Reaction of Enol Ethers with Carbenes. VII.[1] Substituted Allyl Sulfides[2]

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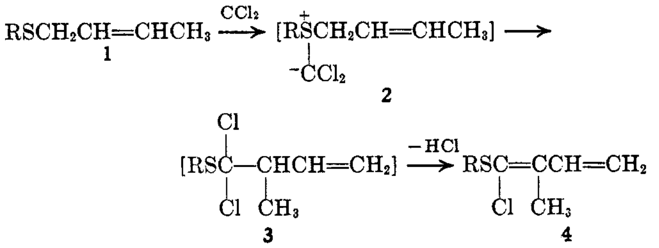
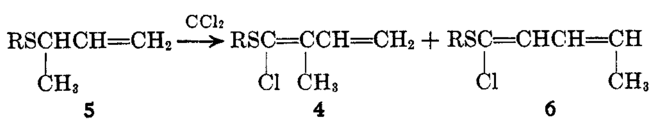
The reactions of ethyl trichloroacetate and sodium methoxide (dichlorocarbene) with γ,γ-dimethylallyl phenyl sulfide, γ,γ-dimethylallyl ethyl sulfide, α,α-dimethylallyl ethyl sulfide, cinnamyl phenyl sulfide, and cinnamyl methyl sulfide are reported. Duality of mechanisms is noted in each case, and products formed by "α-insertion" and by allylic rearrangement of the intermediate sulfur "ylids" are isolated. Direct evidence for α,α-dichloro sulfides, the proposed intermediates in the allylic rearrangement reactions, has been obtained. The mechanism of the α-insertion reaction is considered, and evidence for the Stevens'-type rearrangement is offered.

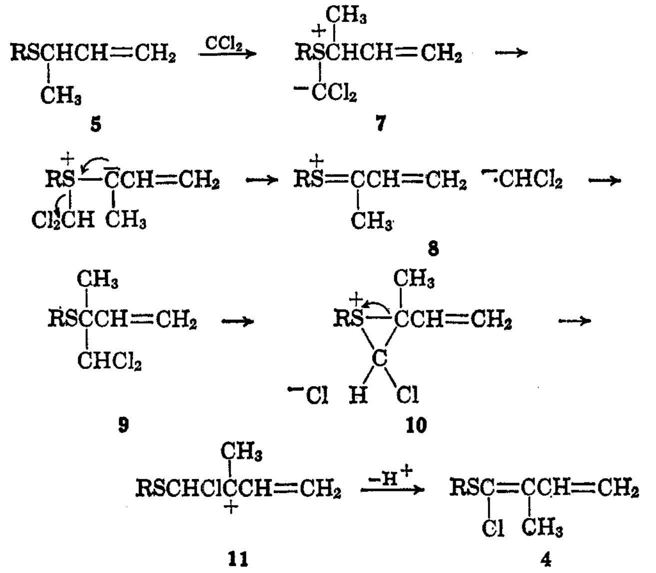
We previously observed that open-chain allyl sulfides,[1,4] such as **1**, reacted with ethyl trichloroacetate and sodium methoxide (dichlorocarbene) to give butadienes (**4**). A duality of mechanisms has been established[1] with appropriately substituted allyl sulfides, such as **5**. The butadienes were formed either totally



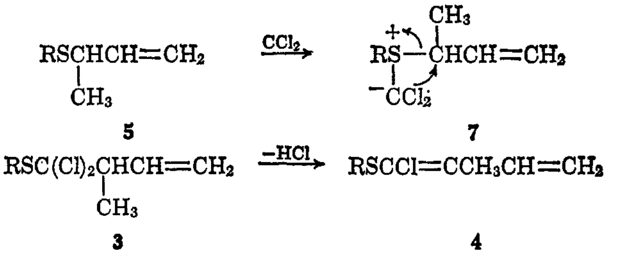


(**1** → **4**) or in part (**5** → **6**) by a process involving an allylic rearrangement of the proposed intermediate "ylid" **2**.[1] For the alternative reaction, the "α insertion" (**5** → **4**), two mechanisms were proposed.[1] Scheme I is a mechanism analogous to the Pummerer reaction,[5] which involved the intermediacy of a phenylmercaptocarbonium ion or ion pair (**8**), and Scheme II is a mechanism analogous to the Stevens' rearrangement.

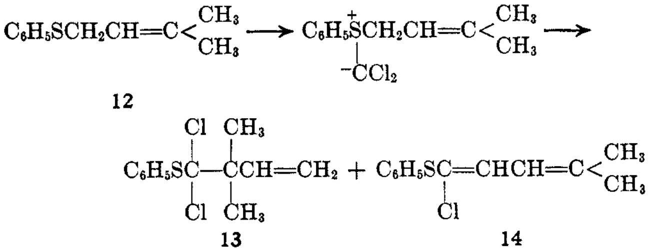
SCHEME I



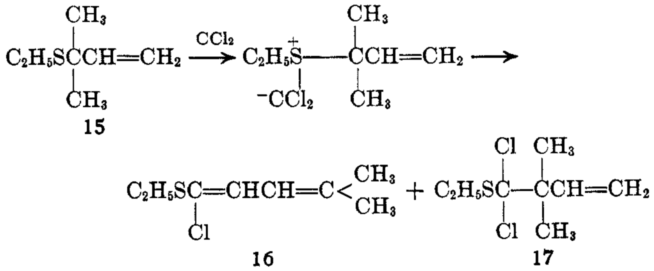
SCHEME II



It was of interest to extend this study to the reaction of γ,γ-dimethylallyl sulfides, such as **12**, since the proposed intermediate dihalide **13**, resulting from allylic rearrangement, could not undergo dehydrochlorination to give a butadiene. The expected product formed by the process of α-insertion was the butadiene **14**.



The reaction of α,α-dimethylallyl ethyl sulfide (**15**) with dichlorocarbene was of interest, since this reaction could not yield **17** by way of Scheme I. A mercaptocarbonium ion such as **8** cannot be formed from an α,α-dimethylallyl sulfide.



To extend the studies of substituted allyl sulfides described in ref 1, the course of the reactions of cinnamyl phenyl sulfide and cinnamyl methyl sulfide with dichlorocarbene was determined.

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[1] For the preceding article in this series, see W. E. Parham and S. H. Groen, *J. Org. Chem.*, **30**, 728 (1965).

[2] Supported by a grant from the U. S. Army Research Office (Durham) (DA-31-124-ARO-D-152).

