The soluble product, 12.5 g., C/(H + Cl) = 1.36, from a similar polymerization (0–5° for 10 hr.) yielded 11 g. of product, C/(H + Cl) = 1.53, on dehydrogenation.

Molecular Weight Determinations.—A vapor pressure osmometer (Mechrolab No. 301A) was used to obtain the average molecular weight of the benzene-soluble fraction of the polymers. The product (0.2 g.) was stirred with 20 ml. of benzene at 25° for 12 hr. in a 50-ml. flask. After the solution was filtered through previously weighed filter paper, the flask was washed with 5 ml. of benzene. The filtrate was transferred into a 25-ml. volumetric flask and diluted to volume. After being dried in air for 24 hr., the filter paper was weighed to obtain the amount of insoluble polymer.

In an alternate procedure the polymer was weighed directly into the volumetric flask, the molecular weight was determined, and the solution then was filtered. The weight of the insoluble polymer was determined. The two procedures gave similar results. In all cases the polymer was initially heated for 6 hr. at 80–90° (1 atm.) and for 15–20 min. at 80–90° (0.4 mm.) to remove traces of *o*-dichlorobenzene and naphthalene. This treatment also removed 5–15% of the 1,1′-binaphthyl. The data are compiled in Table IV.

Isomerization of Binaphthyls.—A standard solution (5 ml.) made up from 20 g. of 1,1′-binaphthyl/l. of *o*-dichlorobenzene or one (10 ml.) composed of 10 g. of 2,2′-binaphthyl/l. was exposed at 20–25° to the following metal halides (0.001 mole of each component): $AlCl_3$, $AlCl_3$–CuCl, $AlCl_3$–$CuCl_2$, $FeCl_3$, $FeCl_3$–$FeCl_2$, $FeCl_3 \cdot H_2O$–$FeCl_2$. After initial agitation, the mixtures were allowed to stand. The extent of isomerization and conversion to higher molecular weight products were followed by periodically analyzing samples of the binaphthyl–metal halide mixtures by gas chromatography (Table V). The rate of disappearance of 1,1′- and 2,2′-binaphthyl by nonisomerization reactions was a function of the metal halide catalyst as indicated: $AlCl_3$–$CuCl_2$, $MoCl_5 > AlCl_3 > AlCl_3$–$CuCl >> FeCl_3 = FeCl_3$–$FeCl_2$.

N.m.r. Analyses.—The studies were made at 60 Mc. on a Varian A-60 spectrometer with 20%, by weight, solutions of the polymers in carbon disulfide. The ferric chloride polymer is described in Table I, entry 9, and the molybdenum pentachloride polymer in Table III, entry 4.

Acknowledgment.—We gratefully acknowledge support of this work by the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and the Sun Oil Company.

The Reaction of Alkyl Aryl Sulfides with Ethyl Trichloroacetate and Sodium Methoxide[1]

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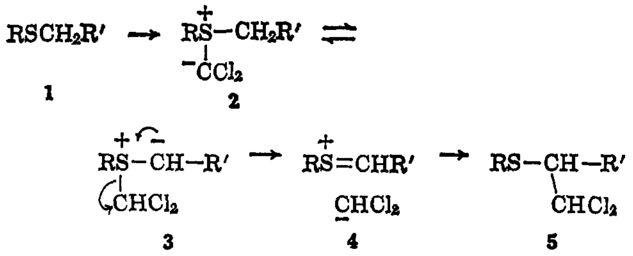
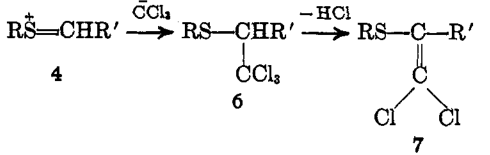
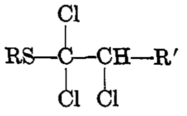
A study of the higher boiling products formed by reactions of ethyl trichloroacetate and sodium methoxide (dichlorocarbene) with ethyl phenyl sulfide, phenyl *n*-propyl sulfide, and methyl phenyl sulfide has shown that trichloromethyl substituted sulfides, and/or products derived from them by loss of hydrogen chloride, are formed. The mechanism of inhibition of addition of dichlorocarbene to olefins by sulfides and the mechanism of insertion of dichlorocarbene and/or the trichloromethyl group into sulfides appear to be related by a process involving a phenylmercaptocarbonium ion intermediate.

The inhibition of the addition of dichlorocarbene to olefins by saturated sulfides[3] and insertion of dichlorocarbene into cyclic allyl sulfides[4,5] may be mechanistically related by a sequence of reactions (Scheme I) formally related to the Pummerer reaction.[6] The unique feature about this reaction sequence, which differentiates it from alternative mechanisms that can be written for these processes, is the intermediacy of the phenylmercaptocarbonium ion (or ion pair) **4**. Evidence for such an intermediate has now been obtained by a study of the higher boiling products formed, in low yields, when ethyl phenyl sulfide, phenyl *n*-propyl sulfide, and methyl phenyl sulfide are allowed to react with ethyl trichloroacetate and sodium methoxide. The products of these reactions are **6** and **7**, but not **8** as previously suggested.[7]

SCHEME I







8

Procedure

Standard conditions were employed in these reactions using approximately 0.2 mole of sulfide, 0.4 mole of sodium methoxide, and 0.36 mole of ethyl trichloro-

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[1] Supported by a grant from the U. S. Army Research Office (Durham), Contract No. DA-31-124-ARO-D-152.

