bicyclo[4.1.0]heptane (XII, 16.35 g., 70% yield, b.p. 71° at 0.75 mm., $n^{25}D$ 1.5604) was distilled through a spiral-wire column.

The infrared and n.m.r. spectrum of XII were consistent with the assigned structure and showed absence of any unsaturation (no insertion detected).

Anal. Calcd. for $C_6H_8Cl_2S$: C, 39.36; H, 4.40. Found: C, 39.53; H, 4.76.

Reaction of Δ^3-Dihydrothiapyran (XIV) with Dichlorocarbene.—The reaction of XIV (6.64 g., 0.066 mole) with ethyl trichloroacetate (25.24 g., 0.13 mole) and commercial sodium methoxide (7.5 g., 0.14 mole) was carried out by a procedure identical with that employed with XI. The product was distilled rapidly (b.p. 65–110° at 0.25 mm., 4.3 g., 35% calcd. as XV or XVI) without use of a fractionating column. The black tarry residue was not further processed. The distillate was fractionated through a spiral-wire column to give (a) 1.0 g., b.p. 52–64° (0.4 mm.), $n^{25}D$ 1.5717, yellow oil which rapidly turned brown; (b) 1.87 g., clear, b.p. 64–68° (0.4 mm.), $n^{25}D$ 1.5700; and (c) 1.28 g., mostly hold up in column, $n^{25}D$ 1.5899. The infrared spectra of all of these fractions showed the presence of considerable unsaturation in the 1608–1680-cm.$^{-1}$ region.

Fraction b showed $\lambda_{max}^{95\%\ alc}$ 233 mμ (ϵ 4970), 248 mμ (ϵ 4330); ν^{neat} C=C (1608 s and 1665 w cm.$^{-1}$); n.m.r. spectrum[13]: strong broad absorption in the region τ 3.6–4.6 (317–362 c.p.s.), consistent with the unsaturated insertion products XV and XVI.

Anal. Calcd. for $C_6H_8Cl_2S$: C, 39.36; H, 4.40. Found: C, 39.62; H, 4.37.

Desulfurization Reactions. A. XV and XVI.—The mixture of XV and XVI (1.4 g., fraction b, above) in 75% ethanol–water (100 ml.) and Raney nickel (about 6 g.)[5] was heated at the reflux temperature for 1.5 hr. Water (25 ml.) was added, and the resulting mixture was distilled. The distillate was diluted with water and then was extracted with ether (5 ml.).

Vapor phase chromatography of the ether extract using a diisodecyl phthalate column (set at 55°, carrier gas helium, flow 15 p.s.i.) showed the presence of three components in addition to solvents. Two of the compounds were identified as n-hexane and 3-methylpentane (approximately equal amounts). The other product (approximately 0.25 peak intensity of n-hexane) was not identified; however, it was shown not to be 2-methylpentane.

B. XII.—Reaction of XII (1.7 g.) with Raney nickel (~6.0 g.) was carried out as described in A, above. Analysis of the ether solution by v.p.c. (same conditions as above) showed n-hexane and 2-methylpentane to be present in the approximate ratio, 3:1.

Reaction of Enol Ethers with Carbenes. IV.[1] Allyl Sulfides and Saturated Sulfides[2]

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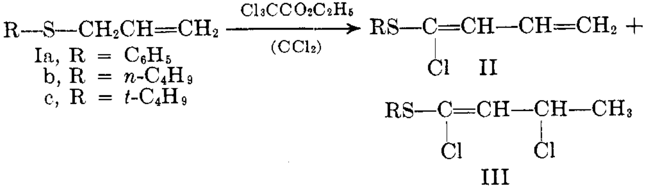
The reaction of ethyl trichloroacetate and sodium methoxide with noncyclic allyl sulfides leads to the formation of 1-chloro 1-substituted mercaptobutadienes in high yields, together with some olefins derived by addition of hydrogen chloride to the butadienes. The course of these reactions is discussed, and additional data concerning reaction of saturated sulfides with ethyl trichloroacetate and sodium methoxide is presented. It is shown that saturated sulfides inhibit the formation of dichlorocyclopropyl adducts from olefins such as cyclohexene. Evidence is also presented for a minor chlorination process in reactions involving ethyl trichloroacetate and sodium methoxide.

In previous reports we have described evidence which shows that dichlorocarbene, generated from ethyl trichloroacetate and sodium methoxide,[4] reacts with vinyl sulfides to give cyclopropanes,[1] and with cyclic allyl sulfides[1,5] to give insertion products. This paper describes reactions of open-chain allyl sulfides with dichlorocarbene precursors, and presents preliminary data concerning reactions of dichlorocarbene with saturated sulfides.

The reaction of the allyl sulfides (I, 1 mole) with ethyl trichloroacetate (1–1.5 moles) and sodium methoxide (1–2 moles) were carried out at ice-bath temperature, and the reaction mixtures were allowed to warm to room temperature overnight. The allyl sulfides studied were allyl phenyl sulfide (Ia), allyl n-butyl sulfide (Ib), and allyl t-butyl sulfide (Ic); evidence will be presented showing that the principal reaction in each case is properly summarized by the equation I → II + III.



$$R{-}S{-}CH_2CH{=}CH_2 \xrightarrow[(CCl_2)]{CH_3O^-,\ Cl_3CCO_2C_2H_5} RS{-}\underset{Cl}{\underset{|}{C}}{=}CH{-}CH{=}CH_2 + RS{-}\underset{Cl}{\underset{|}{C}}{=}CH{-}\underset{Cl}{\underset{|}{CH}}{-}CH_3$$

Ia, R = C_6H_5
b, R = n-C_4H_9
c, R = t-C_4H_9

II

III

A. Reaction of Allyl Phenyl Sulfide.—The reaction of allyl phenyl sulfide (Ia) with ethyl trichloroacetate and sodium methoxide afforded as a principal product a liquid A (IIa) in 46–60% yield with the empirical formula $C_{10}H_9ClS$. Vapor phase chromatography of this product on Reoplex and on Carbowax columns showed only one peak.

The infrared spectrum of the product showed no alkyl hydrogen, but did show olefinic absorption at 1610, 900–910, 980, and 1835 cm.$^{-1}$ characteristic of the —CH=CH$_2$ grouping. The ultraviolet spectrum of IIa (95% alcohol) showed λ_{max} 244 mμ (ϵ 16,370), (shoulder), 274 mμ (ϵ 8680); the n.m.r. spectrum[6] (neat) was complex but showed =CH$_2$ (complex 282–312 c.p.s., weight 2.0), —CH= (complex 363–405 c.p.s., weight 1.9), and aromatic H (complex 408–430 c.p.s., weight 5.4).

The product gave a colorless polymeric sulfone when treated with hydrogen peroxide in acetone, or with 1 equiv. of perbenzoic acid in benzene or chloroform; however, a solid derivative (m.p. 143–144°, >40%

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(1) For the preceeding article in this series, see W. E. Parham, L. Christensen, S. H. Groen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964).

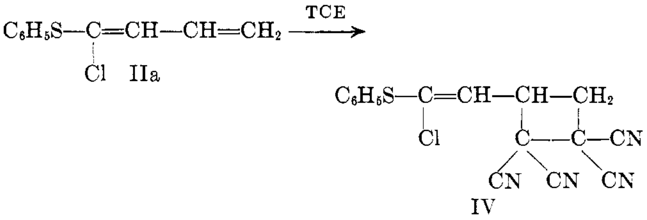
(2) Supported in part by a grant (no. GP-159) from the National Science Foundation, and by a grant from the U. S. Army Research Office (Durham), Contract No. DA-ORD-31-124-61-GB.

(3) 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.).

(4) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

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

(6) The n.m.r. spectra were taken on Varian A60 at 60 Mc. (reference tetramethylsilane). Weights were obtained by integration.

