Treatment of 1.31 g. of XIXa in 40 ml. of acetic anhydride and 10 ml. of acetic acid at 0° over 0.5 hr. with 8.4 g. of sodium nitrite, storage overnight in the refrigerator, and pouring the mixture into 150 g. of ice led to a suspension. Filtration and successive washing with water and ether afforded 1.37 g. of crude XIXb. Attempts at recrystallization led to decomposition. Upon heating it decomposed violently at *ca.* 148°. Infrared spectrum (Nujol) showed no NH, C=O 5.55 (s) and 5.82 (s), and N=O 6.65 (m) μl Treatment of XIXb in methanol with sodium methoxide led, upon evaporation, to a yellow foam which exhibited an infrared spectrum in chloroform with an intense 4.82-μ band. In preliminary experiments, the diazo compound has been treated with several acidic reagents leading to evolution of nitrogen. Although incompletely characterized, the products showed no 4.82-μ band in their infrared spectra.

Acknowledgment.—The authors are indebted to Ciba Pharmaceutical Company and in part to the U. S. Public Health Service for financial support of this work. The able help by Messrs. Thomas E. Wollner, Ronald G. Lewis, and Lloyd H. Woerner, and Miss Patricia G. Gettys is gratefully acknowledged.

Reaction of Enol Ethers with Carbenes. VI.[1] Allylic Rearrangements of Sulfur Ylids[2]

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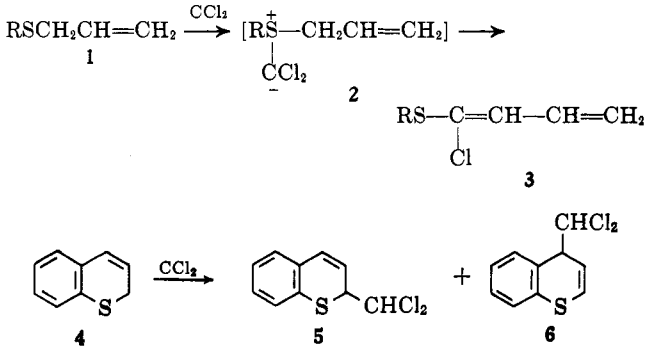
Received September 24, 1964

Evidence is presented for allylic rearrangements of sulfur ylids derived by reaction of ethyl trichloroacetate and sodium methoxide with noncyclic allyl sulfides. The reactions of α-, β-, and γ-methylallyl sulfides with ethyl trichloroacetate and sodium methoxide (dichlorocarbene) are discussed.

We previously observed[4-6] that dichlorocarbene, generated from ethyl trichloroacetate and sodium methoxide, reacts with open-chain allyl sulfides[4] (**1**) to give 1-chloro-1-substituted mercaptobutadienes (**3**) and with



cyclic allyl sulfides,[5,6] such as **4**, to give insertion products **5** and **6**. Sulfur ylids (**2**) were proposed as primary reaction products in these reactions; however, no definitive evidence for ylid formation from sulfides and dihalocarbenes has been noted. A study of the reactions of α-, β-, and γ-methylallyl sulfides with ethyl trichloroacetate and sodium methoxide, which is the subject of this report, has furnished evidence for the intermediate ylids **2** and has permitted definition of the probable mechanism of butadiene formation (**3**) to involve an allylic rearrangement of the ylid **2**. With appropriately substituted allylic sulfides, a duality of mechanism is observed.

(1) For the preceding article in this series, see W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl, and R. M. Dodson, *J. Am. Chem. Soc.*, **87**, 321 (1965).

(2) Supported by the U. S. Army Research Office, Durham, N. C.

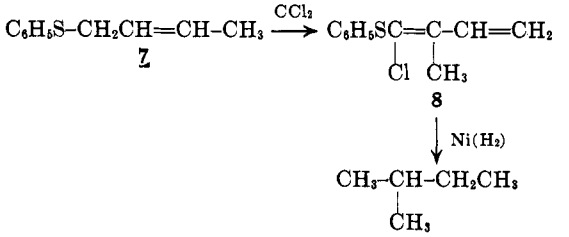
(3) From the dissertation of S. H. Groen, University of Groningen, The Netherlands; O.E.C.D. Postgraduate Travel Grant awarded by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

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

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

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

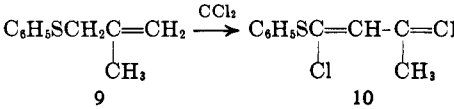
Procedure. A. Reactions of γ-Methylallyl Sulfides.—The reaction of γ-methylallyl phenyl sulfide (**7**), which contained ~6% (by v.p.c.) of the isomeric sul-



fide **11**, with ethyl trichloroacetate and sodium methoxide gave a 52% yield of product composed of >90% 1-chloro-2-methyl-1-phenylmercaptobutadiene (**8**) and <10% 1-chloro-1-phenylmercaptopentadiene-1,3 (**12**). The composition and infrared, ultraviolet, and n.m.r. spectra of the product (see Experimental) were consistent with the assigned structure **8**. Confirmation of the carbon structure of **8** was achieved by its reduction with Raney nickel to isopentane (derived from **8**) and *n*-pentane (derived from **12**) in the ratio of ~12 to 1.

Similar studies were made with *n*-butyl γ-methylallyl sulfide with comparable results (see Experimental). In this case the amount of contaminant (*n*-butyl α-methylallyl sulfide) in the starting sulfide was less. The ratio of derived isopentane to *n*-pentane was ~25 to 1.