[2] From the dissertation of S. H. Groen, the University of Groningen, The Netherlands. O.E.C.D. Postgraduate Travel Grant awarded by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

[3] W. E. Parham and S. H. Groen, *J. Org. Chem.*, **29**, 2214 (1964).

[4] W. E. Parham and R. Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961).

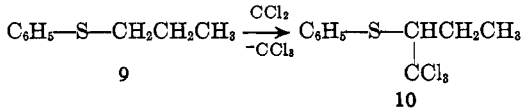
[5] W. E. Parham, L. Christensen, S. H. Groen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964).

[6] The relationship of this scheme to the Pummerer reaction was discussed in an earlier paper: W. E. Parham and S. H. Groen, *ibid.*, **30**, 728 (1965).

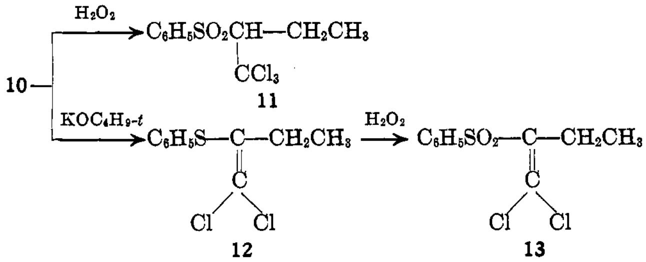
[7] The trichlorosulfide previously isolated from the reaction of *n*-butyl phenyl sulfide with ethyl trichloroacetate, and sodium methoxide was tentatively assigned (see ref. 3) a structure analogous to **8** on the basis of composition and n.m.r. data. A similar product, α,α,β-trichloroethyldimethylamine, was formed from trimethylamine and dichlorocarbene: M. Saunders and R. W. Murray, *Tetrahedron*, **11**, 1 (1960).

acetate. In all cases the yield of recovered sulfide was high (56–75%), and considerable tar formation was noted.

Phenyl *n*-Propyl Sulfide.—The reaction of phenyl *n*-propyl sulfide with ethyl trichloroacetate and sodium methoxide gave, in addition to recovered sulfide (75%), an impure sample of **10** which was characterized by conversion to the sulfone **11**. Reaction of **10** with potassium *t*-butoxide in petroleum ether (b.p. 30–60°) gave a high yield of the olefin **12** which was characterized by conversion to the sulfone **13**.



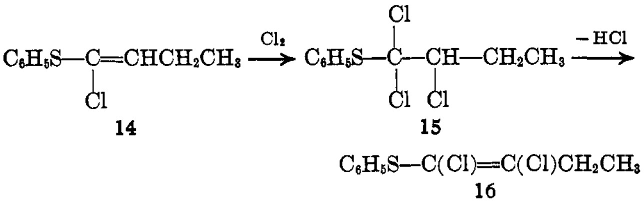
$$\underset{\textbf{9}}{C_6H_5{-}S{-}CH_2CH_2CH_3} \xrightarrow[-CCl_3]{CCl_2} \underset{\textbf{10}}{C_6H_5{-}S{-}\underset{CCl_3}{C}HCH_2CH_3}$$



$$\textbf{10} \xrightarrow{H_2O_2} \underset{\textbf{11}}{C_6H_5SO_2\underset{CCl_3}{C}H{-}CH_2CH_3}$$

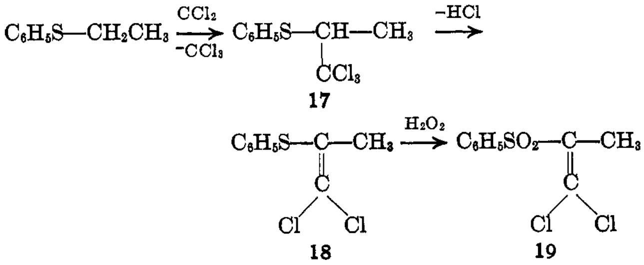
$$\textbf{10} \xrightarrow{KOC_4H_9\text{-}t} \underset{\textbf{12}}{C_6H_5S{-}\underset{\underset{Cl\quad Cl}{C}}{C}{-}CH_2CH_3} \xrightarrow{H_2O_2} \underset{\textbf{13}}{C_6H_5SO_2{-}\underset{\underset{Cl\quad Cl}{C}}{C}{-}CH_2CH_3}$$

Spectral data derived for **11**, **12**, and **13** were quite consistent with the assigned structures; however, such data did not exclude the alternative structures **15** (analogous to **8**) and **16**. This possibility was excluded by a study of the addition of chlorine to the known olefin **14**. The expected trichloride **15**, unlike **10**, appeared to be unstable, for the product isolated was *cis* and *trans* **16**. The sulfone of **16** was not identical with the sulfone **13** derived from phenyl *n*-propyl sulfide.