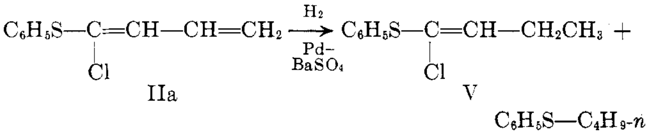


IIa

IV

yield) was formed with tetracyanoethylene.[7] The tetracyanoethylene (TCE) adduct was assigned structure IV[8] on the basis of the following evidence: empirical formula, $C_{16}H_9ClN_4S$; infrared spectrum (halo carbon-Nujol mull): C=C (1600 cm.$^{-1}$), CN (2252 cm.$^{-1}$), absence of CH=CH$_2$ absorption; ultraviolet spectrum (95% alcohol): $\lambda_{\max}$ 215 mμ (ϵ 33,510), 246 mμ (ϵ 19,590); n.m.r. spectrum[9] (<1% in DCCl$_3$): aromatic H (near 423 c.p.s.), =CH—C*H*—C(CN)$_2$ (multiplet, 232–265 c.p.s.), =C*H*-CH (doublet, 315 and 323 c.p.s.), CH$_2$ (multiplet, 150–190 c.p.s.); n.m.r. spectrum[9] (25% in acetone): aromatic H (complex near 422 c.p.s., weight ~5.3), =CH— (doublet, 353 and 360 c.p.s., weight ~1.0, J = 7.2 c.p.s.), =CH—C*H* (multiplet, 248–280 c.p.s., weight ~1.1), CH$_2$ (near solvent absorption). Compound IV gave a red product in boiling methanol[7] which was not further investigated.

Confirmation of the structure of the diene as IIa was achieved by its reduction, with hydrogen in the presence of excess black 5% palladium on barium sulfate, to V. The olefin was obtained in 60–68% yield and structure V was assigned on the basis of the following evidence: empirical formula, $C_{10}H_{11}ClS$; ultraviolet spectrum (95% alcohol): $\lambda_{\max}$ 213 mμ (ϵ 14,590), (shoulder) 221 mμ (ϵ 8070), 248 mμ (ϵ 10,250); infrared spectrum: CH$_2$ (2932 cm.$^{-1}$), CH$_3$ (2970, 2875, and 1370 cm.$^{-1}$), C=C (1600 cm.$^{-1}$), trisubstituted olefin (840 cm.$^{-1}$); n.m.r. spectrum[9] (20% in CCl$_4$): aromatic H (near 408 c.p.s., weight ~4.9), =CH— (triplet, 343, 350, 357 c.p.s., J = 6.9 c.p.s., weight ~1.0), —CH$_2$— (multiplet, 112–147 c.p.s., weight ~2.0), CH$_3$ (triplet, 49, 57, 65 c.p.s., J = 7.7 c.p.s., weight ~3.1). The n.m.r. spectrum is exactly that expected for V and is incompatable with any alternative position isomer. 1-Chloro-1-phenylmercaptobutene-1 was further characterized by oxidation (H$_2$O$_2$) to 1-chloro-1-phenylsulfonylbutene-1 (m.p. 31–32.5°). The infrared and nuclear magnetic resonance spectra of the sulfone are consistent with the assigned structure and are reported in the Experimental section.

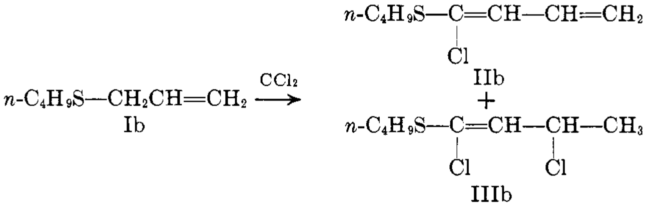


$$\underset{\text{IIa}}{C_6H_5S{-}\underset{\mathrm{Cl}}{\underset{|}{C}}{=}CH{-}CH{=}CH_2} \xrightarrow[\text{Pd–BaSO}_4]{H_2} \underset{\text{V}}{C_6H_5S{-}\underset{\mathrm{Cl}}{\underset{|}{C}}{=}CH{-}CH_2CH_3} + C_6H_5S{-}C_4H_9\text{-}n$$

n-Butyl phenyl sulfide was also isolated from the reduction products of IIa, and was identified by comparison of its infrared spectrum and its palladious chloride complex with those of authentic samples.

The reaction of allyl phenyl sulfide with the dichlorocarbene precursors produced, in addition to the major product IIa, a small amount of higher boiling liquid which eliminated hydrogen chloride upon distillation. When 2 equiv. of base were employed in the reaction, the higher boiling product was not detected, and the diene IIa was isolated pure in 60% yield. The structure IIIa was assigned to this second product by analogy (see IIIb, below) and is thought to form by addition of hydrogen chloride to the diene IIa.

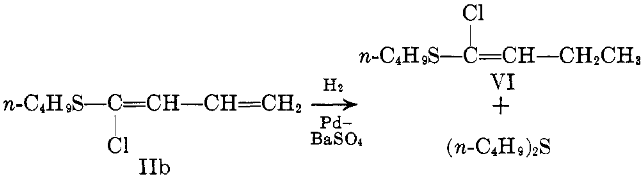
B. Reaction of Allyl *n*-Butyl Sulfide.—Two products were isolated from the reaction of allyl *n*-butyl sulfide and the dichlorocarbene precursors: a liquid A, identified as *cis* and *trans* IIb, and a liquid B, identified as *cis* and *trans* IIIb.



$$\underset{\text{Ib}}{n\text{-}C_4H_9S{-}CH_2CH{=}CH_2} \xrightarrow{CCl_2} \underset{\text{IIb}}{n\text{-}C_4H_9S{-}\underset{\mathrm{Cl}}{\underset{|}{C}}{=}CH{-}CH{=}CH_2} + \underset{\text{IIIb}}{n\text{-}C_4H_9S{-}\underset{\mathrm{Cl}}{\underset{|}{C}}{=}CH{-}\underset{\mathrm{Cl}}{\underset{|}{CH}}{-}CH_3}$$

It was evident from the empirical formula and infrared, ultraviolet, and n.m.r. spectra (see Experimental) that the major product (A, IIb, 68% yield) was structurally related to 1-chloro-1-phenylmercaptobutadiene (IIa). Further evidence for both *cis* and *trans* IIb was the appearance of two close peaks when analytically pure diene was chromatographed (v.p.c.) on Carbowax, and one peak with a shoulder when chromatographed on silicone grease.

Additional evidence for the structure of A as 1-*n*-butylmercapto-1-chlorobutadiene (IIb) was obtained by its reduction, with hydrogen in the presence of excess palladium on barium sulfate, to VI.



$$\underset{\text{IIb}}{n\text{-}C_4H_9S{-}\underset{\mathrm{Cl}}{\underset{|}{C}}{=}CH{-}CH{=}CH_2} \xrightarrow[\text{Pd–BaSO}_4]{H_2} \underset{\text{VI}}{n\text{-}C_4H_9S{-}\overset{\mathrm{Cl}}{\overset{|}{C}}{=}CH{-}CH_2CH_3} + (n\text{-}C_4H_9)_2S$$

The reduction did not proceed as selectively as did that of IIa; a total of 45% by weight of product was recovered which was composed of (1) di-*n*-butyl sulfide (proved by infrared and by vapor phase chromatography), approximately 25%; (2) recovered IIb, a minor component (by v.p.c.); and (3) the olefin VI (principal product by v.p.c.), which was characterized by elemental and spectral (infrared, ultraviolet, and n.m.r.) analysis (see Experimental).

In some runs involving reaction of allyl *n*-butyl sulfide with ethyl trichloroacetate and sodium methoxide a higher boiling liquid was obtained. This product was not obtained analytically pure since it evolved some hydrogen chloride upon distillation. The composition of this product was, however, in agreement with the molecular formula, $C_8H_{14}Cl_2S$. This formula corresponds to two products which could logically be expected from the reaction: (1) the insertion product VIII, IX, or XVIII; or (2) the product IIIb formed by addition of hydrogen chloride to the diene IIb. The

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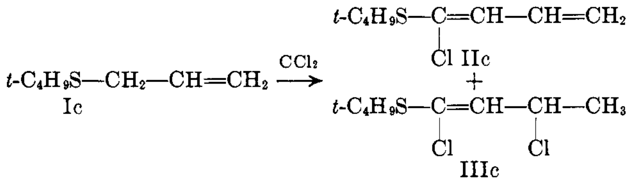
[7] For discussion of reactions of olefins with tetracyanoethylene, see J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962); **84**, 2216 (1962).

