic materials in this respect. Mass spectra were obtained for each of the sulfides collected by g.l.p.c. Each spectrum had a set of parent peaks at m/e 336, 338, 340, and 342 in the expected ratios for five chlorine atoms ( $C_6^{35}Cl_5C_4H_9 = 336$ ). The base peak for each of the isomers was at m/e 57 ( $C_4H_9$ ).

Hexachlorobenzene (identified by g.l.p.c. retention time and by the mass spectrum of a collected sample) was also present in the mixtures. It comprised about 4% (by peak area) for runs 13 and 14, and 5% for runs 15 and 16.

Pentachlorothiophenol was estimated by the acetylation method previously described. For both run 14 and run 16 none of the thiolacetate could be detected by g.l.p.c. Under the analytical conditions employed the upper limit for the yield of pentachlorothiophenol was

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0.5%. Run 14 could be analyzed under the g.l.p.c. conditions as used before. Run 16 was analyzed using a 5 ft  $\times$  1/8 in. QF-1 column at 200°. A summary of the results for runs 13-16 is listed in Table 3.

Photochlorination of Normal Butane and Isobutane

Butane (2 ml, ca. 20 mmol) was photochlorinated at 40° with 2.0 mmol of chlorine in sealed, degassed ampoules with 4.0 ml of carbon tetrachloride as solvent.

Analysis by g.l.p.c. (20 ft  $\times$  1/8 in. SF-96 column) gave, for three reactions, sec-C<sub>4</sub>H<sub>9</sub>Cl/n-C<sub>4</sub>H<sub>9</sub>Cl = 1.65  $\pm$  0.07 for a primary:secondary selectivity/H of 1:2.5  $\pm$  0.1.

Similarly photochlorination of 20 mmol of isobutane with 1.7 mmol of chlorine in 4.0 ml of carbon tetrachloride gave, for two reactions, t-C<sub>4</sub>H<sub>9</sub>Cl/*iso*-C<sub>4</sub>H<sub>9</sub>Cl = 0.358  $\pm$  0.016 for a primary:tertiary ratio of 1:3.2  $\pm$  0.15.

### Reaction of Isobutane with PBSC-Chlorine (Runs 17 and 19)

Two reactions were run at  $40^{\circ}$ . Each reaction mixture consisted of isobutane (5 ml, *ca.* 50 mmol), PBSC (run 17, 0.536 g, 1.69 mmol; run 18, 0.507 g, 1.60 mmol), chlorine (1.37 mmol), Freon 112 (1.00 mmol) and carbon tetrachloride (10.0 ml). Irradiation times of 8–9 h were required for completion of reaction.

The alkyl chlorides were quantitated by g.l.p.c. as before (runs 15 and 16).

The yield, melting point, and mixture melting point (with authentic material) of the disulfide (1) were: run 17, 0.116 g, 234–236, 235–237°; run 16, 0.113 g, 235–237°, none.

The yield of crude sulfide was 0.423 g (1.25 mmol) for run 17 and 0.399 g (1.18 mmol) for run 18.

The n.m.r. spectra (CCl<sub>4</sub>) of the sulfides were qualitatively identical to those previously obtained for the sulfides from runs 15 and 16. Since the spectra did not contain any signals below  $\tau$  7.1 it was concluded that no chlorination of the sulfides had occurred. The ratio (n.m.r.) of 4/5 was 1.44 for run 17 and 1.41 for run 18.

Hexachlorobenzene was estimated by g.l.p.c. analysis as before and found to comprise 4-5% (by peak area) of the crude sulfide mixtures. The peak area ratio (g.l.p.c.) of 4/5 was about 1.3/1 for both runs.