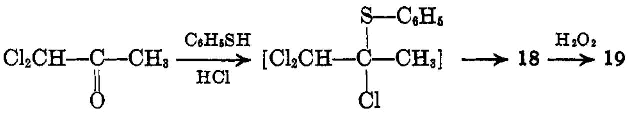


$$\underset{\textbf{14}}{C_6H_5S{-}\underset{Cl}{C}{=}CHCH_2CH_3} \xrightarrow{Cl_2} \underset{\textbf{15}}{C_6H_5S{-}\overset{Cl}{\underset{Cl}{C}}{-}\underset{Cl}{C}H{-}CH_2CH_3} \xrightarrow{-HCl} \underset{\textbf{16}}{C_6H_5S{-}C(Cl){=}C(Cl)CH_2CH_3}$$

Ethyl Phenyl Sulfide.—The reaction of ethyl phenyl sulfide with ethyl trichloroacetate and sodium methoxide gave, in addition to recovered sulfide (75%), a sample of **17** contaminated with the olefin **18**. The trichloride **17** was not dehydrochlorinated by reaction with pyridine in benzene at 45°; however, it was dehydrohalogenated in high yield to a single dihalide (**18**) by reaction with potassium *t*-butoxide in petroleum ether. Olefin **18** was characterized by its composition and spectra (n.m.r. and infrared) and by conversion to the corresponding sulfone **19**. Spectral data derived for **18** and **19** did not permit an absolute assignment of structure. This was achieved by the independent synthesis of **18** and **19** from 1,1-dichloroacetone.

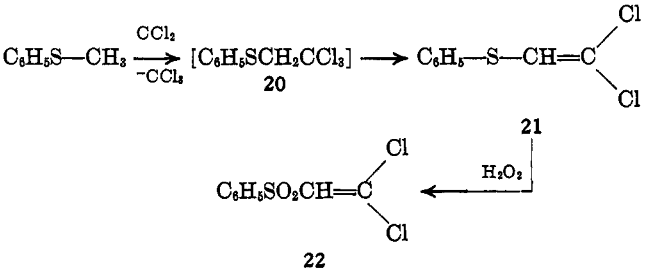


$$C_6H_5S{-}CH_2CH_3 \xrightarrow[-CCl_3]{CCl_2} \underset{\textbf{17}}{C_6H_5S{-}\underset{CCl_3}{C}H{-}CH_3} \xrightarrow{-HCl} \underset{\textbf{18}}{C_6H_5S{-}\underset{\underset{Cl\quad Cl}{C}}{C}{-}CH_3} \xrightarrow{H_2O_2} \underset{\textbf{19}}{C_6H_5SO_2{-}\underset{\underset{Cl\quad Cl}{C}}{C}{-}CH_3}$$



$$Cl_2CH{-}\underset{O}{C}{-}CH_3 \xrightarrow[HCl]{C_6H_5SH} [Cl_2CH{-}\overset{S-C_6H_5}{\underset{Cl}{C}}{-}CH_3] \longrightarrow \textbf{18} \xrightarrow{H_2O_2} \textbf{19}$$

Methyl Phenyl Sulfide.—The trichloromethyl sulfide **20** was not obtained by reaction of methyl phenyl sulfide with ethyl trichloroacetate and sodium methoxide. The product, in addition to recovered sulfide (56%), was the olefin **21**. This olefin, the expected dehydrohalogenation product of **20**, was characterized by conversion to the corresponding sulfone **22**. The only alternative structure which can be considered for the olefin **21** is *cis* or *trans* **23**. This possibility is excluded by (1) comparison of the refractive index of the product with that reported for *cis* and *trans* **23**,[8] (2) comparison of the melting point of the derived sulfone **22** (m.p. 54–55°) with that reported for *cis* and *trans* **23**[8] (m.p. 70–72° and 60–61°, respectively), and (3) by analogy to the products formed from ethyl phenyl sulfide and phenyl *n*-propyl sulfide.

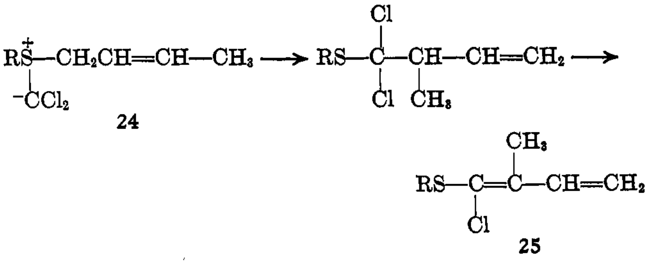


$$C_6H_5S{-}CH_3 \xrightarrow[-CCl_3]{CCl_2} \underset{\textbf{20}}{[C_6H_5SCH_2CCl_3]} \longrightarrow \underset{\textbf{21}}{C_6H_5{-}S{-}CH{=}C\genfrac{}{}{0pt}{}{Cl}{Cl}} \xrightarrow{H_2O_2} \underset{\textbf{22}}{C_6H_5SO_2CH{=}C\genfrac{}{}{0pt}{}{Cl}{Cl}}$$