[8] The 1,4 Diels–Alder adduct seems less probable since vinyl hydrogen absorption in the n.m.r. spectrum would not be expected near 250 c.p.s. for such a product.

[9] The n.m.r. spectra were taken on Varian V 4302 at 56.44 Mc. (reference, tetramethylsilane). Weights are estimates obtained by using a planimeter.

infrared, ultraviolet, and n.m.r. spectra (see Experimental) were consistent with those expected for the diene–HCl addition product IIIb, but not for the insertion products VIII, IX, and XVIII. The structure of this material was shown to be IIIb by its independent synthesis by reaction of 1-*n*-butylmercapto-1-chlorobutadiene (IIb) with anhydrous hydrogen chloride.

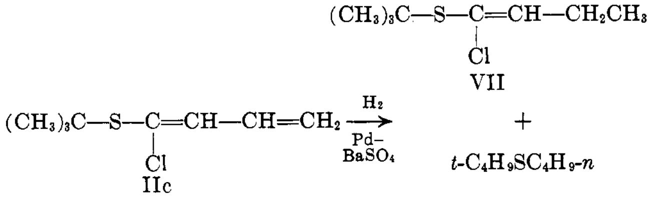
C. Reaction of Allyl *t*-Butyl Sulfide.—The principal product (66% yield) obtained by reaction of allyl *t*-butyl sulfide (Ic) with ethyl trichloroacetate and sodium methoxide was established, by processes similar to those described in A and B, above, to be 1-*t*-butylmercapto-1-chlorobutadiene (IIc). The minor component was identified as *cis* and *trans* IIIc.



$$\underset{\text{Ic}}{t\text{-}C_4H_9S{-}CH_2{-}CH{=}CH_2} \xrightarrow{CCl_2} t\text{-}C_4H_9S{-}\underset{Cl}{C}{=}CH{-}CH{=}CH_2\ \text{IIc} + \underset{\text{IIIc}}{t\text{-}C_4H_9S{-}\underset{Cl}{C}{=}CH{-}\underset{Cl}{CH}{-}CH_3}$$

The major compound showed one main peak, together with one small peak or shoulder, upon vapor phase chromatography using Reoplex, and only one peak using a silicone grease column as well as with two other columns employed. Whether a single isomer of IIc was formed predominantly, or whether the *cis* and *trans* isomers were not well resolved during chromatography, was not established. The diene IIc had the composition calculated for $C_8H_{13}ClS$. The ultraviolet, infrared, and nuclear magnetic resonance spectra (see Experimental) are comparable with those observed for IIa and IIb, and are consistent with the assigned structure IIc.

Reduction of IIc with brown 5% palladium on barium sulfate gave a 30% by weight recovery of product which was shown to be composed of VII and



$$\underset{\text{IIc}}{(CH_3)_3C{-}S{-}\underset{Cl}{C}{=}CH{-}CH{=}CH_2} \xrightarrow[\text{Pd–}BaSO_4]{H_2} \underset{\text{VII}}{(CH_3)_3C{-}S{-}\underset{Cl}{C}{=}CH{-}CH_2CH_3} + t\text{-}C_4H_9SC_4H_9\text{-}n$$

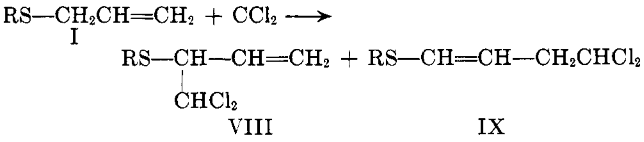
t-butyl *n*-butyl sulfide in the approximate ratio 4 to 1. The principal reduction product was assigned the structure *cis* and *trans* VII on the basis of elemental and spectral (ultraviolet, infrared, n.m.r.) analysis which are discussed in the Experimental section.

The n.m.r. spectrum of VII provided convincing evidence for both *cis* and *trans* isomers. Further evidence for *cis* and *trans* isomers of VII was provided by oxidation to the corresponding mixed sulfones. The n.m.r. spectrum of the mixture of *cis*- and *trans*-sulfone showed a split peak for the *cis* and *trans* $(CH_3)_3C{-}S$ groups, nearly identical triplets for the *cis* and *trans* CH_3 groups, and the —CH= group changed from four peaks (two superimposed triplets, two peaks in common) in the sulfide to five peaks (two superimposed triplets, one peak in common).

The higher boiling product obtained in some reactions with Ic was shown to be structurally related to IIIb and was assigned the structure *cis* and *trans* IIIc by analysis of the n.m.r., infrared, and ultraviolet spectra (see Experimental).

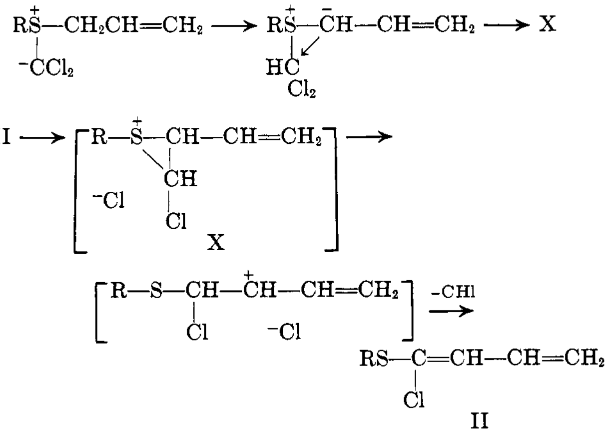
Discussion

By analogy[1,5] to reactions involving cyclic allyl sulfides and dichlorocarbene, the expected products of reaction of I with ethyl trichloroacetate and sodium methoxide are the insertion products VIII and IX.



$$\underset{\text{I}}{RS{-}CH_2CH{=}CH_2} + CCl_2 \longrightarrow \underset{\text{VIII}}{RS{-}\underset{CHCl_2}{CH}{-}CH{=}CH_2} + \underset{\text{IX}}{RS{-}CH{=}CH{-}CH_2CHCl_2}$$

Formation of the substituted butadienes (II), instead, is consistent with this expected course of reaction if it is assumed that the preferred insertion product is VIII,[10]



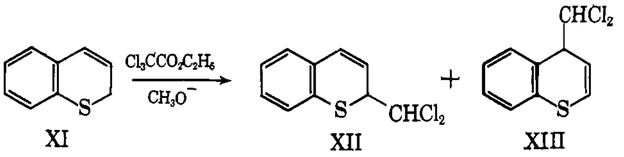
$$R\underset{{}^{-}CCl_2}{\overset{+}{S}}{-}CH_2CH{=}CH_2 \longrightarrow R\underset{HCCl_2}{\overset{+}{S}}{-}\overset{-}{C}H{-}CH{=}CH_2 \longrightarrow \text{X}$$

$$\text{VIII} \longrightarrow \underset{\text{X}}{\left[R{-}\overset{+}{S}{-}\underset{\underset{Cl}{CH}}{CH}{-}CH{=}CH_2\quad {}^{-}Cl\right]} \longrightarrow$$

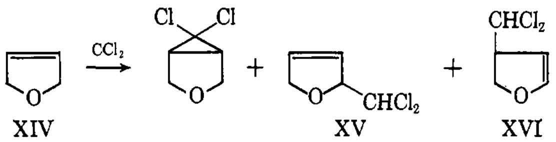
$$\left[R{-}S{-}\underset{Cl}{CH}{-}\overset{+}{C}H{-}CH{=}CH_2\quad {}^{-}Cl\right] \xrightarrow{\text{-CHl}} \underset{\text{II}}{RS{-}\underset{Cl}{C}{=}CH{-}CH{=}CH_2}$$

and that VIII decomposes as shown (VIII → X → II). Both of these assumptions are reasonable ones, although alternatives for the conversion of I to II (*i.e.*, I → XVII → XVIII → II) must be considered.