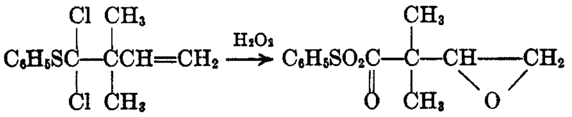
[3] From the Ph.D. dissertation, the University of Groningen, The Netherlands. O.E.C.D. Postgraduate Travel Grant awarded by The Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

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

[5] W. E. Parham and M. D. Bhavsar, *ibid.*, **28**, 2686 (1963).

Procedure

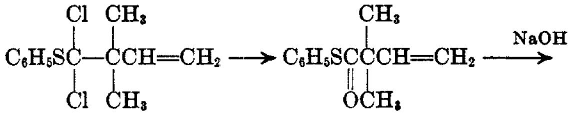
γ,γ-Dimethylallyl Sulfides.—The reaction of γ,γ-dimethylallyl phenyl sulfide (12) with ethyl trichloroacetate and sodium methoxide was carried out essentially as described previously for other allyl sulfides.[1,4] The product of the reaction was a mixture, of which the principal component was 1,1-dichloro-2,2-dimethyl-1-phenylmercapto-3-butene (**13**) with a small amount of 1-chloro-4,4-dimethyl-1-phenylmercaptobutadiene (**14**). The sample was characterized by its spectra (nmr and infrared), and by oxidation with hydrogen peroxide to the epoxide **18** in low yield. Reductive desulfurization of a sample of the crude reaction product with Raney nickel gave a mixture of hydrocarbons consisting of 2-methylbutane (~10%, derived from starting sulfide 12), 2,2-dimethylbutane (~35%, derived from 13), and 2-methylpentane (~55%, derived from 14).



$$C_6H_5S\underset{Cl}{\overset{Cl}{C}}-\underset{CH_3}{\overset{CH_3}{C}}CH=CH_2 \xrightarrow{H_2O_2} C_6H_5SO_2\underset{\overset{\|}{O}}{C}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\diagdown\ O\ \diagup}{CH-CH_2}$$

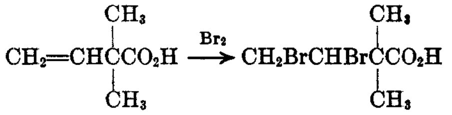
13 18

Confirmation of structure **13**, formed by allylic rearrangement, was obtained by chromatography of the crude reaction mixture on silica gel (100–200 mesh). Vigorous evolution of hydrogen chloride occurred and the thiolester (**19**) was obtained in 31% over-all yield.



$$C_6H_5S\underset{Cl}{\overset{Cl}{C}}-\underset{CH_3}{\overset{CH_3}{C}}CH=CH_2 \longrightarrow C_6H_5S\underset{\overset{\|}{O}}{C}\underset{CH_3}{\overset{CH_3}{C}}CH=CH_2 \xrightarrow{NaOH}$$

13 19



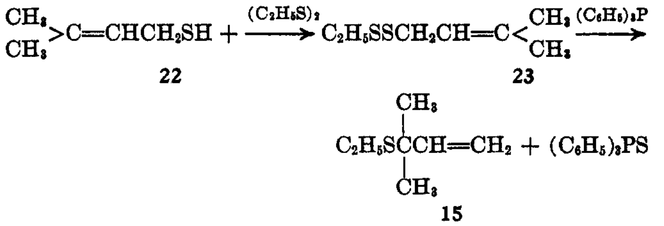
$$CH_2=CH\underset{CH_3}{\overset{CH_3}{C}}CO_2H \xrightarrow{Br_2} CH_2BrCHBr\underset{CH_3}{\overset{CH_3}{C}}CO_2H$$

20 21

The thiolester **19** was characterized by its spectra (nmr and infrared) and by hydrolysis with aqueous sodium hydroxide to 2,2-dimethyl-3-butenoic acid (**20**). The acid **20** was converted to the solid dibromide **21**. The carbene reaction was repeated using γ,γ-dimethylallyl ethyl sulfide and similar results were obtained (see Experimental Section).

α,α-Dimethylallyl ethyl sulfide (**15**) was prepared according to Scheme III which was analogous to the preparation of 1,1-dimethylbut-2-enyl ethyl sulfide described by Moore and Trego.[6] α,α-Dimethylallyl ethyl sulfide (**15**), prepared in this way, contained γ,γ-dimethylallyl ethyl sulfide (<2%) and diethyl disulfide (~7%) as impurities. The latter was reduced with $LiAlH_4$ to the ethyl mercaptan, which was removed by aqueous sodium hydroxide.

SCHEME III

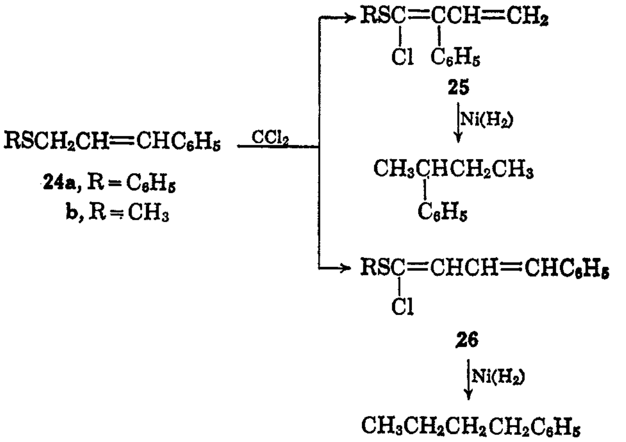


$$\overset{CH_3}{\underset{CH_3}{}}\!\!>C=CHCH_2SH + \xrightarrow{(C_2H_5S)_2} C_2H_5SSCH_2CH=C<\overset{CH_3}{\underset{CH_3}{}} \xrightarrow{(C_6H_5)_3P} C_2H_5S\underset{CH_3}{\overset{CH_3}{C}}CH=CH_2 + (C_6H_5)_3PS$$

22 23 15

The reaction of α,α-dimethylallyl ethyl sulfide (**15**) with dichlorocarbene gave a crude mixture, which on reduction with Raney nickel yielded a small amount of 2-methylbutane (derived from the starting sulfide **15**), 2,2-dimethylbutane (derived from **17**), and 2-methylpentane (derived from **16**). The ratio of 2-methylpentane to 2,2-dimethylbutane (and thus, **16**/**17**) was 93.5/6.5, respectively. Repeated distillations of the crude reaction mixture gave 1-chloro-4,4-dimethyl-1-ethylmercaptobutadiene (**16**) contaminated by a small amount of 1,1-dichloro-2,2-dimethyl-1-ethylmercapto-3-butene (**17**). The mixture was characterized by its spectra (nmr and infrared). Chromatography of this mixture over a silica gel column (100–200 mesh) afforded **16** in 14% over-all yield; however, this material was quite unstable.