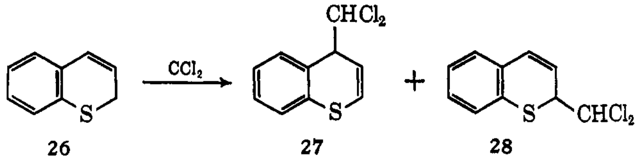
$C_6H_5S{-}C(Cl){=}CHCl$
23

Discussion

The mechanism of insertion of dichlorocarbene into cyclic allyl sulfides,[4,5] and the mechanism of inhibition for the addition of dichlorocarbene to olefins by saturated (alkyl–aryl) sulfides[3] are thought to occur by a process outlined in Scheme I. That an ylid intermediate of type **2** may be involved is supported by the observed[6] allylic rearrangement illustrated by **24** → **25**. Recombination of ions (**4** → **5**) is supported by the formation of the insertion products **27** and **28** from the sulfide **26**.[4] With cyclic sulfides such as **26**, the proposed ion



$$\underset{\textbf{24}}{R\overset{+}{\underset{-CCl_2}{S}}{-}CH_2CH{=}CH{-}CH_3} \longrightarrow RS{-}\overset{Cl}{\underset{Cl}{C}}{-}\underset{CH_3}{C}H{-}CH{=}CH_2 \longrightarrow \underset{\textbf{25}}{RS{-}\underset{Cl}{C}{=}\overset{CH_3}{C}{-}CH{=}CH_2}$$



26 **27** **28**

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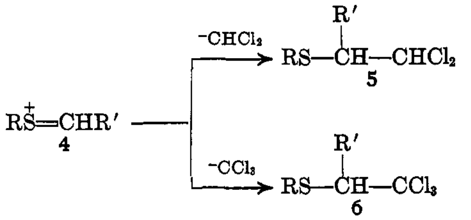
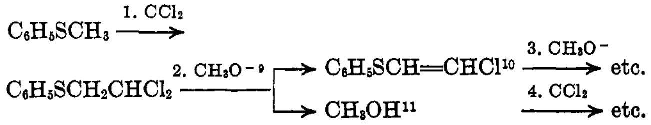
[8] F. Montanari and A. Negrini, *Gazz. chim. ital.*, **87**, 1061 (1957).

4 appears to favor internal return since insertion products (**27** and **28**) are formed in reasonably high yields.

Insertion products of type **5** were not observed with saturated sulfides; however, it is probable that they were formed together with the trichloromethyl sulfides (**6**) which were isolated. Since saturated sulfides inhibit addition of dichlorocarbene to olefins, but are recovered in high yields (75–80%),[3] it appears that 1 equiv. of sulfide must react with several equivalents of dichlorocarbene or reagents (*i.e.*, CH_3O^-, $^-CCl_3$) required for the formation of dichlorocarbene. Such a possibility, as illustrated in the accompanying equations, seems reasonable.



$$RS\overset{+}{=}CHR' \xrightarrow{^-CHCl_2} RS\text{—}CH(R')\text{—}CHCl_2 \; (\mathbf{5}) \qquad RS\overset{+}{=}CHR' \xrightarrow{^-CCl_3} RS\text{—}CH(R')\text{—}CCl_3 \; (\mathbf{6})$$



$$C_6H_5SCH_3 \xrightarrow{1.\ CCl_2} C_6H_5SCH_2CHCl_2 \xrightarrow{2.\ CH_3O^{-\,9}} \begin{cases} C_6H_5SCH{=}CHCl^{10} \xrightarrow{3.\ CH_3O^-} \text{etc.} \\ CH_3OH^{11} \xrightarrow{4.\ CCl_2} \text{etc.} \end{cases}$$

Formation of trichloromethyl sulfides of type **6** constitutes evidence for a phenylmercaptocarbonium ion intermediate (**4** → **6**) in the insertion reaction of sulfides with ethyl trichloroacetate and sodium methoxide.

Experimental

2-Phenylsulfonyl-1,1,1-trichlorobutane (**11**).—Ethyl trichloroacetate (69.9 g., 0.37 mole) was added over a 30-min. period to a cold (ice bath) and stirred mixture, under nitrogen, of phenyl *n*-propyl sulfide (**9**, 30.7 g., 0.20 mole), sodium methoxide (22.7 g., 0.42 mole), and olefin-free petroleum ether (150 ml., b.p. 30–60°). A vigorous reaction, accompanied by tar formation, occurred as the acetate was added. The mixture was stirred at 0° for 4 hr., then allowed to come to room temperature overnight. Water (150 ml.) was added and the layers were separated. The water layer was washed once with ether (100 ml.). The combined organic layers were dried ($MgSO_4$) and concentrated in a rotatory evaporator. Distillation of the residue gave (a) recovered phenyl *n*-propyl sulfide (**9**, 22.9 g., 0.15 mole, 75%) and (b) impure 2-phenylmercapto-1,1,1-trichlorobutane (**10**): 3.7 g.; b.p. 76–80° (0.01 mm.); $n^{19.5}\text{D}$ 1.5736; ν^{neat} 1370 and near 2950 cm.$^{-1}$ (CH_3); n.m.r. spectrum[12] (20% in CCl_4) C_6H_5 (complex, τ 2.39–2.91), CH (four peaks at τ 6.37, 6.41, 6.55, and 6.59), CH_2 (complex, near τ 7.69), CH_3 (complex, near τ 8.67), and strong impurity peaks in the region τ 7.21–9.14.