In the case of 2H-1-benzothiapyran (XI), the insertion products XII and XIII were formed in ratio of



approximately 2 to 1.[5] Furthermore, in the reaction of 2,5-dihydrofuran (XIV) with ethyl trichloroacetate and potassium *t*-butylate, in which both addition and insertion were noted, XV, but not XVI, was formed.[11]



With respect to rearrangement of VIII to II, as shown in VIII → X → II, there is a wealth of analogy for related rearrangements of sulfides substituted in the

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[10] It is possible that X is formed directly from the proposed intermediate "ylid" (XVII). This possibility is considered later in the discussion.

[11] J. C. Anderson and C. B. Reese, *Chem. Ind.* (London), 575 (1963).

TABLE I

REACTION OF SODIUM METHOXIDE (0.13 MOLE), CYCLOHEXENE (0.10 MOLE), AND ETHYL TRICHLOROACETATE (0.13 MOLE) IN PETROLEUM ETHER CONTAINING *n*-BUTYL PHENYL SULFIDE

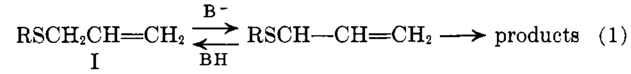
Sulfide added, mole	Yield of dichloronorcarane, %		Recovered cyclohexene (by v.p.c.), %	Recovered sulfide, %	Recovered CCl_4, mole
	Impure	Pure			
0	79	73	<5		0.011
0.013	50	44	28	Small[a]	0.015
0.05	46	36	38	75[b]	0.011
0.10	30	25	48	80[b]	0.021

[a] Not determined quantitatively. [b] A small amount of higher boiling product, formulated as the sulfide corresponding to sulfone XXIV, was detected.

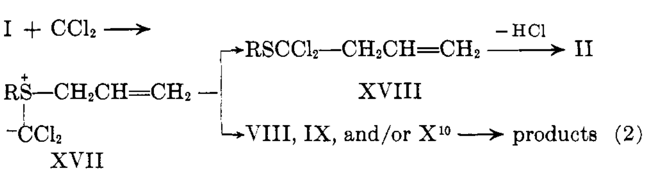
β-position in a manner which permits formation of three-membered ring sulfonium intermediates.[12]

A number of mechanisms can be written for the insertion of dichlorocarbene into allyl sulfides. While the course of this reaction has not been established, we have gained additional information concerning this insertion reaction which we would like to report.

Of the three gross reaction paths shown in eq. 1–3, the first can now be eliminated with some certainty.



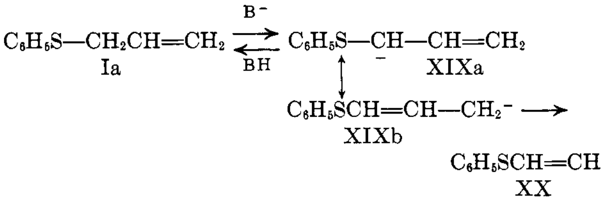
$$\underset{\text{I}}{RSCH_2CH{=}CH_2} \underset{BH}{\overset{B^-}{\rightleftharpoons}} RS\bar{C}H{-}CH{=}CH_2 \longrightarrow \text{products} \quad (1)$$

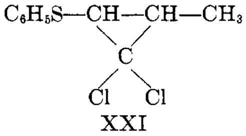


(2)

$$I + CCl_2 \xrightarrow{\text{direct insertion}} \text{products} \quad (3)$$

It was shown in this study that Ia is not isomerized to the vinyl sulfide XX by sodium methoxide under conditions employed for the dichlorocarbene reaction; furthermore, the olefin recovered from the carbene reactions was Ia, uncontaminated by XX.[13] Of more significance, however, was the observation that potassium *t*-butylate in petroleum ether (b.p. 30–60°) does cause isomerization of Ia to XX, and does consequently, involve formation of the anion XIXa ↔ XIXb. When Ia was treated with potassium *t*-butylate and ethyl trichloroacetate, considerable cyclopropane XXI was formed.[14] Since no cyclopropanes were evident in reactions involving I when methoxide was used as base, it was concluded that the carbanion XIXa ↔ XIXb was not an intermediate in these reactions.



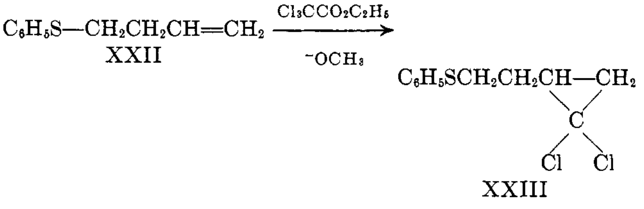


XXI

Reaction path 2 has as its principle feature the formation of an intermediate "ylid", and was suggested originally[5] to explain the difference in behavior of vinyl and allyl sulfides with dichlorocarbene. The formation of an intermediate "ylid" is reasonable in view of the nucleophilic character of sulfur,[15] and in view of the facile formation of stable "ylids" from dichlorocarbene and triphenylphosphorus.[16]

While we have not confirmed the existence of the "ylid" intermediate we have been able to show that divalent sulfur plays a significant role in reactions involving ethyl trichloroacetate and olefins. Specifically, *sulfide sulfur inhibits formation of dichlorocarbene addition products.* For this study the reaction of ethyl trichloroacetate and sodium methoxide in olefin-free petroleum ether was carried out under controlled conditions with cyclohexene containing various quantities of *n*-butyl phenyl sulfide.

It can be seen readily from Table I that the addition of *n*-butyl phenyl sulfide does have a profound effect upon the yield of dichloronorcarane and upon the amount of recovered cyclohexene. The inhibiting effect of sulfide sulfur on dichlorocyclopropane formation was also evident from a study of the reaction of ethyl trichloroacetate and sodium methoxide with 3-butenyl phenyl sulfide (XXII). Under conditions identical with those employed for reactions with cyclohexene, vinyl sulfides,[1] and allyl sulfides, the sulfide XXII gave only a 17% yield of impure cyclopropane (XXIII), characterized by conversion to the corresponding sulfone. Of more significance, however, was the recovery of 50–53% of the starting olefin. That an "ylid" forms, which only slowly reacts with olefin to give adduct, is not born out by studies in which the reaction time with XXII was extended; the yields of cyclopropane XXIII were comparable.



The reaction of ethyl trichloroacetate, sodium methoxide, and saturated sulfides has not provided much useful data to date. With *n*-butyl phenyl sulfide there was obtained (1) much tar, (2) 75% recovery

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[12] *Cf.* (a) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962, p. 9–55; (b) W. E. Parham and M. D. Bhavsar, *J. Org. Chem.*, **28**, 2686 (1963); (c) **29**, 1575 (1964); (d) K. D. Gundermann, *Angew. Chem.*, **75**, 1194 (1963).

[13] Similar results were previously described for the olefin XI and the corresponding isomeric vinyl sulfide. See ref. 5.

[14] The reactions of vinyl sulfides with ethyl trichloroacetate and alkoxide leads to the formation of cyclopropanes; see ref. 1.

[15] For a discussion of the electrophilic character of dichlorocarbene, see (a) W. von E. Doering and W. A. Henderson, *J. Am. Chem. Soc.*, **80**, 5274 (1958); (b) R. C. Woodworth and P. S. Skell, *ibid.*, **79**, 2542 (1957).

[16] A. J. Speziale and K. W. Ratts, *ibid.*, **84**, 854 (1962).