Cinnamyl Sulfides (24).—The reaction of cinnamyl sulfides (**24**) with ethyl trichloroacetate and sodium methoxide gave, in each case, a mixture of two major products, the 1-substituted mercapto-1-chloro-2-phenylbutadiene (**25**) and the 1-substituted mercapto-1-chloro-4-phenylbutadiene (**26**) (below). Reduction of the crude reaction mixtures with Raney nickel gave, in addition to *n*-propylbenzene (derived from the starting sulfide **24**), *sec*-butylbenzene (derived from **25**) and *n*-butylbenzene (derived from **26**) in ratios of approximately 2:1, respectively.



$$RSCH_2CH=CHC_6H_5 \xrightarrow{CCl_2} RS\underset{Cl}{C}=\underset{C_6H_5}{C}CH=CH_2 \xrightarrow{Ni(H_2)} CH_3\underset{C_6H_5}{C}HCH_2CH_3$$

$$RSCH_2CH=CHC_6H_5 \xrightarrow{CCl_2} RS\underset{Cl}{C}=CHCH=CHC_6H_5 \xrightarrow{Ni(H_2)} CH_3CH_2CH_2CH_2C_6H_5$$

24a, R = C_6H_5
b, R = CH_3

25

26

Purification of the butadienes **25** and **26** was very difficult and only **25a** and **25b** were isolated pure. The structures **25** and **26** were assigned on the basis of spectra (infrared, ultraviolet, and nmr) and on the structures of the Raney nickel reduction products (see Experimental Section).

Discussion

Duality in mechanism is indicated in reactions involving γ,γ-dimethylallyl sulfides, α,α-dimethylallyl ethyl sulfide, and the cinnamyl sulfides with ethyl trichloroacetate and sodium methoxide. In all cases products derived by allylic rearrangement and α insertion were observed.

The reaction of γ,γ-dimethylallyl phenyl sulfide (**12**) and dichlorocarbene gave 1-chloro-4,4-dimethyl-1-phenylmercaptobutadiene (**14**), by α insertion, and 1,1-dichloro-2,2-dimethyl-1-phenylmercapto-3-butene (**13**), by allylic rearrangement in the approximate ratio 55:35, respectively. Isolation of the thiolester **19** derived

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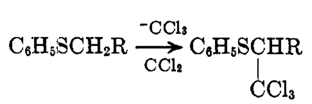
[6] C. G. Moore and B. R. Trego, *Tetrahedron*, **18**, 205 (1962).

from 1,1-dichloro-2,2-dimethyl-1-phenylmercapto-3-butene (**13**) provided direct evidence for the 1,1-dichloro sulfides (**3**), previously[1] proposed as intermediates in the allylic rearrangement process.

The reaction of dichlorocarbene with α,α-dimethylallyl ethyl sulfide (**15**) gave 1-chloro-4,4-dimethyl-1-ethylmercaptobutadiene (**16**), by allylic rearrangement, and 1,1-dichloro-2,2-dimethyl-1-ethylmercapto-3-butene (**17**),[7] by α insertion in the approximate ratio 93.5:6.5, respectively. It was of interest to note that **17**, the α-insertion product, cannot be formed by Scheme I, discussed in the proceeding section, since **15** cannot give a mercaptocarbonium ion of type **8**. This result suggests that a Stevens' type rearrangement (Scheme II) is sufficient to explain the α-insertion products observed with open-chain allyl sulfides. However, studies with cyclic allyl sulfides,[8a-b] which gave appreciable quantities of products formed by insertion of the dichloromethyl group, and studies with aryl alkyl sulfides,[9] which gave insertion products of type **27**, are best explained by Scheme I. Thus,



$$C_6H_5SCH_2R \xrightarrow[CCl_2]{^-CCl_3} \underset{\displaystyle CCl_3}{C_6H_5SCHR}$$

27

there is evidence that the reactions of allyl sulfides with dichlorocarbene involve three distinctly different mechanisms: (1) allylic rearrangement of the sulfur "ylid",[1] (2) Scheme I, as evidenced by the insertion products formed with cyclic allyl sulfides,[8a-b] and (3) Scheme II, to explain the α insertion with α,α-dimethylallyl ethyl sulfide described in this report.

Experimental Section

γ,γ-Dimethylallyl phenyl sulfide (**12**) was prepared from a mixture[10] of α,α-dimethylallyl chloride and γ,γ-dimethylallyl chloride and sodium thiophenolate: 71% yield, bp 70–72° (0.02 mm), $n^{22}{}_\mathrm{D}$ 1.5658 (lit.[11] bp 124–126° at 14 mm; $n^{26}{}_\mathrm{D}$ 1.5644); ν^{neat} 1665 (C=C), 1380 and near 2950 cm^{-1} (CH_3); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 255 mμ (ϵ 6640); nmr spectrum[12] (neat), C_6H_5 (complex, τ 2.57–3.03, wt 5.2), =CH (split triplet, τ 4.53–4.91, wt 1.0), CH_2 (doublet at τ 6.49 and 6.61, wt 2.1), CH_3 (two split peaks near τ 8.40 and 8.52, wt 6.2); vpc [Perkin-Elmer Model 154, silicone oil D.C. 200 (dimethylsiloxane polymer) on Chromosorb W column set at 201°, carrier gas He, pressure of 20 psi used throughout unless noted otherwise] showed one peak.

Anal. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91. Found: C, 74.07; H, 7.82.

γ,γ-Dimethylallyl ethyl sulfide was prepared as described for γ,γ-dimethylallyl phenyl sulfide (**12**) by using ethyl mercaptan instead of thiophenol: yield 63%; bp 76–79° (37 mm); $n^{26.5}{}_\mathrm{D}$ 1.4782; ν^{neat} 1665 (C=C), 1380 and near 2950 cm^{-1} (CH_3); nmr spectrum[12] (neat), =CH (split triplet, τ 4.50–4.87, wt 1.0), SCH_2C= (doublet at τ 6.76 and 6.88, wt 2.0), SCH_2 (quartet at τ 7.34, 7.47, 7.59, and 7.71, wt 2.2), =C(CH_3)$_2$ (two split peaks near τ 8.25 and 8.32, wt 6.3), CH_3 (triplet at τ 8.68, 8.81, and 8.93, wt 3.2); vpc (column set at 168°, pressure 15 psi) showed one peak.