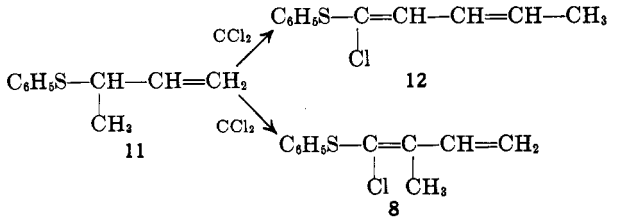
B. Reactions of β-Methylallyl Sulfides.—The reaction of β-methylallyl phenyl sulfide (**9**) with ethyl trichloroacetate and sodium methoxide gave a 42% yield of 1-chloro-3-methyl-1-phenylmercaptobutadiene (**10**). The composition and infrared, ultraviolet, and n.m.r. spectra of the product (see Experimental) were consistent with the assigned structure **10**. The reaction



of **10** with Raney nickel gave, as expected, only isopentane.

Similar studies were made with *n*-butyl β-methylallyl sulfide with comparable results (see Experimental). The butadiene **10** and the *n*-butyl analog were prepared in order to complete the identification of the series of methyl-substituted 1-chloro-1-substituted mercaptobutadienes. It will be noted that butadiene formation from the β-methylallyl sulfides will lead to the same product either by allylic rearrangement or by α insertion (see Discussion section).

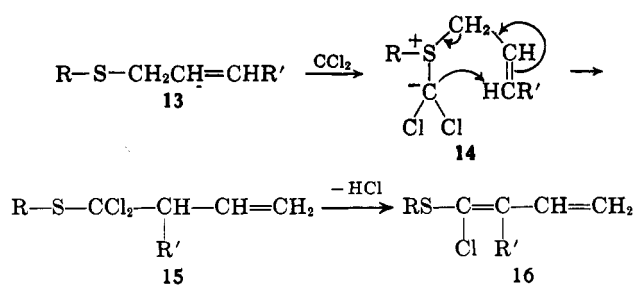
C. Reactions with α-Methylallyl Sulfides.—The reaction of α-methylallyl phenyl sulfide (**11**), containing ~6% (by v.p.c.) of the isomeric sulfide **7**, with ethyl trichloroacetate and sodium methoxide gave a 60% yield of a mixture of 1-chloro-1-phenylmercaptopentadiene-1,3 (**12**) (~64%) and 1-chloro-2-methyl-1-phenylmercaptobutadiene (**8**) (~36%). The composition and infrared, ultraviolet, and n.m.r. spectra of the mixture were consistent with the assigned mixture of **12** and **8**. Reduction of the mixture with Raney nickel gave *n*-pentane and isopentane in the ratio ~1.6 to 1.



Similar results were obtained in a parallel study involving *n*-butyl α-methylallyl sulfide (see Experimental). In this series the starting sulfide was obtained with less contamination by the isomer *n*-butyl γ-methylallyl sulfide. The ratio of derived *n*-pentane to isopentane was ~3.7 to 1.

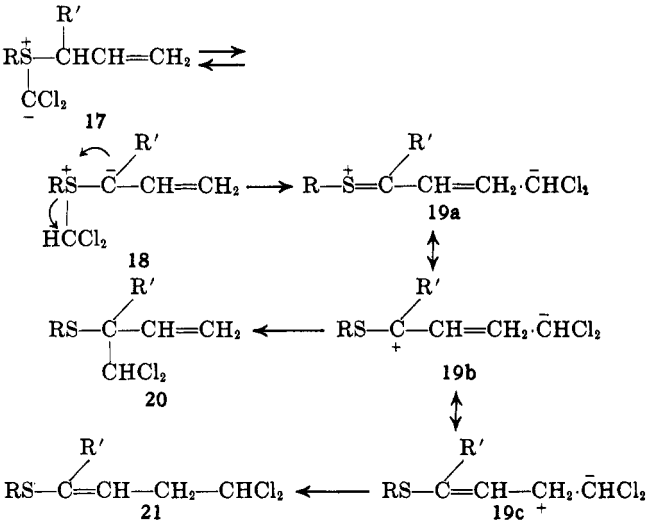
Discussion

The formation (apparently exclusively) of 1-chloro-2-methyl-1-phenylmercaptobutadiene (**8**) from γ-methylallyl phenyl sulfide (**7**) and 1-*n*-butylmercapto-1-chloro-2-methylbutadiene from *n*-butyl γ-methylallyl sulfide constitutes evidence for an allylic rearrangement of the type shown in the accompanying equations.

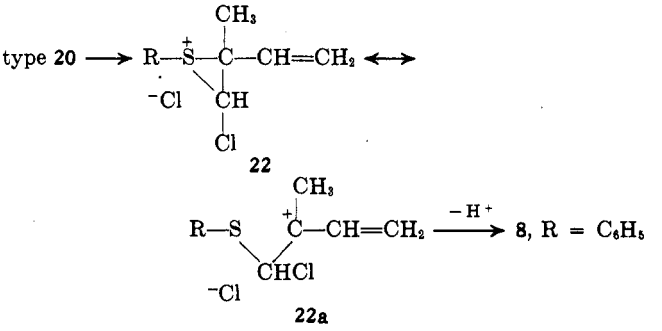


The formation of butadienes of type **16** is then explained by the sequence **13** → **14** → **15** → **16**. This mechanism also explains the marked differences observed for reactions of cyclic[5,6] and open-chain[4] allyl sulfides with dichlorocarbene. The cyclic sulfides cannot, because of geometric limitations, undergo the allylic rearrangement observed for the open-chain analogs.

The formation of butadienes **12** and **8** from α-methylallyl phenyl sulfide (**11**), as well as related butadienes from *n*-butyl α-methylallyl sulfide, in which the ratio of product formed by allylic inversion to α insertion (no inversion) is about 1.8 to 1 and 3.7 to 1, is evidence for duality of mechanism in reactions of allyl sulfides with dichlorocarbene.