TABLE II

REACTION OF ALLYL PHENYL SULFIDE, ALKOXIDE, AND ETHYL TRICHLOROACETATE

Sulfide Ia, mole	Alkoxide, mole	$Cl_3CCO_2C_2H_5$, mole	Recovered olefin, %	Product yield (calcd. on Ia employed, %)
0.18	CH_3O^- (0.28)[a]	0.26	15[b]	IIa (49)
0.20	CH_3O^- (0.20)[a]	0.20	26[b]	IIa (46)
0.10	CH_3O^- (0.20)[c]	0.10	9[b]	IIa (60)
0.22	CH_3O^- (0.30)[c]	0.27	20[b]	IIa + IIIa[d] (~45)
0.207	CH_3O^- (0.32)[c]	0.22	12[b]	IIa (52)[e]
0.10	*t*-$C_4H_9O^-$ (0.20)[h]	0.10	25[f]	Substituted cyclopropane[g]

[a] Dry sodium methoxide was prepared from sodium.[1] [b] No propenyl sulfide was detected in the recovered olefin. [c] Commercial sodium methoxide. [d] The structure of IIIa was not established but was assigned by analogy to IIIb. The impure diene IIa distilled first (16.0 g., b.p. 93–96° at 0.4 mm., $n^{25.5}$D 1.6154); the higher boiling IIIa (6.0 g., b.p. 90–100° at 0.04 mm., $n^{25.5}$D 1.6038) distilled with some evolution of hydrogen chloride. [e] A solution of the crude product (prior to distillation) was refluxed (1 hr.) in pyridine (30 ml.); the resulting mixture was extracted, dried, and distilled. [f] Completely isomerized (infrared and v.p.c.) to phenyl propenyl sulfide. [g] The fractionated product (7.2 g.) was shown to be principally 1,1-dichloro-2-methyl-3-phenylmercaptocyclopropane.[1] [h] Commercial potassium *t*-butoxide.

of sulfide, and (3) a small amount of an impure higher boiling liquid which provided a pure sulfone upon oxidation with hydrogen peroxide. The structure of

$$n\text{-}C_4H_9S\text{—}C_6H_5 \xrightarrow[\text{(2) } H_2O_2]{\text{(1) } ^-OCH_3,CCl_3CO_2C_2H_5} C_6H_5SO_2CCl_2CHClCH_2CH_2CH_3$$

XXIV

the sulfone ($C_{11}H_{13}Cl_3O_2S$) has not been established; however, the corresponding n.m.r. spectrum suggests XXIV. The formation of the trichloro sulfide is, however, of questionable significance to the mechanism of the insertion reaction in view of the low yield, and the fact that a chlorination process is known to occur in reactions of ethyl trichloroacetate and sodium methoxide.[17,18] The reaction of saturated sulfides with dichlorocarbene precursors will, however, be the subject of further study.

Experimental

Allyl phenyl sulfide (**Ia**) was prepared in 87% yield by the method of Hurd and Greengard[19a] and had the following properties: b.p. 102.5–103.5° (12 mm.), n^{20}D 1.5770 (lit.[19b] n^{20}D 1.5760); $\lambda_{\max}^{95\%\ \text{alc}}$ 254 mμ (ϵ 7130); ν^{neat} C═C (1628 cm.$^{-1}$), CH═CH_2 (908, 976, 1840 cm.$^{-1}$); n.m.r. spectrum[6] (neat): aromatic H (complex, 397–423 c.p.s., weight 4.9), ═CH (complex 308–348 c.p.s., weight 1.0), ═CH_2 (three split peaks of ~ equal intensity at 272, 280, and 288 c.p.s., total weight 1.9), —S—CH_2 (split doublet, 179 and 186 c.p.s., weight 1.8).

Isomerization of Allyl Phenyl Sulfide.—A mixture of Ia (11.25 g., 0.075 mole), potassium *t*-butoxide (17.2 g., 0.15 mole), and petroleum ether (100 ml., b.p. 30–60°) was treated exactly as in reactions containing ethyl trichloroacetate (see synthesis of II). There was obtained 9.8 g. (87% yield) of phenyl propenyl sulfide (b.p. 46–50° at 0.07 mm., n^{24}D 1.5840). Comparison of the infrared spectrum and vapor phase chromatogram (silicone grease column set at 200°, carrier He, flow ~15 p.s.i.) of the product with authentic phenyl propenyl sulfide indicated that isomerization was complete. When sodium methoxide was used in place of potassium *t*-butoxide no isomerization was detected.

1-Chloro-1-phenylmercaptobutadiene (**IIa**).—The procedure employed was essentially identical with that previously described for the preparation of 1,1-dichlorocyclopropanes from vinyl sulfides.[1] The effect of changes of mole ratio of reactants is summarized in Table II. Spectra are described in the text.

Vapor phase chromatogram showed one peak (8.9% Reoplex on Chromosorb 60–80 M at 200°, flow 30 ml. He/min. and on Carbowax 20 M on Fluoropak, 245°, carrier He at ~40 p.s.i.).

Anal. Calcd. for $C_{10}H_9ClS$: C, 61.06; H, 4.61; Cl, 18.03; S, 16.30. Found: C, 60.93; H, 4.72; Cl, 18.09; S, 16.13.

Reaction of IIa with Tetracyanoethylene (**TCE**).—The violet solution prepared from IIa (6.2 g., 0.032 mole), tetracyanoethylene (3.45 g., 0.027 mole), and ethyl acetate (30 ml.) was allowed to stand for 3 days, then was concentrated, and petroleum ether (b.p. 30–60°, 20 ml.) was added. The solid obtained was partially sublimed (80° at 0.05 mm.) to remove TCE, and the residue (6.2 g., m.p. 125–131°, 70% yield) was recrystallized several times from benzene and benzene–petroleum ether (b.p. 30–60°). The white solid thus obtained weighed 3.8 g. (43% yield) and melted at 143–144°. Structure IV was assigned to this product on the basis of the spectra described in the text.

Anal. Calcd. for $C_{16}H_9ClN_4S$: C, 59.16; H, 2.79; N, 17.25. Found: C, 59.37; H, 2.89; N, 17.55.

Compound IV decomposed in hot methanol (16 hr.) to a dark red solid, m.p. 186–187° dec. (from CCl_4), which was not identified.

Anal. Found: C, 67.41; H, 3.55; N, 11.34.

Reduction of 1-Chloro-1-phenylmercaptobutadiene (**IIa**) **to 1-Chloro-1-phenylmercaptobutene-1** (**V**).—1-Chloro-1-phenylmercaptobutadiene (IIa, 7.0 g., 0.036 mole) was reduced with hydrogen (50 p.s.i.) in absolute ethanol (100 ml.) using 5% palladium on barium sulfate (black, 28 g.) as catalyst. After 2 hr. at room temperature 0.053 mole of hydrogen was consumed. The catalyst was removed (Filter-cell) and the residue was distilled to give (1) *n*-butyl phenyl sulfide, 0.4 g., b.p. 35–48° (0.03 mm.), n^{20}D 1.5500, and (2) 1-chloro-1-phenylmercaptobutene-1, 4.8 g., 68% yield, b.p. 48–51.5° (0.03 mm.), n^{26}D 1.5704.

n-**Butyl phenyl sulfide**, fraction 1, was identified by infrared (comparison with authentic), and by conversion to the palladium chloride complex (m.p. and m.m.p. 104–106°).[20]

Fraction 2 was redistilled (b.p. 44–46.5° at 0.02 mm., $n^{25.5}$D 1.5740) and was assigned the structure **1-chloro-1-phenylmercaptobutene-1** (**V**) on the basis of the spectral data described in the text. The vapor phase chromatogram showed one peak (column, Carbowax 20 M on Fluoropak, 245°, carrier He at ~40 p.s.i.).

Anal. Calcd. for $C_{10}H_{11}ClS$: C, 60.44; H, 5.58. Found: C, 60.20; H, 5.77.

The olefin V was further characterized by conversion to 1-chloro-1-phenylsulfonylbutene-1.

1-Chloro-1-phenylsulfonylbutene-1.—A mixture of V (6.6 g., 0.033 mole), acetic acid (15 ml.), and hydrogen peroxide (5 ml., 30%) was heated at 100° for 1 hr., and water (50 ml.) then was added. The resulting mixture was extracted with ether and the ether solution was washed with five portions of saturated sodium carbonate and one portion of water. The ether was dried ($MgSO_4$) and the residue (6.0 g., 79% yield) was distilled to give 4.1 g. (54% yield) of 1-chloro-1-phenylsulfonylbutene-1 (b.p. 96–99° at 0.04 mm., $n^{25.5}$D 1.5513, m.p. 31–32.5° from absolute alcohol–petroleum ether at Dry Ice temperature).