Anal. Calcd for $C_7H_{14}S$: C, 64.55; H, 10.83. Found: C, 64.48; H, 10.74.

The Reaction between γ,γ-Dimethylallyl Phenyl Sulfide (**12**) **and Dichlorocarbene.**—Ethyl trichloroacetate (42.0 g, 0.22 mole) was added in 45 min to a cold (ice bath) and stirred mixture, under nitrogen, of γ,γ-dimethylallyl phenyl sulfide (**12**, 30.0 g, 0.17 mole), sodium methoxide (22.0 g, 0.41 mole), and olefin-free petroleum ether (200 ml, bp 30–60°). The mixture was stirred at 0° during 4 hr, then allowed to come to room temperature overnight. Water (200 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 rotary evaporator. Repeated distillations of the residue gave a mixture (16.6 g, bp 81.5–82.5° at 0.01 mm, $n^{23.5}{}_\mathrm{D}$ 1.5790–1.5836), which could not be purified by further distillation. The principal product in this mixture was 1,1-dichloro-2,2-dimethyl-1-phenylmercapto-3-butene (**13**) according to the infrared and nmr spectra: ν^{neat} 925 and 995 (CH=CH_2), 1640 cm^{-1} (C=C); nmr spectrum[12] (neat), C_6H_5 (complex near τ 2.80), =CH (four peaks at τ 3.42, 3.59, 3.72, and 3.88), =CH_2 (complex, τ 4.67–5.00), CH_3 (singlet at τ 8.50), small impurity peaks near τ 2.30 (complex), 3.17 (two close peaks), 8.40 (two split peaks) probably due to the presence of $C_6H_5SC(Cl)=CHCH=C(CH_3)_2$ (**14**), and near τ 7.20, 8.87, and 9.05.

The mixture (5.0 g) was refluxed with hydrogen peroxide (20 ml, 30%) in acetic acid (40 ml) for 3.5 hr. The oil obtained subsequent to addition of water was extracted with ether (70 ml). The ether extract was washed with saturated sodium carbonate solution. The dried ($MgSO_4$) ether solution was concentrated in a rotatory evaporator, and the oily residue (3.7 g) was chromatographed on a silica gel (100–200 mesh) column. Elution of the column with benzene–ether (2:1) yielded the sulfone **18**: 0.3 mg; mp 108–109° (crystallized from ethanol); ν^{Nujol} 1790 (C=O), near 1155 and 1330 (SO_2), no absorption near 900 and 1000 cm^{-1} (no CH=CH_2); nmr spectrum[12] (10% in $DCCl_3$), C_6H_5 (complex, τ 2.00–2.60, wt 5.1), $CHCH_2$ (multiplet, τ 5.34–6.42, wt 3.0), CH_3 (two peaks at τ 8.42 and 8.61, wt 6.2).

Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.67; H, 5.55. Found: C, 56.95; H, 5.33.

Phenyl Thiolester of 2,2-Dimethyl-3-butenoic Acid (**19**).—The dichlorocarbene reaction was repeated with γ,γ-dimethylallyl phenyl sulfide (**12**, 31.6 g, 0.177 mole), ethyl trichloroacetate (49.0 g, 0.256 mole), sodium methoxide (27.1 g, 0.50 mole), and olefin-free petroleum ether (250 ml, bp 30–60°). Distillation of the crude reaction mixture which was processed as described in the proceeding experiment gave a fraction (34.7 g, bp 115–145° at 0.1 mm, $n^{19}{}_\mathrm{D}$ 1.5818), which was chromatographed in portions of 11.0 g, under vigorous evolution of hydrogen chloride, on a silica gel (100–200 mesh) column with petroleum ether (bp 60–68°)-benzene (2:1) as elution solvent. Distillation of the concentrated solution gave, in addition to an unidentified higher boiling fraction (1.2 g, bp 94–95° at 0.02 mm, $n^{22}{}_\mathrm{D}$ 1.5760), the phenyl thiolester **19**: 11.3 g, 0.055 mole, 31% yield calculated on **12**; bp 67–68° (0.04 mm); $n^{21}{}_\mathrm{D}$ 1.5533; ν^{neat} 1690 (C=O), 1630 (C=C), 910 and 960 cm^{-1} (CH=CH_2); nmr spectrum[12] (neat), C_6H_5 (complex, τ 2.56–2.90, wt 5.2), =CH (four peaks at τ 3.70, 3.87, 3.99, and 4.16, wt 1.0), =CH_2 (complex, τ 4.68–5.01, wt 2.0), CH_3 (singlet at τ 8.70, wt 6.1). A sample was redistilled for analysis (bp 56–57° at 0.01 mm, $n^{22.5}{}_\mathrm{D}$ 1.5520).

Anal. Calcd for $C_{12}H_{14}OS$: C, 69.85; H, 6.83; S, 15.55. Found: C, 69.65; H, 6.63; S, 15.45.

2,2-Dimethyl-3-butenoic Acid (**20**).—The phenyl thiolester of 2,2-dimethyl-3-butenoic acid (**19**, 4.2 g, 0.02 mole) was refluxed with a solution of sodium hydroxide (8.0 g, 0.2 mole) in a mixture of water (10 ml) and ethanol (40 ml) for 4 hr. Water (100 ml) was added and the mixture was washed twice with ether (50 ml). The water layer was acidified with 2 *N* sulfuric acid and extracted twice with ether (75 ml). The dried ($MgSO_4$) organic layers were concentrated in a rotatory evaporator. Distillation of the residue through a spiral-wire column gave **20**: 1.4 g, 0.012 mole, 60% yield; bp 88° (16 mm); $n^{20}{}_\mathrm{D}$ 1.4309 (lit.[13a] bp 100–102° at 28 mm, $n^{20}{}_\mathrm{D}$ 1.4295); ν^{neat} 1700–1720 (C=O), 2500–3000 (OH), 1645 cm^{-1} (C=C); the infrared spectrum was identical with no. 6208 in "The Sadtler Standard Spectra;[13b] nmr spec-

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[7] The sulfide **17** was formed in higher yield than could be accommodated by the assumption that **17** was formed from γ,γ-dimethylallyl ethyl sulfide, present as a contaminate (<2%) in the starting sulfide **15**, by a process involving an allylic rearrangement.