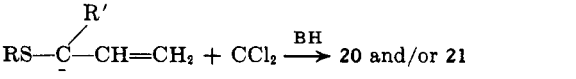


An attractive mechanism for the insertion reaction (*i.e.*, no inversion) is outlined in gross detail in the accompanying equations. Butadiene formation without allylic rearrangement, as also observed with α-methylallyl phenyl sulfide (**11**) and *n*-butyl α-methylallyl sulfide, could then proceed as shown (type **20** → **22**[7] → **22a** → **8**). Precedent for rearrangements of the type **20** → **22** → **8** are discussed in detail in an earlier

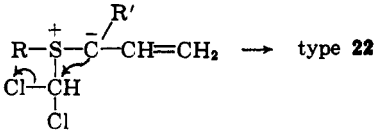


discussion.[4] This insertion reaction sequence is analogous to the Pummerer reaction in which sulfoxides are converted into α-acetoxysulfides (**24**) by reaction with anhydrides. Evidence for the carbonium ion **23**, free enough to undergo molecular rearrangement with suitably substituted sulfoxides, has recently been presented.[8] This gross reaction mechanism, which in-

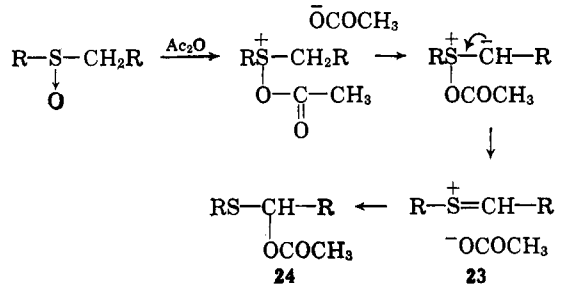
(7) In preceding articles of this series (*cf.* ref. 4), we showed that reaction of allyl sulfides, ethyl trichloroacetate, and sodium methoxide does not involve formation of the carbanion of the sulfide. Thus, insertion as shown in the following equation would appear to be precluded.



Alternative pathways for formation of bridged ions of type **22** can, however, be considered.

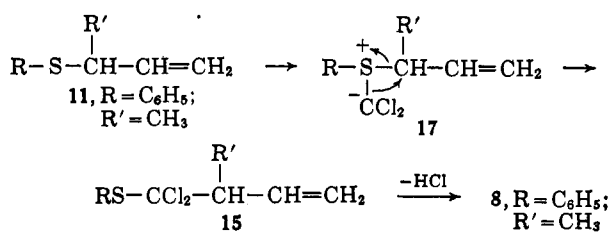


(8) W. E. Parham and M. D. Bhavsar, *J. Org. Chem.*, **28**, 2686 (1963).



volves the carbonium ion, or ion-pair, intermediate **19**, also accounts for insertion reactions at both the α and γ positions in cyclic allyl sulfides such as **4**[5] (*i.e.*, formation of **5** and **6**). Furthermore, existence of intermediate ions of type **19** is also consistent with the observed fact that allylic inversion is more pronounced with γ-methylallyl sulfides (**7**) than with α-methylallyl sulfides (**11**). α-Alkyl substitution should increase ease of formation of the corresponding carbonium ion (*i.e.*, a tertiary carbonium ion as compared with a secondary carbonium ion). The fact that γ insertion was not observed with the α-methylallyl sulfide (**11**) is not unreasonable since, in the proposed ion-pair intermediate **19**, the hypothetical structure **19b** may be of more significance than **19c**. With the γ-methylallyl sulfides only allylic rearrangement is observed.

Attractive alternative mechanisms can, however, be formulated to explain the partial formation of butadienes of type **8** (no allylic rearrangement) from α-methylallyl sulfides. The sequence shown **11** → **17** → **15** → **8**



is formally analogous to the well-known Stevens rearrangement[9,10] and cannot be ruled out with existing data. The only tangible objection to this alternative sequence is that it does not explain the observed formation of insertion products of type **5** and **6** with cyclic allyl sulfides. However, a Stevens-type reaction with cyclic sulfide of type **4** would involve an unfavorable ring expansion from a six- to a seven-membered ring.

Experimental

cis- and *trans*-γ-**methylallyl phenyl sulfide** (**7**) was prepared as described by Cope, Morrison, and Field[11]: 70% yield; b.p. 42–46° (0.04 mm.); n^{17}D 1.5720 (reported[11] 75% yield; b.p. 69.6–70° at 13 mm.; n^{25}D 1.5680); $\lambda_{max}^{95\%\ EtOH}$ 255 mμ (ϵ 6630); ν^{neat} 965 (*trans* CH=CH), 1380, and near 2900 cm.$^{-1}$ (CH_3); n.m.r. spectrum[12] (neat) C_6H_5 (complex 418–443 c.p.s., wt. 5.3), CH=CH (multiplet 318–332 c.p.s., wt. 2.0), S-CH_2 (complex, 196–210 c.p.s., wt. 2.1), CH_3 (complex, 82–94 c.p.s., wt. 3.0), minor impurities at 73, 80, and near 220, 300, and 345 c.p.s. due to the isomer α-methylallyl phenyl sulfide (**11**); v.p.c. (Perkin-Elmer Model 154, silicone oil D.C. 200 on Chromosorb W, column set at 203°, carrier gas, He, pressure of 15 p.s.i.) showed a major peak and a minor peak (~6%, proved by injection to be α-methylallyl phenyl sulfide).