1-Chloro-1-phenylsulfonylbutene-1 showed ν^{neat} C═C (1600–1610 cm.$^{-1}$), —SO_2 (near 1310 and 1135 cm.$^{-1}$); n.m.r. spec-

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(17) That a chlorination process can be involved in reactions involving ethyl trichloroacetate and sodium methoxide is evidenced by formation of carbon tetrachloride in reactions summarized in Table I.

(18) A chlorination process has also been observed in reactions involving sodium trichloroacetate. *Cf.* W. M. Wagner, H. Kloosterziel, and H. F. Bickel, *Rec. trav. chim.*, **81**, 925 (1962).

(19) (a) C. D. Hurd and H. Greengard, *J. Am. Chem. Soc.*, **52**, 3356 (1930); (b) D. S. Tarbell and M. A. McCall, *ibid.*, **74**, 48 (1952).

(20) V. N. Ipatieff, H. Pines, and B. S. Friedman, *ibid.*, **60**, 2731 (1938).

trum[9] (20% in CCl_4): aromatic H (complex near 441 and 428 c.p.s., weight ~5.0), =CH— (triplet, 396, 403, 410 c.p.s., J = 7.3 c.p.s., weight ~1.0), CH_3 (triplet, 53, 60, and 67 c.p.s., J = 7.3 c.p.s., weight ~3), CH_2 (complex, 115–146 c.p.s., weight ~1.8).

Anal. Calcd. for $C_{10}H_{11}ClO_2S$: C, 52.05; H, 4.81. Found: C, 51.76; H, 4.93.

Allyl *n*-butyl sulfide (Ib) was prepared in 69% yield as previously described[21] and had b.p. 66–67° (29 mm.), $n^{25.5}$D 1.4652, lit.[21] n^{20}D 1.4677; ν^{neat} C=C (1630 cm.$^{-1}$), $CH{=}CH_2$ (905, 980, and 1830 cm.$^{-1}$); $\lambda_{\max}^{95\%\ \text{alc}}$ 207 mμ (ϵ 1400), 218 mμ (ϵ 1280); n.m.r. spectrum[9] (20% in CCl_4): CH_3 (complex 43–58 c.p.s., weight ~2.9), CH_3-$\mathit{CH_2}$-$\mathit{CH_2}$ (complex 64–94 c.p.s., weight ~3.8), $-SCH_2$ (complex, 127–143 c.p.s., weight ~1.8), —S-$\mathit{CH_2}$-CH= (doublet, 168 and 175 c.p.s., J = 7.0 c.p.s., weight ~2.0), —CH= (complex 304–346 c.p.s., weight ~1.0), $=CH_2$ (complex, 270–292 c.p.s., weight ~2.1).

1-*n*-Butylmercapto-1-chlorobutadiene (IIb).—The reaction of Ib (20.0 g., 0.154 mole), ethyl trichloroacetate (38.3 g., 0.20 mole), and commercial sodium methoxide (11.6 g., 0.21 mole, weighed in a drybox) in olefin-free petroleum ether (150 ml., b.p. 30–60°) was carried out as described for Ia. Distillation of the crude product gave 18.5 g. (68%) yield) of 1-*n*-butylmercapto-1-chlorobutadiene (b.p. 44–48° at 0.8 mm., n^{26}D 1.5301).

The diene IIb showed $\lambda_{\max}^{95\%\ \text{alc}}$ 234 mμ (ϵ 14,450), 280 mμ (ϵ 11,500); ν^{neat} C=C (1610 cm.$^{-1}$), $CH{=}CH_2$ (900, 980, and 1825 cm.$^{-1}$): n.m.r. spectrum[9] (20% in CCl_4): CH_3 (complex 43–61 c.p.s., weight ~2.9), CH_2 (complex 68–102 c.p.s., weight ~3.8), $\mathit{CH_2}$S (complex 150–168 c.p.s., weight ~2.0), $=CH_2$ (complex 280–303 c.p.s., weight ~2.2), =CH (complex 362–396 c.p.s., weight ~2.1); v.p.c.: one peak with shoulder (column, Dow-Corning silicone grease, carrier He ~ 40 p.s.i., 195°), two unresolved peaks (Carbowax 20 M on Fluoropak, carrier He ~40 p.s.i., 191°) of approximate peak ratio 7:8.

Anal. Calcd. for $C_8H_{13}ClS$: C, 54.37; H, 7.42. Found: C, 54.43; H, 7.59.

***cis,trans*-1-*n*-Butylmercapto-1,3-dichlorobutene-1 (IIIb). A.**—In another reaction involving Ib (27.6 g., 0.21 mole), commercial sodium methoxide (15.0 g., 0.28 mole), and ethyl trichloroacetate (48.1 g., 0.25 mole) some hydrogen chloride was evolved during distillation. There was obtained, in addition to IIb (b.p. 59–62° at 1.3 mm., n^{26}D 1.5272, 15.0 g., yield 40%), a higher boiling liquid (1.3 g., b.p. 48–50° at 0.01 mm., n^{26}D 1.5060) which was shown to be principally IIIb. This product evolved some hydrogen chloride upon repeated distillation and was not obtained pure.

Impure IIIb showed $\lambda_{\max}^{95\%\ \text{alc}}$ 208 mμ (ϵ 6210), λ (shoulder) 225 mμ (ϵ 3010), $\lambda_{\max}$ 254 mμ (ϵ 2400); ν^{neat} C=C (1600 cm.$^{-1}$), and weak absorption in the region 905, 980, 1835 cm.$^{-1}$ (weak $CH{=}CH_2$, probably butadiene impurity); n.m.r. spectrum[9] (20% in CCl_4): $\mathit{CH_3}$–$(CH_2)_3$– (complex, 47–60 c.p.s., weight ~2.7), $CH_3\mathit{CH_2}\mathit{CH_2}CH_2$ and $\underset{\text{Cl}}{\underset{|}{\text{CH}}}\text{–}\mathit{CH_3}$ (complex, 70–96 c.p.s., weight ~6.7), S–$\mathit{CH_2}$ (complex, 150–167 c.p.s., weight ~1.8), $\underset{\text{Cl}}{\underset{|}{\text{–CH}}}$ (complex, 258–291 c.p.s., weight ~1.0), =CH (two doublets, 334, 343, and 338, 348 c.p.s., J_1 = J_2 = 9.4 c.p.s., weight ~1.0).

Anal. Calcd. for $C_8H_{14}Cl_2S$: C, 45.07; H, 6.62; Cl, 33.26; S, 15.04. Found: C, 45.90; H, 6.05; Cl, 31.91; S, 14.94.

B.—A cold (ice bath), stirred solution of 1-*n*-butylmercapto-1-chlorobutadiene (IIb, 6.0 g., 0.034 mole) in petroleum ether (30 ml., b.p. 30–60°) was treated with gaseous hydrogen chloride for 2.5 hr. The solvent was removed (rotatory evaporator), and the residue was distilled. Some hydrogen chloride was evolved during distillation; there was obtained 3.1 g. of recovered IIb and 1.9 g. of impure IIIb. Redistillation of IIIb afforded a product (0.5 g., n^{24}D 1.5090, b.p. 51–52° at 0.05 mm.), which had essentially identical n.m.r. and infrared spectra as the product described in A above.

Reduction of 1-*n*-Butylmercapto-1-chlorobutadiene (IIb) to 1-*n*-Butylmercapto-1-chlorobutene-1. (VI).—The reduction of IIb (5.5 g., 0.031 mole) with hydrogen (50 p.s.i.) in absolute ethanol (50 ml.) was carried out as described for the reduction of IIa using 5% palladium on barium sulfate (black, 25 g.) as catalyst. Distillation of the crude product gave 2.5 g. of combined product which was shown by vapor phase chromatography (Carbowax 20 M on Fluoropak column, 215°, carrier He ~40 p.s.i.) to contain di-*n*-butyl sulfide (25%), IIb (small amount), and a principal product subsequently identified as VI. Fractionation of the total distillate gave pure di-*n*-butyl sulfide (b.p. 30–34° at 1.2 mm., $n^{25.5}$D 1.4510), identified by comparison (v.p.c. and infrared spectrum) with an authentic sample, and VI (b.p. 93–94° at 19 mm., n^{23}D 1.4885).