### Photochlorination of Normal Butane (Runs 19 and 20) and Isobutane (Runs 21 and 22) in the Presence of n-Butyl Pentachlorophenyl Sulfide (7)

Each reaction mixture contained 2 ml (20 mmol) of hydrocarbon (3.3 *M*), 1.20 mmol of chlorine (0.20 *M*), 0.60 mmol of 7 (0.10 *M*), 2.00 mmol of Freon 112, and 4.0 ml of carbon tetrachloride. The chlorinations were carried out at 40° and required about 0.25 h of irradiation. The alkyl chlorides were analyzed by g.l.p.c. as before. For runs 19 and 20, the molar ratio sec-C<sub>4</sub>H<sub>9</sub>Cl/ n-C<sub>4</sub>H<sub>9</sub>Cl was 1.78 ± 0.06 for a primary :secondary selectivity/H of 1:2.7 ± 0.1. The total yield of alkyl chlorides was 0.72 mmol or about 60% of the theoretical, based on chlorine.

The reaction mixtures from runs 19 and 20 were combined and the solvent removed to give 0.454 g of colorless oil. When the n.m.r. spectrum of this oil was obtained in carbon tetrachloride solution it showed that the sulfide had undergone chlorination. The signal at  $\tau$  4.6 (triplet) was assigned to the  $\alpha$ -chlorinated product, and the signal at 5.8 was assigned to the  $\beta$ -chlorinated product. The ratio of  $\alpha$ -chlorination to  $\beta$ -chlorination was about 2:1. From a comparison of the integrated intensities of the chlorinated sulfides and the unchlorinated starting material it was estimated that about 40% of the sulfide had been chlorinated. Because the  $\alpha,\alpha$ -dichlorosulfide could not be observed by n.m.r., it was not known for certain if any dichlorosulfide was produced in the reaction.

Runs 21 and 22 were analyzed in the same way. The ratio t-C<sub>4</sub>H<sub>9</sub>Cl/*iso*-C<sub>4</sub>H<sub>9</sub>Cl was  $0.388 \pm 0.023$  for a primary:tertiary ratio of  $1:3.5 \pm 0.2$ . The total yield of chlorides was 0.60 mmol, about 50% of theoretical. The combined yield of (chlorinated) sulfides was 0.450 g. The n.m.r. spectrum was qualitatively identical to that obtained from the chlorinated sulfides in runs 19 and 20. Again the ratio of  $\alpha$ -chlorination to  $\beta$ -chlorination was 2:1. About 50% of the sulfide had been chlorinated.

### Photolysis of Bispentachlorophenyl Disulfide, 1, in Isobutane – Carbon Tetrachloride

Mixtures of 0.17 g ( $3.02 \times 10^{-4}$  mol) of bispentachlorophenyl disulfide, 3 ml  $(3.0 \times 10^{-2} \text{ mol})$  of isobutane, and 5 ml of carbon tetrachloride were degassed and sealed in Pyrex ampoules. The ampoules were placed in a thermostat at 80 °C and irradiated with a 200 W tungsten lamp for the appropriate times (0.5-32 h). The ampoules were cooled in liquid nitrogen, opened, and the reaction mixtures were filtrated by suction to remove unreacted bispentachlorophenyl disulfide. Analysis of the filtrates by g.l.p.c. (SE 30, 230°) showed three products which were collected and identified by a comparison of their i.r. spectra with those of authentic samples. The compounds were shown to be pentachlorobenzenethiol, t-butyl pentachlorophenyl sulfide, and isobutyl pentachlorophenyl sulfide. The reactions were quantitated by adding known amounts of hexachlorobenzene and determining the yields of the products by the use of standard calibration curves constructed for the products and the standard. Product ratios of *t*-butyl pentachlorophenyl sulfide to isobutyl pentachlorophenyl sulfide were determined by comparison of the corresponding peak areas. Results are given in Fig. 1. In typical runs the products were isolated by g.l.p.c. and the structures were determined by their i.r. and n.m.r. spectra. A control experiment carried out without irradiation resulted in complete recovery of the starting disulfide after 24 h.