Anal. Calcd. for $C_{10}H_{12}S$: C, 73.11; H, 7.37. Found: C, 73.29; H, 7.56.

cis- and *trans-n*-**butyl** γ-**methylallyl sulfide** was prepared as described for *cis-* and *trans*-γ-methylallyl phenyl sulfide (**7**) by using *n*-butylmercaptan instead of thiophenol: 50% yield; b.p. 72.5–74.5° (13 mm.); n^{22}D 1.4711 (reported[13] b.p. 72° at 14 mm.; n^{20}D 1.4742); ν^{neat} 965 cm.$^{-1}$ (*trans* CH=CH); n.m.r. spectrum[12] (neat) CH=CH (multiplet, 318–335 c.p.s., wt. 2.1), S-CH_2-C= (complex, 175–185 c.p.s., wt. 2.0), S-CH_2 (complex, 135–153 c.p.s., wt. 2.1), CH_2-CH_2 and =C-CH_3 (complex, 70–103 c.p.s., wt. 7.4), -CH_3 (complex, 45–60 c.p.s., wt. 3.3), minor impurities showed up near 190, 300, and 340 c.p.s., due to the isomer *n*-butyl α-methylallyl sulfide; v.p.c. (Perkin-Elmer Model 154, silicone oil D.C. 200, on Chromosorb W, column set at 175°, carrier gas, He, pressure of 15 p.s.i.) showed a major peak and a minor peak (~3.5%, proved by injection to be *n*-butyl α-methylallyl sulfide).

Anal. Calcd. for $C_8H_{16}S$: C, 66.59; H, 11.18. Found: C, 66.36; H, 11.43.

β-**Methylallyl phenyl sulfide** (**9**) was prepared as described for *cis-* and *trans*-γ-methylallyl phenyl sulfide (**7**) by using β-methylallyl chloride instead of γ-methylallyl bromide: 81% yield; b.p. 63–65° (0.15 mm.); $n^{20.5}$D 1.5658; $\lambda_{max}^{95\%\ EtOH}$ 255 mμ (ϵ 6510); ν^{neat} 1645 (C=C), 1380 and near 2900 (CH_3), and 895 and 1790 cm.$^{-1}$ (C=CH_2); n.m.r. spectrum[12] (neat) C_6H_5 (complex, 418–445 c.p.s., wt. 5.1), =CH_2 (complex, 282–290 c.p.s., wt. 2.1), SCH_2 (singlet, 203 c.p.s., wt. 2.0), and =C-CH_3 (split peak, 110 c.p.s., wt. 3.1); v.p.c. (Perkin-Elmer Model 154, silicone oil D.C. 200, on Chromosorb W, column set at 203°, carrier gas, He, pressure of 15 p.s.i.) showed one peak.

Anal. Calcd. for $C_{10}H_{12}S$: C, 73.11; H, 7.37. Found: C, 73.25; H, 7.64.

n-**Butyl** β-**methylallyl sulfide** was prepared as described for β-methylallyl phenyl sulfide (**9**) by using *n*-butylmercaptan instead of thiophenol: 55% yield; b.p. 93–96° (50 mm.); $n^{25.5}$D 1.4662; ν^{neat} 1645 (C=C), 895, and 1790 cm.$^{-1}$ (-C=CH_2); n.m.r. spectrum[12] (neat) =CH_2 (split peak, 288 c.p.s., wt. 2.1), S-CH_2-C= (singlet, 184 c.p.s., wt. 2.1), S-CH_2 (complex, 135–150 c.p.s., wt. 2.0), =C-CH_3 (split peak, 108 c.p.s., wt. 3.2), CH_2-CH_2 (complex, 75–98 c.p.s., wt. 4.0), and CH_3 (complex, 45–61 c.p.s., wt. 3.2); v.p.c. (Perkin-Elmer Model 154, silicone oil D.C. 200, on Chromosorb W, column set at 175°, carrier gas, He, pressure of 15 p.s.i.) showed one peak.

Anal. Calcd. for $C_8H_{16}S$: C, 66.59; H, 11.18. Found: C, 66.44; H, 11.22.

α-**Methylallyl phenyl sulfide** (**11**) was prepared as described by Cope, Morrison, and Field[11] from α-methylallyl chloride[14] and sodium thiophenolate: 50% yield; b.p. 35–36 (0.05 mm.); n^{23}D 1.5564 (reported[11] 51% yield; b.p. 56–58° at 1.2 mm.; n^{25}D 1.5546); $\lambda_{max}^{95\%\ EtOH}$ 256 mμ (ϵ 4350); ν^{neat} 1635 (C=C), 915, 990, and 1830 (CH=CH_2), and 1370 and near 2900 cm.$^{-1}$ (CH_3); n.m.r. spectrum[12] (neat) C_6H_5 (complex, 420–450 c.p.s., wt. 4.9), =CH (multiplet, 325–365 c.p.s., wt. 1.0), =CH_2 (complex, 280–302 c.p.s., wt. 1.8), -CH (multiplet, 200–235 c.p.s., wt. 1.0), CH_3 (doublet, 73 and 80 c.p.s., wt. 2.9), and minor impurities showed up near 90, 200, and 325 c.p.s. due to the isomer γ-methylallyl phenyl sulfide (**7**); v.p.c. (Perkin-Elmer Model 154, silicone oil D.C. 200, on Chromosorb W, column set at 203°, carrier gas, He, pressure of 15 p.s.i.) showed a major peak and a minor peak (~6%, proved by injection to be γ-methylallyl phenyl sulfide).