[8] (a) W. E. Parham and R. Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961); (b) W. E. Parham, L. Christensen, S. H. Groen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964).

[9] W. E. Parham and S. H. Groen, *ibid.*, **30**, 3181 (1965).

[10] A. J. Ultée, *J. Chem. Soc.*, 530 (1948).

[11] P. B. D. de la Mare and C. A. Vernon, *ibid.*, 3555 (1953).

[12] The nmr spectra were taken on a Varian A-60 at 60 Mc (internal standard, tetramethylsilane). Weights were obtained by integration.

[13] (a) H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **76**, 5403 (1954); (b) "The Sadtler Standard Spectra," Midget Edition, Philadelphia, Pa., Spectrum No. 6208.

trum[12] (neat), $\mathrm{CO_2}H$ (singlet at τ −2.50, wt 1.0), $=\mathrm{C}H$ (four peaks at τ 3.61, 3.78, 3.91, and 4.08, wt 1.0), $=\mathrm{C}H_2$ (complex, τ 4.68–5.00, wt 2.0), $\mathrm{C}H_3$ (peak at τ 8.70, wt 6.2). A sample was redistilled for analysis (bp 87° at 16 mm, $n^{20}\mathrm{D}$ 1.4291).

Anal. Calcd for $\mathrm{C_6H_{10}O_2}$: C, 63.13; H, 8.84. Found: C, 63.28; H, 8.81.

3,4-Dibromo-2,2-dimethylbutanoic acid (**21**) was prepared from **20** as described by Kwart and Miller:[13a] 70% yield; mp 91–92° (lit.[13a] mp 89–91°); ν^{Nujol} 1715 cm^{-1} (C=O); nmr spectrum[12] (30% in $\mathrm{DCCl_3}$), $\mathrm{CO_2}H$ (broad peak near τ −2.03, wt 1.0), $\mathrm{C}H$ (four peaks at τ 5.32, 5.40, 5.47 and 5.55, wt 1.1), $\mathrm{C}H_2$ (multiplet, τ 5.94–6.55, wt 2.0), $\mathrm{C}H_3$ (two peaks at τ 8.58 and 8.63, wt 6.2).

Anal. Calcd for $\mathrm{C_6H_{10}Br_2O_2}$: C, 26.30; H, 3.68; Br, 58.34. Found: C, 26.49; H, 3.62; Br, 58.02.

Reduction of the Dichlorocarbene Reaction Mixture of γ,γ-Dimethylallyl Phenyl Sulfide (**12**).—The dichlorocarbene reaction mixture (bp 115–145° at 0.1 mm; $n^{19}\mathrm{D}$ 1.5818, 1.7 g), dissolved in 75% ethanol–water (100 ml), was refluxed with Raney nickel (about 30 g) for 4 hr. Water (300 ml) was added and the mixture distilled with steam. About 20 ml of distillate was collected. The distillate was diluted with water (20 ml) and extracted with isooctane (5 ml). The isooctane extract was dried over calcium chloride. A sample, analyzed by vpc (column set at 49°, pressure 15 psi) showed the absence of 3-methylpentane and the presence of 2-methylbutane (derived from starting sulfide **12**), 2,2-dimethylbutane (derived from **13**), and 2-methylpentane (derived from **14**) in the approximate ratio of 10:35:55, respectively.

The reaction between γ,γ-dimethylallyl ethyl sulfide and dichlorocarbene and the isolation of the ethyl thiolester of 2,2-dimethyl-3-butenoic acid were carried out as described for γ,γ-dimethylallyl phenyl sulfide (**12**), using γ,γ-dimethylallyl ethyl sulfide (20.3 g, 0.156 mole), ethyl trichloroacetate (49.0 g, 0.256 mole), sodium methoxide (19.7 g, 0.365 mole), and olefin-free petroleum ether (250 ml, bp 30–60°). A fraction[14] (23.5 g, bp 60° at 15 mm, 120° at 0.05 mm) was chromatographed as described for the dichlorocarbene reaction product of γ,γ-dimethylallyl phenyl sulfide (**12**). Distillation of the concentrated eluent solution gave, in addition to a higher boiling fraction (1.6 g, bp 40–45° at 0.01 mm, $n^{23.5}\mathrm{D}$ 1.5160), the ethyl thiolester of 2,2-dimethyl-3-butenoic acid: 6.3 g, 0.04 mole, 26% yield; bp 67–69° (12 mm); $n^{23}\mathrm{D}$ 1.4770; ν^{neat} 1675 (C=O), 1635 (C=C), 915, 965, and 1820 cm^{-1} ($\mathrm{CH{=}CH_2}$); nmr spectrum[12] (neat), $=\mathrm{C}H$ (four peaks at τ 3.72, 3.89, 4.01, and 4.18, wt 0.9), $=\mathrm{C}H_2$ (complex, τ 4.68–5.03, wt 1.9), $\mathrm{SC}H_2$ (quartet at τ 7.02, 7.14, 7.26, and 7.39, wt 2.0), $\mathrm{C(C}H_3)_2$ + $\mathrm{C}H_3$ (singlet at τ 8.72 and triplet at τ 8.72, 8.83, and 8.94, wt 9.0). A sample was redistilled for analysis (bp 71–72° at 15 mm).

Anal. Calcd for $\mathrm{C_8H_{14}OS}$: C, 60.71; H, 8.92; S, 20.27. Found: C, 60.41; H, 8.93; S, 19.94.

The ethyl thiolester of 2,2-dimethyl-3-butenoic acid was hydrolyzed as described for the phenyl thiolester (**19**). 2,2-Dimethyl-3-butenoic acid (**20**) was obtained in 69% yield (bp 85–87° at 16 mm, $n^{22}\mathrm{D}$ 1.4291).

γ,γ-Dimethylallylmercaptan (**22**) **was prepared as described for 4-methylpent-3-ene-2-thiol**[15] by using isoprene instead of 2-methylpenta-1,3-diene: 30% yield, bp 125–128° (lit.[16] bp 125–127°).