A stirred mixture of fraction b (3.7 g.), acetic acid (18 ml.), and hydrogen peroxide (8 ml., 30%) was heated at 100° for 3 hr. The mixture was cooled and water (100 ml.) was added. The oil was extracted with ether and the ether extract was washed with saturated sodium carbonate. The dried ($MgSO_4$) ether extracts were concentrated in a rotatory evaporator and the crude oily sulfone was dissolved in ethanol (two parts)–petroleum ether (one part, b.p. 30–60°) and cooled in Dry Ice–acetone. The solid sulfone (1.3 g., 2% yield, based on phenyl *n*-propyl sulfide) was crystallized from ethanol (one part)–petroleum ether (one part, b.p. 30–60°). 2-Phenylsulfonyl-1,1,1-trichlorobutane (**11**) had m.p. 70.5–71.5°; $\nu^{\text{halocarbon-Nujol}}$ near 1150 and 1320 cm.$^{-1}$ (SO_2); n.m.r. spectrum[12] (20% in $DCCl_3$) C_6H_5 (complex, τ 1.93–2.55, wt. ~5), CH (four peaks at τ 6.05, 6.11, 6.16, and 6.22; wt. ~1), CH_2 (complex, τ 7.96–7.33, wt. ~2), and CH_3 (triplet at τ 8.93, 8.80, and 8.67; wt. ~3).

Anal. Calcd. for $C_{10}H_{11}Cl_3O_2S$: C, 39.82; H, 3.68; Cl, 35.27; S, 10.63. Found: C, 40.03; H, 3.73; Cl, 35.18; S, 10.79.

1,1-Dichloro-2-phenylmercaptobutene-1 (**12**).—The reaction of phenyl *n*-propyl sulfide (**9**, 62.8 g., 0.41 mole), ethyl trichloroacetate (119.2 g., 0.62 mole), and sodium methoxide (57.0 g., 1.06 mole) in petroleum ether (400 ml., b.p. 30–60°) was repeated as described above, and gave (a) recovered phenyl *n*-propyl sulfide (**9**, 47.1 g., 0.31 mole, 75%) and (b) impure 2-phenylmercapto-1,1,1-trichlorobutane (**10**, 4.7 g., b.p. 110–120° (0.2 mm.), $n^{24}\text{D}$ 1.5674). Fraction b (4.7 g.) was added over a period of 10 min. to a cold (ice bath) and stirred mixture of potassium *t*-butoxide (11.0 g.) and petroleum ether (100 ml., b.p. 30–60°). The mixture was stirred for an additional 2 hr. in an ice bath and 1 hr. at room temperature. Water (100 ml.) was added and the layers were separated. The water layer was washed once with ether (100 ml.). The combined organic layers were dried ($MgSO_4$) and concentrated in a rotatory evaporator. Distillation of the residue gave 1,1-dichloro-2-phenylmercaptobutene-1 (**12**): 2.7 g., 3% yield (based on phenyl *n*-propyl sulfide); b.p. 75–76.5° (0.03 mm.); $n^{22}\text{D}$ 1.5885; ν^{neat} 1370 and near 2950 cm.$^{-1}$ (CH_3); n.m.r. spectrum[13] (neat) C_6H_5 (complex, τ 2.95–2.66, wt. 5.4), CH_2 (quartet at τ 7.92, 7.80, 7.68, and 7.55; wt. 2.0), and CH_3 (triplet at τ 9.21, 9.08, and 8.96; wt. 3.1).

The sulfone was prepared as described for 2-phenylsulfonyl-1,1,1-trichlorobutane (**11**). **1,1-Dichloro-2-phenylsulfonylbutene-1** (**13**) was collected in 45% yield, based on **12**: b.p. 98° (0.01 mm.); m.p. 33–35°; $n^{24}\text{D}$ 1.5708; ν^{neat} near 1160 and 1320 cm.$^{-1}$ (SO_2); n.m.r. spectrum[13] (neat) C_6H_5 (complex, τ 2.67–2.00, wt. 5.2), CH_2 (quartet at τ 7.45, 7.33, 7.21, and 7.09; wt. 2.0), and CH_3 (triplet at τ 8.93, 8.81, and 8.69; wt. 3.0).

Anal. Calcd. for $C_{10}H_{10}Cl_2O_2S$: C, 45.29; H, 3.80; S, 12.09. Found: C, 45.57; H, 3.67; S, 12.00.