The photolysis of bispentachlorophenyl disulfide in isobutane – carbon tetrachloride was carried out with added pentachlorobenzenethiol (12 mol %). The reactions were carried out to 0.1, 2.7, 3.3, and 20.2% conversion and were analyzed in the usual manner. The ratio of 4/5 was 96.5  $\pm$  0.5/4  $\pm$  0.5 for these four independent reactions.

### Photolysis of Bispentachlorophenyl Disulfide in n-Butane – Carbon Tetrachloride

Mixtures of 0.17 g  $(3.02 \times 10^{-4} \text{ mol})$  of bispentachlorophenyl disulfide, 3 ml  $(3.0 \times 10^{-2} \text{ mol})$  of *n*butane, and 5 ml of carbon tetrachloride were degassed and sealed in Pyrex ampoules. The ampoules were placed in a thermostat at 80° and preheated before irradiation for 3 h. Irradiation with a 200 W tungsten bulb was continued for the appropriate times (1–115 h). G.l.p.c. analysis (SE 30, 230°) of the reaction mixtures showed

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three products identified by retention times as pentachlorobenzenethiol, *sec*-butyl pentachlorophenyl sulfide, and *n*-butyl pentachlorophenyl sulfide in the order of elution. In some typical cases products were isolated and their structures determined by comparison of their i.r.  $(CS_2)$  and n.m.r. spectra with those of authentic samples. Percent conversion of the disulfide into sulfides and the ratio of *sec*-butyl to *n*-butyl derivatives in each ampoule were determined by g.l.p.c. using calibration curves (standard/hexachlorobenzene). The results of these experiments are given in Fig. 2. A control experiment carried out without irradiation resulted in complete recovery of the starting disulfide.

Photolysis of bispentachlorophenyl disulfide in *n*butane – carbon tetrachloride was carried out with added pentachlorobenzenethiol (12 mol %). The reactions were carried out and analyzed in the usual manner. Reactions run to 0.7, 1.0, and 2.4% conversion showed ratios of 6/7 of 93.3  $\pm$  0.3/6.7  $\pm$  0.3.

### Photolysis of PBSC in Carbon Tetrachloride

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PBSC (0.487 g, 1.54 mmol) was photolyzed at  $40^{\circ}$  for 24 h in a sealed, degassed ampoule using 5 ml of carbon tetrachloride as solvent. The volatile components were removed by vacuum transfer at room temperature and 0.05 mm. By iodometric titration, 0.10 mmol of active halogen was found in the distillate, and 0.94 mmol was found in the residue. After titration, the organic layer was removed and evaporated leaving a pale yellow solid. Analysis of this solid by g.l.p.c. (SE-30 at 200°) showed hexachlorobenzene as the sole volatile product. By sublimation at 150° and 15 mm, 0.075 g (17%) of hexachlorobenzene was obtained, m.p. 223-226° (sealed tube). After one crystallization from carbon tetrachloride it had m.p. 228-229° (sealed tube) and mixture m.p. with authentic material 228-229° (sealed tube). The i.r. spectrum (Nujol mull) was identical to that of authentic material.

### The Rate of the Reaction Between Pentachlorobenzenesulfenyl Chloride and Pentachlorobenzenethiol

The solutions of pentachlorobenzenesulfenyl chloride (1.316 g, 0.052 M) in 80 ml of carbon tetrachloride – cyclohexane mixture (5:3 in volume) and pentachlorobenzenethiol (1.174 g, 0.052 M) in 80 ml of the same mixture were separately equilibrated at 40° for 10 min

and then were mixed together in the dark. The pentachlorobenzenesulfenyl chloride remaining in the solution was monitored by withdrawing aliquot portions of the solution and subjecting them to iodometric titration with standard sodium thiosulfate solution. A second order rate constant of  $1.8 \pm 0.2 \times 10^{-2} \, \mathrm{l} \, \mathrm{mol}^{-1} \, \mathrm{s}^{-1}$  was obtained.

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