γ,γ-Dimethylallyl ethyl disulfide (**23**) was prepared as described for 1,3-dimethylbut-2-enyl ethyl disulfide[6] by using γ,γ-dimethylallyl mercaptan (**22**) instead of 4-methylpent-3-ene-2-thiol: 37% yield; bp 94–99° (15 mm); $n^{29.5}\mathrm{D}$ 1.5203; ν^{neat} 1660 cm^{-1} (C=C); nmr spectrum[12] (neat), $=\mathrm{C}H$ (split triplet at τ 4.56–4.95, wt 1.0), $\mathrm{SC}H_2\mathrm{C}=$ (doublet at τ 6.61 and 6.74, wt 2.1), $\mathrm{SC}H_2$ (quartet at τ 7.17, 7.30, 7.42, and 7.54, wt 2.1), $=\mathrm{C(C}H_3)_2$ (split peak near τ 8.31, wt 5.4), $\mathrm{C}H_3$ (triplet at τ 8.62, 8.74, and 8.86, wt 2.8); vpc (column set at 199°, pressure of 15 psi) showed one peak. A sample was redistilled for analysis (bp 95–98° at 16 mm, $n^{25}\mathrm{D}$ 1.5230).

Anal. Calcd for $\mathrm{C_7H_{14}S_2}$: C, 51.79; H, 8.69; S, 39.52. Found: C, 52.08; H, 8.84; S, 39.62.

α,α-Dimethylallyl ethyl sulfide (**15**) was prepared as described for 1,1-dimethylbut-2-enyl ethyl sulfide[6] by using γ,γ-dimethylallyl ethyl disulfide (**23**, 35.5 g, 0.22 mole) instead of 1,3-dimethylbut-2-enyl ethyl disulfide and triphenylphosphine (90.0 g, 0.34 mole). α,α-Dimethylally ethyl sulfide (**15**) contaminated with diethyl disulfide (~7%) and γ,γ-dimethylallyl ethyl sulfide (<2%) was collected: 14.0 g, ~45% yield; bp 51–56° (32 mm); $n^{25}\mathrm{D}$ 1.4658; ν^{neat} 1630 (C=C), 905, 990, and 1810 cm^{-1} ($\mathrm{CH{=}CH_2}$); nmr spectrum[12] (neat), $=\mathrm{C}H$ (multiplet, τ 3.95–4.43, wt 1.0), $=\mathrm{C}H_2$ (complex, τ 5.00–5.31, wt 2.0), $\mathrm{SC}H_2$ of diethyl disulfide + $\mathrm{SC}H_2$ of **15** (two partly superimposed quartets of τ 7.17, 7.30, 7.42, and 7.54 and 7.50, 7.62, 7.74, and 7.86, wt 2.3), $\mathrm{C}H_3$ of diethyl disulfide + $\mathrm{C}H_3$ and $\mathrm{C(C}H_3)_2$ of **15** (partly superimposed triplets τ 8.62–9.00 and singlet τ 8.69, wt 8.5); vpc (Beckman G.C. 4, silicone oil S.E. 30 on Chromosorb W 80–100 column set at 90°, carrier gas He, flow 17 cc/min) showed the presence of **15**, diethyl disulfide (~7%), and γ,γ-dimethylallyl ethyl sulfide (<2%).

The impure α,α-dimethylallyl ethyl sulfide (**15**, 14.0 g, 0.11 mole) was refluxed with $\mathrm{LiAlH_4}$ (1.0 g) in ether (80 ml) during 2 hr. Water (10 ml) was added and the mixture was extracted twice with 10% sodium hydroxide in water (50 ml). The dried ($\mathrm{MgSO_4}$) ether solution was concentrated in a rotatory evaporator. Distillation of the residue through a spiral-wire column gave **15**: 6.6 g; bp 48–50° (29 mm); $n^{24.5}\mathrm{D}$ 1.4624; ν^{neat} 1630 (C=C), 905, 990, and 1810 cm^{-1} ($\mathrm{CH{=}CH_2}$); nmr nmr spectrum[12] (neat), $=\mathrm{C}H$ (multiplet τ 3.92–4.38, wt 1.0), $=\mathrm{C}H_2$ (complex, τ 4.96–5.28, wt 2.0), $\mathrm{SC}H_2$ (quartet at τ 7.47, 7.59, 7.72, and 7.84, wt 2.2), $\mathrm{C}H_3$ and $\mathrm{C(C}H_3)_2$ (partly superimposed triplet at τ 8.75, 8.88, and 9.00, and singlet at τ 8.69, wt 9.2); vpc (column used for **15** set at 100° carrier gas He, flow 17 cc/min) showed a strong peak (**15**) with minor impurity (<2%, γ,γ-dimethylallyl ethyl sulfide). A sample was redistilled for analysis (bp 47° at 22 mm, $n^{22.5}\mathrm{D}$ 1.4636).

Anal. Calcd for $\mathrm{C_7H_{14}S}$: C, 64.55; H, 10.83; S, 24.62. Found: C, 64.95; H, 10.83; S, 24.89.

Reaction between α,α-dimethylallyl ethyl sulfide (**15**) **and dichlorocarbene** was carried out as described for γ,γ-dimethylallyl phenyl sulfide (**12**) with α,α-dimethylallyl ethyl sulfide (**15**, 6.0 g, 0.046 mole), ethyl trichloroacetate (14.0 g, 0.073 mole), sodium methoxide (7.7 g, 0.14 mole), and olefin-free petroleum ether (100 ml, bp 30–60°). The reaction mixture was not washed with water, but was filtered. Distillation of the concentrated filtrate gave a fraction, 5.5 g, bp 65–110° (0.8 mm), $n^{24}\mathrm{D}$ 1.5263–1.5362. Redistilltion of this fraction (4.0 g) gave 1-chloro-4,4-dimethyl-1-ethylmercaptobutadiene (**16**) with a small amount of 1,1-dichloro-2,2-dimethyl-1-ethylmercapto-3-butene (**17**): 1.7 g; bp 74.5–76.5° (0.7 mm); $n^{24.5}\mathrm{D}$ 1.5376; ν^{neat} 1640 cm^{-1} (C=C); nmr spectrum[12] (neat), $\mathrm{C_2H_5SCCl{=}C}H\mathrm{CH{=}C(CH_3)_2}$ (four peaks at τ 3.13, 3.19, 3.32, and 3.38), $=\mathrm{CHC}H\mathrm{{=}C(CH_3)_2}$ + $\mathrm{C_2H_5SCCl_2C(CH_3)_2C}H\mathrm{{=}CH_2}$ (complex τ 3.45–4.00), $\mathrm{C}H_2\mathrm{SCCl}=$ (quartet at τ 7.03, 7.16, 7.28, and 7.40), $=\mathrm{C(C}H_3)_2$ (split doublet near τ 8.25), $\mathrm{C}H_3\mathrm{CH_2SCCl}=$ (triplet at τ 8.67, 8.80, and 8.92), $\mathrm{C_2H_5SCCl_2C(CH_3)_2CH{=}C}H_2$ (complex, τ 4.58–5.00) $\mathrm{CH_3C}H_2\mathrm{SCCl_2}$ (quartet at τ 6.70, 6.82, 6.94, 7.05), $\mathrm{C(C}H_3)_2\mathrm{CCl_2}$ (peak at τ 8.55), $\mathrm{C}H_3\mathrm{CH_2SCCl_2}$ (in region of other methyl hydrogens near τ 8.65).