1,2-Dichloro-1-phenylmercaptobutene-1 (**16**).—Dry chlorine, generated from potassium permanganate (4.0 g.) and hydrochloric acid (35 ml., 37%) was led, over a 2-hr. period, into a stirred and cooled (ice bath) solution of 1-chloro-1-phenylmercaptobutene-1[3] (**14**, 4.2 g., 0.0212 mole) in chloroform (30 ml.). Water (100 ml.) was added and the layers were separated. The dried ($MgSO_4$) organic layer was concentrated in a rotatory evaporator. Distillation of the residue gave slightly impure 1,2-dichloro-1-phenylmercaptobutene-1 (**16**): 3.5 g., 70% yield; b.p. 99–104° (0.1 mm.); $n^{22}\text{D}$ 1.5885; ν^{neat} 1375 and near 2950 cm.$^{-1}$ (CH_3), the spectrum was different from that of the 1,1-dichloro-2-phenylmercaptobutene-1 (**12**), derived from phenyl *n*-propyl sulfide; n.m.r. spectrum[13] (50% in CCl_4) C_6H_5 (complex, τ 2.83–2.50, wt. 5.5), CH_2 (two partly superimposed quartets due to *cis–trans* isomers at τ 7.51, 7.39, 7.27, and 7.14, and a weaker one at τ 7.35, 7.23, 7.10, and 6.97; wt. 2.0), CH_3 (probably two partly superimposed triplets between τ 9.05–8.63, wt. 3.3), impurity peaks near τ 2.25 and four small peaks at τ 6.03, 5.99, 5.85, and 5.81, probably due to $C_6H_5SCCl_2CHClC_2H_5$.

The sulfone was prepared as described for 2-phenylsulfonyl-1,1,1-trichlorobutane (**11**). **1,2-Dichloro-1-phenylsulfonylbutene-1** was collected in 28% yield: b.p. 104–105° (0.01 mm.); $n^{22.5}\text{D}$ 1.5706, ν^{neat} near 1160 and 1320 cm.$^{-1}$ (SO_2), the spectrum was not identical with that of 1,1-dichloro-2-phenylsulfonylbutene-1 (**13**), derived from phenyl *n*-propyl sulfide; n.m.r. spectrum[13] (30% in CCl_4) C_6H_5 (complex, τ 2.58–1.92, wt. 5.2), CH_2 (two quartets at τ 6.97, 6.85, 6.73, 6.60 and τ 7.56, 7.43, 7.31, and 7.19; wt. 2.0), CH_3 (two partly superimposed triplets at τ 9.02, 8.90, 8.78, 8.76, and 8.63; wt. 3.1). This n.m.r. solution was mixed with 1,1-dichloro-2-phenylsulfonylbutene-1 (**13**), derived from phenyl *n*-propyl sulfide; the quartet of the CH_2 and the triplet of the CH_3 of the latter did not coincide with one of the two quartets of the CH_2 or with one of the two triplets of the CH_3 of 1,2-dichloro-1-phenylsulfonylbutene-1, respectively.

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(9) The trichloromethyl anion could logically function as the base for such elimination reactions.

(10) Olefins of this type are known to be quite reactive toward nucleophilic reagents: W. E. Truce, M. M. Boudakian, R. F. Heine, and R. J. McManimie, *J. Am. Chem. Soc.*, **78**, 2743 (1956).

(11) Alcohols are known to react with dichlorocarbene: *cf.* J. Hine, E. L. Pollitzer, and H. Wagner, *ibid.*, **75**, 5607 (1953).

(12) The n.m.r. spectra were taken on a Varian V4302 at 56.44 Mc. (reference, tetramethylsilane). Weights were estimates obtained by using a planimeter.

(13) The n.m.r. spectra were determined on a Varian A-60 at 60 Mc. (reference, tetramethylsilane). Weights were obtained by use of an integrator.

Anal. Calcd. for $\mathrm{C_{10}H_{10}Cl_2O_2S}$: C, 45.29; H, 3.80; Cl, 26.75; S, 12.09. Found: C, 45.33; H, 3.55; Cl, 27.79, 27.57; S, 11.99.

2-Phenylmercapto-1,1,1-trichloropropane (17) and 1,1-Dichloro-2-phenylmercaptopropene-1 (18).—The reaction of ethyl trichloroacetate (67.0 g., 0.35 mole), sodium methoxide (21.6 g., 0.40 mole), and ethyl phenyl sulfide (27.6 g., 0.20 mole) in olefin-free petroleum ether (100 ml., b.p. 30–60°), carried out as described for phenyl *n*-propyl sulfide (**9**), gave recovered ethyl phenyl sulfide (21.1 g., 0.15 mole, 75%) and a mixture of 2-phenylmercapto-1,1,1-trichloropropane (**17**) and 1,1-dichloro-2-phenylmercaptopropene-1 (**18**): 4.4 g.; b.p. 90–95° (0.05 mm.); $n^{22.5}\mathrm{D}$ 1.5792; ν^{neat} 1370 and near 2950 cm.$^{-1}$ ($\mathrm{CH_3}$); n.m.r. spectrum[12] (15% in $\mathrm{CCl_4}$) $\mathrm{C_6}H_5$ (complex, τ 2.86–2.52), $\mathrm{C_6H_5SC}H\mathrm{(CCl_3)CH_3}$ (quartet at τ 5.96, 6.08, 6.20, and 6.32), $\mathrm{C_6H_5SC({=}CCl_2)C}H_3$ (singlet at τ 8.10), $\mathrm{C_6H_5SCH(CCl_3)C}H_3$ (doublet at τ 8.23 and 8.35). The ratio of **17** to **18** was approximately 3 to 1.