Anal. Calcd. for $C_{10}H_{12}S$: C, 73.11; H, 7.37. Found: C, 73.13; H, 7.12.

n-**Butyl** α-**methylallyl sulfide** was prepared as described for α-methylallyl phenyl sulfide (**11**) by using *n*-butylmercaptan instead of thiophenol: 49% yield; b.p. 70–72° (23 mm.); n^{23}D 1.4622 (reported[13] b.p. 61° at 15 mm.; n^{20}D 1.4655); ν^{neat} 1635 (C=C), 915, 990, and 1830 cm.$^{-1}$ (CH=CH_2); n.m.r. spectrum[12] (neat) =CH (multiplet, 325–360 c.p.s., wt. 1.0), =CH_2 (com-

(9) T. S. Stevens, E. M. Creighton, A. B. Gordon, and M. McNicol, *J. Chem. Soc.*, 3193 (1928).

(10) M. Saunders and R. W. Murray, *Tetrahedron*, **11**, 1 (1960).

(11) A. C. Cope, D. E. Morrison, and L. Field, *J. Am. Chem. Soc.*, **72**, 59 (1950).

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

(13) L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 1596 (1955).

(14) α-Methylallyl chloride was prepared from buten-1-ol-3 as described by L. F. Hatch and S. S. Nesbitt, *J. Am. Chem. Soc.*, **72**, 728 (1950). The mixture of α-methylallyl chloride and γ-methylallyl chloride was separated by repeated distillations through a 5-in. column filled with helices: yield 15%; b.p. 60–63°; n^{25}D 1.4155.

plex, 287–305 c.p.s., wt. 2.1), –CH (multiplet, 182–211 c.p.s., wt. 1.0), S–CH_2 (complex, 138–153 c.p.s., wt. 2.0), CH_2–CH_2 and >CH–CH_3 (complex, 72–100 c.p.s., wt. 7.4), CH_3 (complex, 45–60 c.p.s., wt. 3.2); v.p.c. (Perkin-Elmer Model 154, silicone oil D. C. 200 on Chromosorb W, column at 175°, carrier gas, He, pressure of 15 p.s.i.) showed a major peak and a minor peak (~2%, proved by injection to be *n*-butyl γ-methylallyl sulfide).

Anal. Calcd. for $C_8H_{16}S$: C, 66.59; H, 11.18. Found: C, 66.27; H, 11.15.

1-Chloro-2-methyl-1-phenylmercaptobutadiene (8). The Reaction between Dichlorocarbene and γ-Methylallyl Phenyl Sulfide (7).—Ethyl trichloroacetate (26.0 g., 0.14 mole) was added in 45 min. to a cold (ice bath) and stirred mixture, under nitrogen, of γ-methylallyl phenyl sulfide (21.4 g., 0.13 mole), sodium methoxide (14.1 g., 0.26 mole), and olefin-free petroleum ether (160 ml., b.p. 30–60°). The mixture was stirred at 0° during 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 (magnesium sulfate) and concentrated in a rotatory evaporator. Distillation of the residue through a 3-in. Vigreux column gave (a) recovered **7**, 5.5 g., 0.034 mole, b.p. 40–46° (0.01 mm.), and $n^{25.5}D$ 1.5670; and (b) 1-chloro-2-methyl-1-phenylmercaptobutadiene (**8**), 14.4 g., 0.068 mole, 52% yield, b.p. 98–104° (0.08 mm.), and $n^{24}D$ 1.6160–1.6182. Fraction b was redistilled through a spiral-wire column to give 11.1 g. (0.053 mole) of product: 41% yield; b.p. 82–84° (0.02 mm.); $n^{20.5}D$ 1.6218; $\lambda_{max}^{95\% EtOH}$ 249 mμ (ε 20,790), shoulder 280 mμ (ε 9760); ν^{neat} 1605 (C=C), 915, 990, and 1830 (CH=CH_2), 1375 and near 2900 cm.$^{-1}$ (CH_3); n.m.r. spectrum[12] (neat) C_6H_5 and =CH (complex, 414–455 c.p.s., wt. 6.4), =CH_2 (multiplet, 304–329 c.p.s., wt. 2.0), –CH_3 (doublet due to *cis* and *trans* isomers, 121 c.p.s. and 126 c.p.s., wt. 2.9), minor impurities showed up near 100 and 400 c.p.s. due to the isomer 1-chloro-1-phenylmercaptopentadiene-1,3 (**12**); v.p.c. (Perkin-Elmer Model 154, silicone oil D. C. 200, on Chromosorb W, column set at 202° carrier gas, He, pressure of 15 p.s.i.) showed one major peak with shoulder (<10%, proved to be **12** by injection).

Anal. Calcd. for $C_{11}H_{11}ClS$: C, 62.69; H, 5.26; S, 15.22. Found: C, 62.79; H, 5.09; S, 15.34.

Reduction of 1-Chloro-2-methyl-1-phenylmercaptobutadiene (8) with Raney Nickel.—1-Chloro-2-methyl-1-phenylmercaptobutadiene (**8**, 2.5 g.), dissolved in 75% ethanol–water (100 ml.), was refluxed for 4 hr. with Raney nickel (30 g., W-2). Water (250 ml.) was added and the mixture was distilled with steam. About 20 ml. of distillate was collected. The distillate was diluted with water (20 ml.) and extracted with heptane. This solution was dried with calcium chloride. A sample was analyzed in a Perkin-Elmer Model 154 vapor phase chromatograph using a silicone oil D. C. 200 on Chromosorb W column set at 40°, and a carrier gas (He) pressure of 15 p.s.i. The spectrum showed the presence of four components (other than heptane). The compounds were identified by the injection of authentic samples as isopentane, *n*-pentane, cyclohexane, and benzene. The ratio of isopentane to *n*-pentane was ~12 to 1.