The crude fraction (bp 65–110° at 0.8 mm, 1.0 g), dissolved in absolute alcohol (80 ml), refluxed for 2 hr with Raney nickel (about 30 g). The mixture was distilled and 25 ml of distillate was collected. Water (75 ml) was added and the mixture was extracted with heptane (5 ml). A sample of the dried ($\mathrm{CaCl_2}$) heptane solution analyzed in a Beckman G.C. 4 vapor phase chromatograph using a 20% diisodecyl phthalate on Chromosorb W 80–100 column set at 40°, carrier gas He, flow 17 cc/min, showed the presence of a small amount of 2-methylbutane (derived from **15**), 2,2-dimethylbutane (derived from **17**), and 2-methylpentane (derived from **16**). The ratio of 2,2-dimethylbutane:2-methylpentane was 7:93, respectively.

The carbene reaction was repeated with α,α-dimethylallyl ethyl sulfide (**15**, 6.2 g, 0.048 mole), ethyl trichloroacetate (14.0 g, 0.073 mole), sodium methoxide (8.0 g, 0.15 mole), and olefin-free petroleum ether (100 ml, bp 30–60°). The filtered reaction

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[14] No pure products could be isolated by distillation of an analogous fraction in a parallel experiment. However, upon fractional distillation, a sample (bp 54–58° at 0.6 mm, $n^{23}\mathrm{D}$ 1.5155) was collected, which contained 1,1-dichloro-2,2-dimethyl-1-ethylmercapto-3-butene and a small amount of 1-chloro-4,4-dimethyl-1-ethylmercaptobutadiene according to infrared and nmr spectra: ν^{neat} 925 and 995 ($\mathrm{CH{=}CH_2}$), 1640 cm^{-1} (C=C); nmr spectrum[12] (neat), $=\mathrm{C}H\mathrm{C(CH_3)_2}$ (four peaks at τ 3.51, 3.68, 3.81, and 3.98), $=\mathrm{CH_2}$ (complex, τ 4.67–5.00), $\mathrm{C}H_2\mathrm{SCCl_2}$ (quartet at τ 6.68, 6.81, 6.93, and 7.06), $\mathrm{CCl_2C(C}H_3)_2$ (peak at τ 8.54), $\mathrm{C}H_3\mathrm{CH_2SCCl_2C(CH_3)_2CH{=}CH_2}$ and $\mathrm{C}H_3\mathrm{CH_2SCCl{=}CHCH{=}C(CH_3)_2}$ (complex, τ 8.57–8.90), $\mathrm{CH_3CH_2SCCl{=}C}H\mathrm{CH{=}C(CH_3)_2}$ (four peaks at τ 3.18, 3.22, 3.37, and 3.41), $=\mathrm{CHC}H\mathrm{{=}C(CH_3)_2}$ (complex, τ 3.75–4.00), $\mathrm{CH_3C}H_2\mathrm{SCCl}=$ (with impurity peaks near τ 7.20), $=\mathrm{C(C}H_3)_2$ (split doublet near τ 8.22), small impurity peaks near τ 4.20, 5.10, 7.10–7.70.

[15] B. Saville, *J. Chem. Soc.*, 5040 (1962).

[16] J. V. Braun and T. Plate, *Ber.*, **67**, 281 (1934).

mixture was concentrated at 80° (40 mm), residue 5.1 g. Distillation of the residue (4.5 g) gave a fraction (3.0 g, bp 70–110° at 0.7 mm, $n^{24}\text{D}$ 1.5292–1.5278), which was chromatographed on a silica gel (100–200 mesh) column. The column was washed with 100 ml of petroleum ether (bp 60–68°)–benzene (4:1). The eluent solution was concentrated in a rotatory evaporator. Distillation of the residue (1.9 g) yielded slightly impure 1-chloro-4,4-dimethyl-1-ethylmercaptobutadiene (**16**): 1.0 g, 14% yield calculated on **15**: bp 52–53.5° (0.1 mm); $n^{29}\text{D}$ 1.5482; ν^{neat} 1640 cm^{-1} (C=C); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 244.5 mμ (ϵ 12,400), 281.5 mμ (ϵ 15,200); nmr spectrum[12] (neat), CCl=C*H* (four peaks at τ 3.13, 3.19, 3.32, and 3.38, wt 0.8), C*H*=C(CH$_3$)$_2$ (complex, τ 3.66–4.02, wt 0.8), SC*H*$_2$ (quartet at τ 7.02, 7.15, 7.28, and 7.40, wt 1.9), =C(C*H*$_3$)$_2$ (split doublet near τ 8.25, wt 5.2), C*H*$_3$ (triplet at τ 8.65, 8.77, and 8.89, wt 3.0). This material was quite unstable and could not be sent out for analysis.

Raney nickel reduction of the dichlorocarbene reaction mixture from α,α-dimethylallyl ethyl sulfide (**15**) was carried out as described for the fraction with bp 65–110° (0.8 mm) using the concentrated reaction mixture (0.6 g). Vapor phase chromatography showed the absence of 3-methylpentane, the presence of a small amount of 2-methylbutane (derived from **15**), 2,2-dimethylbutane (derived from **17**), and 2-methylpentane (derived from **16**). The ratio of 2-methylpentane:2,2-dimethylbutane was 93.5:6.5, respectively.

Cinnamyl phenyl sulfide (**24a**) was prepared from cinnamyl bromide and sodium thiophenolate: 60% yield; mp 77.5–78.5° (lit.[17] mp 77–78°); ν^{Nujol} 960 cm^{-1} (*trans* CH=CH); nmr spectrum[18] (20% in DCCl$_3$), C$_6$*H*$_5$ (complex, τ 2.61–2.92), =C*H* (complex, τ 3.66–3.90, wt ~2.0), C*H*$_2$ (doublet at τ 6.32 and 6.43, wt ~2.0).