The olefin VI showed $\lambda_{\max}^{95\%\ \text{alc}}$ 209 mμ (ϵ 7430), λ (shoulder) 225 mμ (ϵ 3130), $\lambda_{\max}$ 254 mμ (ϵ 2610); ν^{neat} C=C (1590–1600 cm.$^{-1}$), absence of absorption at 980 and 1830 cm.$^{-1}$ (no $—CH{=}CH_2$), trisubstituted olefin (835 cm.$^{-1}$); n.m.r. spectrum[9] (20% in CCl_4): CH_3 (two triplets, 45–68 c.p.s., weight ~5.4), $CH_3\mathit{CH_2}$-$\mathit{CH_2}$ (complex, 68–99 c.p.s., weight ~3.7), $—SCH_2—$(complex, 144–167 c.p.s., weight ~2.0), =CH— (triplet, 331, 339, 347 c.p.s., J = 7.6, weight ~1.0), =CH-$\mathit{CH_2}$ (complex, 108–144 c.p.s., weight ~2.0).

Anal. Calcd. for $C_8H_{15}ClS$: C, 53.76; H, 8.46. Found: C, 53.87; H, 8.69.

Allyl *t*-butyl sulfide (Ic) was prepared (67% yield) as previously described[22] and showed b.p. 142.5–144°, n^{20}D 1.4651 (lit.[22] b.p. 139–141.5°, n^{20}D 1.4638); $\lambda_{\max}^{95\%\ \text{alc}}$ 208 mμ (ϵ 1410), λ (shoulder) 216 mμ (ϵ 850); ν^{neat} C=C (1636 cm.$^{-1}$), $CH{=}CH_2$ (908, 985, and 1830 cm.$^{-1}$); n.m.r. spectrum[9] (20% in CCl_4): $(CH_3)_3C$ (singlet, 73 c.p.s.), CH_2 (doublet, 173 and 179 c.p.s., J = 6.3 c.p.s., weight ~1.9), =CH (multiplet, 309–350 c.p.s., weight ~1.0), $=CH_2$ (triplet of nearly equal intensity, 278, 287, 296 c.p.s., weight ~1.9).

1-*t*-Butylmercapto-1-chlorobutadiene (IIc).—The reaction of Ic (12.0 g., 0.09 mole), ethyl trichloroacetate (24.0 g., 0.13 mole), and sodium methoxide (from 3.2 g., 0.14 g.-atom of sodium) was carried out as described for IIa. 1-*t*-Butylmercapto-1-chlorobutadiene (10.4 g., 66% yield) was collected at 83–85° (12 mm.) and showed n^{20}D 1.5272; ν^{neat} C=C (1610 cm.$^{-1}$), $CH{=}CH_2$ (905, 985, and 1830 cm.$^{-1}$); $\lambda_{\max}^{95\%\ \text{alc}}$ 246 mμ (ϵ 18,820), $\lambda_{\max}$ 285 mμ (ϵ 4490); n.m.r. spectrum (pure liquid)[6]: $(CH_3)_3C$ (split peak, 74 c.p.s., weight 9.4), $=CH_2$ (complex, 300–338 c.p.s., weight 2.0), =CH (complex 380–416 c.p.s., weight 2.0); v.p.c.: two nearly superimposed peaks (8.9% Reoplex on Chromosorb 60–80 M., He flow 30 ml./min., 150°) of relative heights 1:10, one peak (Dow-Corning silicone grease column, carrier flow He ~40 p.s.i., 195°), one peak (diisodecylphthalate column, carrier flow He ~15 p.s.i., 173°).

Anal. Calcd. for $C_8H_{13}ClS$: C, 54.37; H, 7.42; Cl, 20.06; S, 18.15. Found: C, 54.38; H, 7.64; Cl, 20.37; S, 17.87.

***cis,trans*-1-*t*-Butylmercapto-1,3-dichlorobutene-1 (IIIc).**—In another reaction of Ic (32.5 g., 0.25 mole) with ethyl trichloroacetate (68.3 g., 0.36 mole) and commercial sodium methoxide (20.4 g., 0.38 mole), distillation of the product was accompanied by elimination of some hydrogen chloride. The yield of IIc was 54% (24.0 g.). There was also obtained 2.1 g. of higher boiling material (b.p. 58–61° at 1.8 mm., n^{25}D 1.5050) which was not obtained pure since it lost some hydrogen chloride upon repeated distillation. This higher boiling material was assigned structure IIIc by comparison of the following properties with those of IIIb: $\lambda_{\max}^{95\%\ \text{alc}}$ 211 mμ (ϵ 10,590), $\lambda_{\max}$ 255 mμ (ϵ 3000); ν^{neat} C=C (1590 cm.$^{-1}$), weak or no absorption near 905, 915, and 1830 cm.$^{-1}$ indicating absence of $—CH{=}CH_2$; n.m.r. spectrum[9] (20% in CCl_4): *cis–trans* $(CH_3)_3C$– (split peak at 82 c.p.s.), *cis–trans* CH_3– (two split doublets 91, 98 c.p.s.), =CH— (two doublets, 347, 356 and 351, 360 c.p.s.), $-CHCl$ (complex 257–302 c.p.s.).

Reduction of IIc to *t*-Butyl *n*-Butyl Sulfide and *cis,trans*-1-*t*-Butylmercapto-1-chlorobutene-1 (VII).—The diene IIc (10.0 g., 0.057 mole) was reduced in absolute alcohol (140 ml.) with hydrogen (50 p.s.i.) and 5% palladium on barium sulfate[23] (26 g.) as described for the reduction of IIa and IIb. Distillation of the reaction residue gave two products (A and B).

Product A (0.6 g., 6% yield, b.p. 60–65° at 24 mm., n^{25}D 1.4498) was shown to be identical (v.p.c., infrared) with authentic *t*-butyl *n*-butyl sulfide (prepared, 54% yield, b.p. 62–63° at 20 mm., n^{25}D 1.4453, from *t*-butylmercaptane and *n*-butyl bromide).

Product B (2.45 g., 24% yield, b.p. 35–43° at 1 mm., n^{25}D 1.4860) showed by v.p.c. two peaks (ratio ~9:1, neither due to *t*-butyl *n*-butyl sulfide, on silicon oil DC-200 column set at 180°); $\lambda_{\max}^{95\%\ \text{alc}}$ 212 mμ (ϵ 10,360), 258 mμ (ϵ 1440); ν^{neat} C=C (1590–1600 cm.$^{-1}$), absence of absorption near 905, 980, 1830 cm.$^{-1}$ (no $CH{=}CH_2$); n.m.r. spectrum[9] (20% CCl_4): $—CH_3$ (triplets, 50,

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[21] L. Bateman and J. G. Cunneen, *J. Chem. Soc.*, 1596 (1955).

[22] D. S. Tarbell and W. E. Lovett, *J. Am. Chem. Soc.*, **78**, 2259 (1956).

[23] The Pd–$BaSO_4$ was brown (Engelhard Co.) and was more active than that employed for reduction of IIa and IIb.

57, 64 c.p.s., and 52, 59, 66 c.p.s., $J_1 = J_2 = 7.0$ c.p.s., weight ~3.3), *t*-butyl (two peaks, 78 and 80 c.p.s.), $=CH-$ (four peaks, 339, 346, 353, 360 c.p.s., due to two nearly superimposed triplets, $J = 7.0$ c.p.s., weight ~1.0), CH_2 (split quintet 113–147, $J = 7.0$ c.p.s., weight ~2.2).

Anal. Calcd. for $C_8H_{15}ClS$: C, 53.76; H, 8.46. Found: C, 53.39; H, 8.43.