The mixture of 2-phenylmercapto-1,1,1-trichloropropane (**17**) and 1,1-dichloro-2-phenylmercaptopropene-1 (**18**) was oxidized to the sulfones as described for 2-phenylsulfonyl-1,1,1-trichlorobutane (**11**). A mixture of **2-phenylsulfonyl-1,1,1-trichloropropane and 1,1-dichloro-2-phenylsulfonylpropene-1 (19)** was collected: b.p. 99–105° (0.01 mm.); $n^{27}\mathrm{D}$ 1.5767; ν^{neat} near 1150 and 1320 cm.$^{-1}$ ($\mathrm{SO_2}$); n.m.r. spectrum[12] (20% in $\mathrm{CCl_4}$) $\mathrm{C_6}H_5$ (complex, τ 1.94–2.57), $\mathrm{C_6H_5SO_2C}H\mathrm{(CCl_3)CH_3}$ (quartet at τ 6.05, 5.93, 5.82, and 5.70), $\mathrm{C_6H_5SO_2C({=}CCl_2)C}H_3$ (singlet at τ 7.76), $\mathrm{C_6H_5SO_2CH(CCl_3)C}H_3$ (doublet at τ 8.32 and 8.20). The ratio of dichlorosulfone to trichlorosulfone was slightly greater than 1.

The reaction of ethyl phenyl sulfide (30.0 g., 0.22 mole), ethyl trichloroacetate (72.2 g., 0.38 mole), and sodium methoxide (24.0 g., 0.44 mole) in petroleum ether (150 ml., b.p. 30–60°) was repeated as described above. In addition to recovered ethyl phenyl sulfide (21.5 g., 0.16 mole, 72%) an impure mixture of 2-phenylmercapto-1,1,1-trichloropropane (**17**) and 1,1-dichloro-2-phenylmercaptopropene-1 (**18**, 5.9 g., b.p. 97–115° at 0.2 mm., $n^{23}\mathrm{D}$ 1.5750) was collected. This mixture was heated with pyridine (3 ml.) and benzene (20 ml.) at 45° for 1 hr. Water (50 ml.) was added and the layers were separated. The organic layer was washed with three 30-ml. portions of 2 *N* hydrochloric acid and dried ($\mathrm{MgSO_4}$). Careful distillation of the product through a spiral-wire column gave slightly impure **2-phenylmercapto-1,1,1-trichloropropane** (**17**): 3.2 g., 6% yield, based on ethyl phenyl sulfide; b.p. 74–76° (0.03 mm.); $n^{26}\mathrm{D}$ 1.5772; ν^{neat} 1370 and near 2950 cm.$^{-1}$ ($\mathrm{CH_3}$); n.m.r. spectrum[12] (20% in $\mathrm{CCl_4}$) $\mathrm{C_6}H_5$ (complex, τ 2.41–2.91, wt. ~5), $\mathrm{C}H$ (quartet at τ 6.34, 6.22, 6.10, and 5.97; wt. ~1), $\mathrm{C}H_3$ (doublet at τ 8.33 and 8.21; wt. ~3), and a small peak from $\mathrm{C_6H_5S{-}C({=}CCl_2){-}C}H_3$ at τ 8.10.

1,1-Dichloro-2-phenylmercaptopropene-1 (18).—The mixture of 2-phenylmercapto-1,1,1-trichloropropane (**17**) and 1,1-dichloro-2-phenylmercaptopropene-1 (**18**) was treated with potassium *t*-butoxide in petroleum ether (b.p. 30–60°), as described for 1,1-dichloro-2-phenylmercaptobutene-1 (**12**). 1,1-Dichloro-2-phenylmercaptopropene-1 (**18**) was collected in 5% yield, based on ethyl phenyl sulfide: b.p. 58–60° (0.02 mm.); $n^{22}\mathrm{D}$ 1.6013; ν^{neat} 1375 and near 2950 cm.$^{-1}$ ($\mathrm{CH_3}$); n.m.r. spectrum[13] (neat) $\mathrm{C_6}H_5$ (peak at τ 2.58, wt. 5.4), $\mathrm{C}H_3$ (singlet at τ 8.07; wt. 3.0).

Anal. Calcd. for $\mathrm{C_9H_8Cl_2S}$: C, 49.32; H, 3.68. Found: C, 49.56; H, 3.83.

1,1-Dichloro-2-phenylmercaptopropene-1 (**18**) was oxidized to the sulfone, as described for 2-phenylsulfonyl-1,1,1-trichlorobutane (**11**). **1,1-Dichloro-2-phenylsulfonylpropene-1 (19)** was collected in 67% yield: b.p. 92° (0.01 mm.); $n^{20}\mathrm{D}$ 1.5825; ν^{neat} near 1160 and 1320 cm.$^{-1}$ ($\mathrm{SO_2}$); n.m.r. spectrum[13] (neat) $\mathrm{C_6}H_5$ (complex, τ 2.48–1.80, wt. 5.1), $\mathrm{C}H_3$ (singlet at τ 7.68, wt. 3.0).