1-*n*-Butylmercapto-1-chloro-2-methylbutadiene. The Reaction between Dichlorocarbene and *n*-Butyl γ-Methylallyl Sulfide.—The reaction was carried out as described for **7** using *n*-butyl γ-methylallyl sulfide (14.4 g., 0.10 mole), ethyl trichloroacetate (19.5 g., 0.10 mole), sodium methoxide (10.8 g., 0.20 mole), and olefin-free petroleum ether (140 ml., b.p. 30–60°). In addition to recovered sulfide (3.5 g., 0.024 mole; b.p. 72–75° at 14 mm.; $n^{28}D$ 1.4690), crude 1-*n*-butylmercapto-1-chloro-2-methylbutadiene (6.4 g., 0.034 mole, 34% yield; b.p. 110–116° at 15 mm.; $n^{26}D$ 1.5304) was collected. This crude fraction was redistilled through a spiral-wire column to give 5.8 g. (0.30 mole) of product: 30% yield; b.p. 37–39° (0.01 mm.); $n^{24}D$ 1.5340; $\lambda_{max}^{95\% EtOH}$ 237 mμ (ε 13,870) and 282 mμ (ε 10,970); ν^{neat} 1610 (C=C), 910, 990, and 1820 cm.$^{-1}$ (CH=CH_2); n.m.r. spectrum[12] (neat) =CH (two quadruplets, due to *cis* and *trans* isomers, at 410, 419, 421, and 430 and at 428, 437, 439, and 448 c.p.s., wt. 1.0), =CH_2 (multiplet, 302–327 c.p.s., wt. 2.0), S–CH_2 (complex, 160–178 c.p.s., wt. 2.1), =C–CH_3 (doublet, 120 and 123 c.p.s., wt. 3.0), CH_2–CH_2 (complex, 75–105 c.p.s., wt. 4.3), and CH_3 (complex, 45–60 c.p.s., wt. 3.2); v.p.c. (Perkin-Elmer Model 154, silicone oil D. C. 200, on Chromosorb W, column set at 189°, carrier gas, He, pressure of 15 p.s.i.) showed a major peak with very small shoulder.

Anal. Calcd. for $C_9H_{15}ClS$: C, 56.67; H, 7.93. Found[15]: C, 56.28; H, 7.87.

Reduction of 1-*n*-Butylmercapto-1-chloro-2-methylbutadiene with Raney Nickel.—The reduction was carried out as described for **8**. Vapor phase chromatography of the heptane solution showed the presence of three compounds (other than heptane). The compounds were identified as *n*-butane, isopentane, and *n*-pentane. The ratio of isopentane to *n*-pentane was ~25 to 1.

1-Chloro-3-methyl-1phenylmercaptobutadiene (10). The Reaction between Dichlorocarbene and β-Methylallyl Phenyl Sulfide (9).—The reaction was carried out as described for **7** using β-methylallyl phenyl sulfide (24.6 g., 0.15 mole), ethyl trichloroacetate (30.0 g., 0.16 mole), sodium methoxide (18.0 g., 0.33 mole), and olefin-free petroleum ether (200 ml., b.p. 30–60°). In addition to recovered **9** (2.3 g., 0.014 mole; b.p. 36–40° at 0.01 mm.; $n^{25}D$ 1.5632), crude 1-chloro-3-methyl-1-phenylmercaptobutadiene (**10**) (13.2 g., 0.063 mole, 42% yield; b.p. 110–112° at 0.15 mm.; $n^{22}D$ 1.6058–1.6073) was collected. This crude fraction was redistilled through a spiral-wire column to give 9.0 g. (0.043 mole) of product: 29% yield; b.p. 81–83° (0.01 mm.); $n^{21.5}D$ 1.6102; $\lambda_{max}^{95\% EtOH}$ 251 mμ (ε 15,150), shoulder 280 mμ (ε 8350); ν^{neat} 1605 (C=C), 900 and 1800 (C=CH_2), and 1375 and near 2900 cm.$^{-1}$ (CH_3); n.m.r. spectrum[12] (neat) C_6H_5 (complex, 424–450 c.p.s., wt. 4.8), =CH (two peaks due to *cis* and *trans* isomers, 400 and 403.5 c.p.s., wt. 1.0), =CH_2 (complex, 302–311 c.p.s., wt. 2.0), CH_3 (split peak, 117.5 c.p.s., wt. 2.9); v.p.c. (Perkin-Elmer Model 154, silicone oil D. C. 200, on Chromosorb W, column set at 204°, carrier gas, He, pressure of 15 p.s.i.) showed one peak.

Anal. Calcd. for $C_{11}H_{11}ClS$: C, 62.69; H, 5.26; S, 15.22. Found: C, 62.79; H, 5.54; S, 15.04.

Reduction of 1-Chloro-3-methyl-1-phenylmercaptobutadiene (10) with Raney Nickel.—The reduction was carried out as described for **8**. Vapor phase chromatography of the heptane solution showed the presence of two compounds (other than heptane). The compounds were identified as isopentane and cyclohexane.