These data are consistent with the assigned structure *cis-trans* 1-*t*-butylmercapto-1-chlorobutene (VII). The butene VII (0.8 g.) was oxidized to the sulfone (0.3 g., oil), *cis,trans*-1-*t*-butylsulfonyl-1-chlorobutene-1, which showed ν^{neat} $C{=}C$ (1590–1605 cm.$^{-1}$), no $CH{=}CH_2$ (absence of absorption near 985 and 1830 cm.$^{-1}$); n.m.r. spectrum[9] (20% in CCl_4): CH_3 (two triplets, 53, 61, 68 c.p.s. and 56, 67, 71 c.p.s.), *t*-butyl (split singlet, 79 c.p.s.), $=CH-$ (five peaks, probably two triplets at 367, 375, 383 c.p.s. and 383, 391, and 399 c.p.s., weight ~1.0), CH_2 (multiplet 117–165 c.p.s., weight ~1.8).

Anal. Calcd. for $C_8H_{15}ClO_2S$: C, 45.49; H, 7.18. Found: C, 45.60; H, 7.04.

4-Phenylmercaptobutene-1 (XXII).—This sulfide (b.p. 72–74° at 1.4 mm., $n^{25}\text{D}$ 1.5621) was prepared (86% yield) from 1-bromobutene-3[24] and thiophenol as described[22] for the preparation of allyl *t*-butyl sulfide. This sulfide (XXII) showed ν^{neat} $C{=}C$ (1635 cm.$^{-1}$), $-CH{=}CH_2$ (905, 983, and 1840 cm.$^{-1}$).

Anal. Calcd. for $C_{10}H_{12}S$: C, 73.11; H, 7.37. Found: C, 73.30; H, 7.61.

1,1-Dichloro-2-(2-phenylmercaptoethyl)cyclopropane (XXIII).—The reaction of XXII (16.4 g., 0.10 mole) with ethyl trichloroacetate (28.7 g., 0.15 mole) and commercial sodium methoxide (8.7 g., 0.16 mole), as described for olefins Ia–c, gave recovered sulfide XXII (8.3 g., 50%), the cyclopropane XXIII (impure, b.p. 110–130° at 0.1–0.6 mm., $n^{26}\text{D}$ 1.5771, 4.2 g., 17% yield), and residual tar (5.6 g.).

The cyclopropane XIII, after redistillation (b.p. 85–87° at 0.01 mm., $n^{26}\text{D}$ 1.5754) showed weak absorption at ν^{neat} 1635, 910, and 985 cm.$^{-1}$ assigned to olefin impurity. The cyclopropane XXIII (1.7 g., 0.006 mole) was characterized by conversion to 1,1-dichloro-2-(2-phenylsulfonylethyl)cyclopropane by oxidation with hydrogen peroxide in acetic acid. The crude oily sulfone was crystallized by cooling its solution in ethanol to Dry Ice temperature. The solid sulfone was then recrystallized from ethanol–petroleum ether (30–60°) and melted at 64.5–65.5° (0.7 g., 36% yield from XXIII).

1,1-Dichloro-2-(2-phenylsulfonylethyl)cyclopropane showed absence of olefin in its infrared and n.m.r. spectra. The n.m.r. spectrum[9] (20% in $DCCl_3$) showed aromatic H (complex, 438–453 c.p.s., weight ~4.9), SCH_2 (complex, 177–197 c.p.s., weight ~2.0), other H (complex, 57–126 c.p.s., weight ~5.2).

Anal. Calcd. for $C_{11}H_{12}Cl_2O_2S$: C, 47.32; H, 4.33. Found: C, 47.40; H, 4.48.

The reaction XXII with dichlorocarbene precursors was carried out as described above; however, the reaction time was increased to 66 hr. Essentially identical results were obtained.

Reaction of *n*-Butyl Phenyl Sulfide with Dichlorocarbene.—The reaction of ethyl trichloroacetate (38.0 g., 0.20 mole), commercial sodium methoxide (10.8 g., 0.20 mole), and *n*-butyl phenyl sulfide (20.0 g., 0.12 mole) in olefin-free petroleum ether (90 ml., b.p. 30–60°) was carried out as described for Ia. Distillation of the residue gave recovered *n*-butyl phenyl sulfide (15.0 g., 75%). A small amount of higher boiling material (2.1 g., $n^{26}\text{D}$ 1.5596) was obtained which was not obtained pure by fractionation (b.p. 75–80° at 0.05 mm., $n^{22}\text{D}$ 1.5656). This product (2.1 g.) was oxidized with hydrogen peroxide in acetic acid and the crude sulfone was dissolved in ethanol and cooled in Dry Ice–acetone. The crude solid sulfone (0.6 g., m.p. 85–91°) was recrystallized from alcohol–petroleum ether (b.p. 30–60°); the product melted at 100–102°.

The sulfone showed $\nu^{CCl_4-CS_2}$ $-SO_2-$ (1335–1345 and 1155 cm.$^{-1}$); n.m.r. spectrum[9] (20% in $DCCl_3$): CH_3 (triplet, 47, 53, and 60 c.p.s., $J = 6.7$ c.p.s., weight ~3.2), aromatic H (two split peaks, 419–429 and 429–457 c.p.s., weight ~5.1), $-\underset{\displaystyle \mathrm{Cl}}{\underset{|}{\mathrm{CH}}}-$ (four peaks of equal intensity, probably two doublets, 218, 220, 224, and 227 c.p.s., weight ~1.0), CH_2 (multiplet, 75–111 c.p.s., weight ~2.1), CH_2 (multiplet, 111–147 c.p.s., weight ~2.0).

Anal. Calcd. for $C_{11}H_{13}Cl_3O_2S$: C, 41.85; H, 4.15; Cl, 33.70; S, 10.16. Found: C, 41.80; H, 4.12; Cl, 33.63; S, 10.07.

This product has not been identified but is tentatively assigned the structure 1-phenylsulfonyl-1,1,2 trichloropentane (XXIV).

The reaction of cyclohexene (8.2 g., 0.10 mole), ethyl trichloroacetate (24.8 g., 0.13 mole), commercal sodium methoxide (7.2 g., 0.13 mole), and *n*-butyl phenyl sulfide (0–0.10 mole) was carried out as described for Ia. The results are described in Table I. Impure **7,7-dichloronorcarane** was collected, ~b.p. 85–88° at 20 mm., $n^{24}\text{D}$ 1.4992, and showed ester carbonyl in the infrared spectrum. The material was purified by washing with two portions of concentrated sulfuric acid and with two portions of water.

The **carbon tetrachloride** and **recovered cyclohexene** were collected with solvent petroleum ether by stripping the volatile components (rotatory evaporator) from the dried reaction mixture. Known amounts of tetrachloroethylene (absent in the mixture) were added, and the carbon tetrachloride and cyclohexene were analyzed by vapor phase chromatography (column, silicone grease set at 67°, carrier He, flow ~15 p.s.i.).

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The Radiation-Induced Addition Reaction of Ethers to Chlorofluoroolefins

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The radiation-induced addition reactions of tetrahydrofuran, dioxane, and diethyl ether to chlorofluoroolefins such as 1,2,2-trichloro-2-fluoroethylene, 1,2-dichloro-1,2-difluoroethylene, and 1,1-dichloro-2,2-difluoroethylene were carried out. While the addition of tetrahydrofuran and dioxane gave mainly 1:1 adducts in appreciable yields, diethyl ether added to the olefins to give a 1:1 adduct and a 1:2 adduct in a molar ratio of about 1:1. The structures of the adducts were determined by proton n.m.r. spectroscopy.

Among the various methods[1] of preparing fluorine-containing ethers, the addition of alcohols to fluoroolefins by an ionic mechanism using sodium alkoxides was most extensively studied. On the other hand, little attention has been paid to the free-radical addition of ethers to fluoroolefins, and the only report[2] available was on the peroxide-induced addition of certain cyclic ethers to $CF_2{=}CF_2$ to give 1:1 adducts and telomers.

This study is concerned with the addition of tetrahydrofuran, 1,4-dioxane, and diethyl ether to $CFCl{=}CCl_2$, $CFCl{=}CFCl$, and $CF_2{=}CCl_2$ by γ-ray irradia-

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[1] For a review of the syntheses of fluorine-containing ethers, see A. M Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p. 155.

[2] W. E. Hanford, U. S. Patent 2,433,844 (1948).