Anal. Calcd. for $\mathrm{C_9H_8Cl_2O_2S}$: C, 43.04; H, 3.21; Cl, 28.24; S, 12.77. Found: C, 43.30; H, 3.39; Cl, 28.46; S, 12.87.

1,1-Dichloroacetone was prepared as described in Friedländer[14]: b.p. 113–116; $n^{19}\mathrm{D}$ 1.4480; ν^{neat} 1740 cm.$^{-1}$ (C=O); n.m.r. spectrum[13] (neat) $\mathrm{C}H_3$ (singlet at τ 7.55, wt. 3.0), $\mathrm{C}H\mathrm{Cl_2}$ (singlet at τ 3.90, wt. 1.0).

1,1-Dichloro-2-phenylmercaptopropene-1 (18), Prepared from Dichloroacetone and Thiophenol.—Dry hydrochloric acid was led in a cold (ice bath) mixture of 1,1-dichloroacetone (19.1 g., 0.15 mole) and thiophenol (5.5 g., 0.05 mole). To the stirred mixture was added thiophenol (11.0 g., 0.10 mole) over a period of 45 min. After the addition of thiophenol was completed, the hydrochloric acid was led in for 1 additional hr. The reaction mixture was added to potassium *t*-butoxide (30.0 g.) in petroleum ether (200 ml., b.p. 30–60°). Water (150 ml.) was added to the mixture and the layers were separated. The organic layer was dried ($\mathrm{MgSO_4}$) and concentrated in a rotatory evaporator. Distillation of the residue gave 1,1-dichloro-2-phenylmercaptopropene-1 (**18**), 6.1 g., 18% yield, b.p. 96–101° (0.15 mm.), $n^{26.5}\mathrm{D}$ 1.5987. The infrared and n.m.r. spectra of this product were identical with those of the 1,1-dichloro-2-phenylmercaptopropene-1 (**18**), derived from ethyl phenyl sulfide. A sample was redistilled for analysis (b.p. 62° at 0.03 mm., $n^{19}\mathrm{D}$ 1.6020).

Anal. Calcd. for $\mathrm{C_9H_8Cl_2S}$: C, 49.32; H, 3.68. Found: C, 49.60; H, 3.76.

1,1-Dichloro-2-phenylmercaptopropene-1 (**18**) was oxidized to the sulfone as described for 2-phenylsulfonyl-1,1,1-trichlorobutane (**11**). **1,1-Dichloro-2-phenylsulfonylpropene-1 (19)** was collected in 65% yield, b.p. 98–99° (0.01 mm.), $n^{26.5}\mathrm{D}$ 1.5792. The infrared and n.m.r. spectra of this product were identical with those of 1,1-dichloro-2-phenylsulfonylpropene-1 (**19**), derived from ethyl phenyl sulfide.

Anal. Calcd. for $\mathrm{C_9H_8Cl_2O_2S}$: C, 43.04; H, 3.21. Found: C, 42.91; H, 3.14.

1,1-Dichloro-2-phenylmercaptoethene (21).—The reaction of ethyl trichloroacetate (76.7 g., 0.40 mole), sodium methoxide (24.8 g., 0.46 mole), and methyl phenyl sulfide (28.5 g., 0.23 mole) in olefin-free petroleum ether (200 ml., b.p. 30–60°), carried out as described for phenyl *n*-propyl sulfide (**9**), gave recovered methyl phenyl sulfide (16.0 g., 0.13 mole, 56%) and 1,1-dichloro-2-phenylmercaptoethene (**21**): 2.7 g.; 6% yield; b.p. 60–62° (0.01 mm.); $n^{24}\mathrm{D}$ 1.6050; ν^{neat} no absorption at 1370 and near 2950 cm.$^{-1}$ (no $\mathrm{CH_3}$); n.m.r. spectrum[12] (15% in $\mathrm{CCl_4}$) $\mathrm{C_6}H_5$ (peak at τ 2.70, wt. ~5), $\mathrm{{=}C}H$ (singlet at τ 3.50, wt. ~1).

1,1-Dichloro-2-phenylmercaptoethene (**21**) was oxidized to the sulfone as described for 2-phenylsulfonyl-1,1,1-trichlorobutane (**11**). **1,1-Dichloro-2-phenylsulfonylethene (22)** was collected in 58% yield: m.p. 54–55°; $\nu^{\mathrm{halocarbon\text{-}Nujol}}$ near 1150 and 1330 cm.$^{-1}$ ($\mathrm{SO_2}$); n.m.r. spectrum[12] (15% in $\mathrm{DCCl_3}$) $\mathrm{C_6}H_5$ (complex, τ 1.91–2.52, wt. ~5), $\mathrm{{=}C}H$ (singlet at τ 3.04, wt. ~1).

Anal. Calcd. for $\mathrm{C_8H_6Cl_2O_2S}$: C, 40.52; H, 2.55; Cl, 29.91; S, 13.52. Found: C, 40.59; H, 2.59; Cl, 29.98; S, 13.43.

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(14) Friedländer, "Fortschritte der Teefarbenfabrikation und verwandter Industriezweige," Vol. XVIII, Julius Springer, Berlin, 1931; German Patent 547 642.