1-*n*-Butylmercapto-1-chloro-3-methylbutadiene. The Reaction between Dichlorocarbene and *n*-Butyl β-Methylallyl Sulfide.—The reaction was carried out as described for **7** using *n*-butyl β-methylallyl sulfide (28.8 g., 0.20 mole), ethyl trichloroacetate (48.0 g., 0.25 mole), sodium methoxide (26.0 g., 0.48 mole), and olefin-free petroleum ether (250 ml., b.p. 30–60°). In addition to recovered sulfide (5.0 g., 0.035 mole; b.p. 69–71° at 20 mm.; $n^{24}D$ 1.4665), impure 1-*n*-butylmercapto-1-chloro-3-methylbutadiene was collected: 14.7 g., 0.077 mole, 39% yield; b.p. 109–114° (23 mm.); $n^{26}D$ 1.5130–1.5170; ν^{neat} 1605 (C=C), 895, and 1790 cm.$^{-1}$ (>C=CH_2); n.m.r. spectrum[12] (neat) =CH (singlet, 391 c.p.s., wt. 1.0), =CH_2 (complex, 300–310 c.p.s., wt. 2.0), S–CH_2 (complex, 160–180 c.p.s., wt. 2.0), =C–CH_3 (split peak, 120 c.p.s., wt. 3.0), CH_2–CH_2 (complex, 77–97 c.p.s., wt. 4.2), CH_3 (complex, 45–62 c.p.s., wt. 3.1), and small impurity peaks at 105, 150, 214, 287, and 197 c.p.s. (singlet).

The lower boiling impurity was difficult to remove from the butadiene, but after several distillations, essentially pure 1-*n*-butylmercapto-1-chloro-3-methylbutadiene was collected: 3.5 g., 0.018 mole, 9% yield; b.p. 54–55° (1 mm.); $n^{25}D$ 1.5216; $\lambda_{max}^{95\% EtOH}$ 236 mμ (ε 10,160) and 278 mμ (ε 8570); v.p.c. (Perkin-Elmer Model 154, silicone oil D. C. 200, on Chromosorb W, column set at 198°, carrier gas, He, pressure of 15 p.s.i.) showed one peak with small impurity peak (<3%, not the starting sulfide or the addition product of the diene and hydrogen chloride).

Anal. Calcd. for $C_9H_{15}ClS$: C, 56.67; H, 7.93; S, 16.81. Found[15]: C, 57.25; H, 7.91; S, 17.12.

Reduction of 1-*n*-Butylmercapto-1-chloro-3-methylbutadiene with Raney Nickel.—The reduction was carried out as described for **8**. Vapor phase chromatography of the heptane solution showed the presence of two compounds (other than heptane). The compounds were identified as *n*-butane and isopentane.

1-Chloro-1-phenylmercaptopentadiene-1,3 (12) and 1-Chloro-2-methyl-1-phenylmercaptobutadiene (8). The Reaction between Dichlorocarbene and α-Methylallyl Phenyl Sulfide (11).—The reaction was carried out as described for **7** using α-methylallyl phenyl sulfide (16.6 g., 0.10 mole), ethyl trichloroacetate (24.4 g., 0.13 mole), sodium methoxide (13.8 g., 0.26 mole),

(15) This compound was extremely unstable and probably decomposed before and during the analysis.

and olefin-free petroleum ether (150 ml., b.p. 30–60°). A mixture of 1-chloro-1-phenylmercaptopentadiene-1,3 (**12**) and 1-chloro-2-methyl-1-phenylmercaptobutadiene (**8**) was collected in 60% yield (12.7 g., 0.060 mole) and had the following properties: b.p. 74–77° (0.1 mm.); $n^{25}D$ 1.6202; $\lambda_{max}^{95\%\ EtOH}$ 252 mμ (ε 20,930), shoulder 280 mμ (ε 10,950); ν^{neat} 1635 and 1605 (C=C), 1375 and near 2900 (CH_3), and 915 and 990 cm.$^{-1}$ (weak $CH=CH_2$); n.m.r. spectrum[12] (neat) C_6H_5 (complex, 423–445 c.p.s.), =CH (complex, partly under phenyl hydrogens, 453–330 c.p.s.), $=CH_2$ (complex, 304–328 c.p.s.), $C_6H_5CCl=C(CH_3)-CH=CH_2$ (doublet, 121 and 126 c.p.s., wt. 1.0), and $C_6H_5-S-CCl=CH-CH=CH-CH_3$ (complex, 90–103 c.p.s., wt. 1.9); v.p.c. (Perkin-Elmer Model 154, silicone oil D. C. 200, on Chromosorb W, column set at 204°, carrier gas, He, pressure of 20 p.s.i.) showed two partly superimposed peaks, the smaller one being 1-chloro-2-methyl-1-phenylmercaptobutadiene (**8**) proved by injection of an authentic sample. A sample of the reaction mixture was redistilled through a spiral-wire column for analysis: b.p. 70–71° (0.01 mm.); $n^{23}D$ 1.6208.

Anal. Calcd. for $C_{11}H_{11}ClS$: C, 62.69; H, 5.26; S, 15.22. Found: C, 62.41; H, 4.99; S, 15.26.

Reduction of the Mixture of 1-Chloro-2-methyl-1-phenylmercaptobutadiene (8) and 1-Chloro-1-phenylmercaptopentadiene-1,3 (12) with Raney Nickel.—The reduction was carried out as described for **8**. Vapor phase chromatography of the heptane solution showed the presence of three compounds (other than heptane). The compounds were identified as cyclohexane, isopentane, and *n*-pentane. The ratio of isopentane to *n*-pentane was 1 to 1.6 (according to n.m.r. spectrum, the ratio of **8** to **12** was 1 to 1.9).

1-*n*-Butylmercapto-1-chloropentadiene-1,3 and 1-*n*-Butylmercapto-1-chloro-2-methylbutadiene. The Reaction between Dichlorocarbene and *n*-Butyl α-Methylallyl Sulfide.—This reaction was carried out as described for **7** using *n*-butyl α-methylallyl sulfide (14.4 g., 0.10 mole), ethyl trichloroacetate (26.5 g., 0.14 mole), sodium methoxide (16.4 g., 0.30 mole), and olefin-free petroleum ether (175 ml., b.p. 30–60°). In addition to impure recovered sulfide (proved by v.p.c.; 3.1 g., 0.022 mole), there was obtained a crude mixture of 1-*n*-butylmercapto-1-chloropentadiene-1,3 and 1-*n*-butylmercapto-1-chloro-2-methylbutadiene (8.2 g., 0.043 mole, 43% yield; b.p. 73–75° at 0.7 mm.; $n^{22}D$ 1.5278). This fraction was redistilled through a spiral-wire column to give 5.9 g. (0.031 mole) of product: 31% yield; b.p. 67–71 (0.7 mm.); $n^{23}D$ 1.5313; $\lambda_{max}^{95\%\ EtOH}$ 237 mμ (ε 12,200) and 279 mμ (ε 10,300); ν^{neat} 1610 and 1635 cm.$^{-1}$ (weak, C=C); n.m.r. spectrum[12] (neat) $H_2C=CH$ (two quartets, 410, 419, 421, and 430 c.p.s. and 428, 437, 439, and 448 c.p.s.), =CH–CH=CH– (complex, 333–418 c.p.s.), $=CH_2$ (complex, 303–329 c.p.s.), SCH_2 (complex, 151–176 c.p.s., wt. 9.5), *n*-$C_4H_9-S-CCl=C(CH_3)CH=CH_2$ (doublet, 120 and 123 c.p.s.; wt. 3.0), *n*-$C_4H_9-S-CCl=CH-CH=CHCH_3$ (complex, 97–110 c.p.s.), CH_2-CH_2 (complex, 72–97 c.p.s.), CH_3 (complex, 42–61 c.p.s.), and small impurity peaks near 195 and 215 c.p.s.; v.p.c. (Perkin-Elmer Model 154, silicone oil D. C. 200, on Chromosorb W, column set at 198°, carrier gas, He, pressure of 15 p.s.i.) showed two nearly superimposed peaks, probably due to *cis*- and *trans*-1-*n*-butylmercapto-1-chloropentadiene-1,3 with a shoulder on the first peak, proved to be 1-*n*-butylmercapto-1-chloro-2-methylbutadiene by injection, and small peak due to an unknown impurity.

This lower-boiling impurity was very difficult to remove from the mixture of butadienes. After two distillations through a spiral-wire column a fraction (2.5 g., 0.013 mole, 13%; b.p. 68–69° at 0.7 mm.; $n^{29}D$ 1.5300) was collected, which showed only a small impurity (<3%) in the v.p.c. and the n.m.r. spectrum.

Anal. Calcd. for $C_9H_{15}ClS$: C, 56.67; H, 7.93; S, 16.81. Found: C, 56.55; H, 8.15; S, 16.71.

Reduction of the Mixture of 1-*n*-Butylmercapto-1-chloropentadiene-1,3 and 1-*n*-Butylmercapto-1-chloro-2-methylbutadiene with Raney Nickel.—The reduction was carried out as described for **8** with the mixture of butadienes (fraction, b.p. 67–71° at 0.7 mm.; $n^{23}D$ 1.5313). Vapor phase chromatography of the heptane solution showed the presence of three compounds (other than heptane). The compounds were identified as *n*-butane, isopentane, and *n*-pentane. The ratio of isopentane to *n*-pentane was 1 to 3.7 (according to n.m.r. spectrum the ratio of 1-*n*-butylmercapto-1-chloro-2-methylbutadiene to 1-*n*-butylmercapto-1-chloropentadiene-1,3 was 1 to 3.75).

Dithiolium Derivatives. V.[1] 1,3-Dithiol-2-ylidenes[2]

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Received October 8, 1964

The synthesis of 1,3-dithiol-2-ylidene derivatives from dithiocarboxylic acids and α-halo ketones is described. Dithiocarboxylic acids derived from compounds with active methylene groups and carbon disulfide, in their tautomeric form as α,β-unsaturated *gem*-dithiols, were condensed with α-halo ketones at room temperature to give 4-hydroxy-1,3-dithiolan-2-ylidene derivatives. Dehydration of these derivatives under mild conditions afforded the corresponding 1,3-dithiol-2-ylidenes, which also were prepared in some cases by the condensation of 2-methylthio-1,3-dithiolium perchlorates with active methylene compounds. 1,3-Dithiol-2-ylidenes were converted into 1,3-dithiolium perchlorates. N.m.r. and infrared data of the new products are discussed.

1,3-Dithiol-2-ylidene derivatives have been prepared by the condensation of 2-methylthio-1,3-dithiolium cations with compounds containing an active methylene group.[1b] Recently[3] it has been shown that α-halo ketones readily form 1,3-dithiols with a *gem*-dithiol. Since condensation of carbon disulfide with active methylene derivatives leads to dithio acids, which exist as α,β-unsaturated *gem*-dithiols,[4,5] condensation of these derivatives with α-halo ketones should provide a convenient alternate pathway for the synthesis of certain 1,3-dithiol-2-ylidene derivatives, some of which could not be obtained by the earlier method. It is interesting to note that these β-keto dithio acids can also serve as intermediates in the synthesis of 1,2-dithiolium systems.[4]

Dithio acids have been shown to condense with α-halo ketones to produce β-keto dithio esters, which require strongly acidic conditions to be cyclized to 1,3-dithiolium salts.[1d,6] It was therefore surprising to find that, in several instances, reaction of α-halo ketones (**1**) with β-keto dithio acids (**2**) in alcohol under mild alkaline conditions resulted in spontaneous ring closure to form the 4-hydroxy-1,3-dithiolan-2-ylidene derivatives **3**, and, in one case, the unsaturated 1,3-dithiol-2-ylidene (**4d**).

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(2) Contribution No. 1263. This research was supported by a grant from the Mead-Johnson Corp., Evansville, Ind. We gratefully acknowledge this support.

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