Anal. Calcd for C$_{15}$H$_{14}$S: C, 79.60; H, 6.23. Found: C, 79.57; H, 6.48.

Cinnamyl methyl sulfide (**24b**) was prepared from cinnamyl bromide and the sodium salt of methyl mercaptan: bp 80–83° (0.08 mm); $n^{23}\text{D}$ 1.5972 (lit.[19] bp 142–144° at 144 mm); ν^{neat} 960 cm^{-1} (*trans* CH=CH); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 254 mμ (ϵ 17,430), 284 (sh) (2350), 293.5 (1480); nmr spectrum[12] (50% in CCl$_4$), C$_6$*H*$_5$ (complex, τ 2.65–2.90, wt 5.2), =C*H* (multiplet, τ 3.48–4.20, wt 2.1), C*H*$_2$ (doublet at τ 6.83 and 6.93, wt 2.0), C*H*$_3$ (singlet at τ 8.08, wt 3.1).

Anal. Calcd for C$_{10}$H$_{12}$S: C, 73.11; H, 7.37. Found: C, 73.11; H, 7.55.

The reaction between cinnamyl phenyl sulfide (**24a**) **and dichlorocarbene** was carried out as described for γ,γ-dimethylallyl phenyl sulfide (**12**) using cinnamyl phenyl sulfide (**24a**, 13.5 g, 0.06 mole), ethyl trichloroacetate (22.0 g, 0.11 mole), sodium methoxide (7.0 g, 0.13 mole), and benzene (85 ml). The concentrated (rotatory evaporator) reaction mixture was chromatographed on silica gel (100–200 mesh) using petroleum ether (bp 60–68°)–benzene (10:1) as eluent. An oil was obtained, which was chromatographed again, and 1-chloro-2-phenyl-1-phenylmercaptobutadiene (**25a**) was obtained in low yield: 210 mg; mp 86–87° (from ethanol); ν^{Nujol} 920 and 985 cm^{-1} (CH=CH$_2$); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 226 mμ (ϵ 15,470), 254 (16,340), 280 (sh) (10,400); nmr spectrum[12] (10% in DCCl$_3$), C$_6$*H*$_5$ + =C*H* (complex, τ 2.53–2.98, wt 11.4), =CH$_2$ (four doublets at τ 4.53 and 4.56, 4.71 and 4.74, 4.99 and 5.02, 5.27 and 5.30, wt 2.0).

Anal. Calcd for C$_{16}$H$_{13}$ClS: C, 70.44; H, 4.80; S, 11.70. Found: C, 70.17; H, 5.08; S, 11.51.

Reduction of the Mixture from the Reaction of Cinnamyl Phenyl Sulfide (**24a**) **and Dichlorocarbene.**—The concentrated reaction mixture (3.0 g), dissolved in 75% ethanol–water (100 ml), was refluxed for 4 hr with Raney nickel (about 30 g). Water (500 ml) was added and the mixture was distilled with steam. About 300 ml of distillate was collected. The distillate was diluted to 500 ml with water and extracted twice with pentane (50 ml). The dried (MgSO$_4$–CaCl$_2$) mixture was concentrated to approximately 3 ml. A sample, analyzed by vpc (silicone grease, column set at 140°, pressure of 15 psi) showed the presence of *n*-propylbenzene (~15%, derived from **24a**), iso- or *sec*-butylbenzene (~60%, the latter derived from **25a**) and *n*-butylbenzene (~25%, probably derived from **26a**). A capillary column coated with di-*n*-decyl phthalate separated iso- and *sec*-butylbenzene and showed that in the reduction mixture, no isobutylbenzene (derived from the cyclopropane formed by addition of dichlorocarbene to the double bond of cinnamyl phenyl sulfide) was present.

The reaction between cinnamyl methyl sulfide (**24b**) **and dichlorocarbene** was carried out as described for γ,γ-dimethylallyl phenyl sulfide (**12**) using cinnamyl methyl sulfide (**24b**, 32.8 g, 0.20 mole), ethyl trichloroacetate (48.0 g, 0.25 mole), sodium methoxide (22.1 g, 0.41 mole), and petroleum ether (200 ml, bp 30–60°). Repeated distillations of the concentrated reaction mixture gave two fractions.

A.—1-Chloro-1-methylmercapto-2-phenylbutadiene (**25b**, ~75%) and cinnamyl methyl sulfide (**24b**, ~25%): 11.3 g; bp 74–77° (0.01 mm); $n^{22.5}\text{D}$ 1.6081–1.6112; nmr spectrum[12] (50% in CCl$_4$), C$_6$*H*$_5$ of **24b** and **25b** + =CH of **25b** (complex, τ 2.45–3.03, wt 7.4), =C*H*$_2$ of **25b** (two triplets at τ 4.70, 4.72, and 4.75 and 4.89, 4.91, and 4.93 and two quartets, each peak of approximately the same intensity at τ 5.09, 5.11, 5.13, 5.15 and 5.39, 5.41, 5.43, 5.45, wt 2.0), C*H*$_3$ of **25b** (doublet at τ 7.68 and 7.81, wt 3.0), =C*H* of **24b** (multiplet at τ 3.46–4.20, wt 0.7), SC*H*$_2$ of **24b** (doublet at τ 6.82 and 6.93, wt 0.65), C*H*$_3$ of **24b** (singlet at τ 8.07, wt 1.0). A sample of A was chromatographed on silica gel (100–200 mesh) with petroleum ether (bp 60–68°)–benzene (4:1) as eluent. Distillation of the concentrated eluent solution gave reasonably pure 1-chloro-1-methylmercapto-2-phenylbutadiene (**25b**): bp 65–66° (0.02 mm); $n^{24}\text{D}$ 1.6170; ν^{neat} 915 and 990 cm^{-1} (CH=CH$_2$); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 234 mμ (ϵ 11,980), 288 mμ (ϵ 10,670); nmr spectrum[12] (10% in CCl$_4$), C$_6$*H*$_5$ + =C*H* (complex, τ 2.50–3.06, wt 6.2), =C*H*$_2$ (two triplets at τ 4.70, 4.72, and 4.75 and 4.89, 4.91, and 4.93 and two quartets, each peak of approximately the same intensity at τ 5.10, 5.12, 5.14, 5.17 and 5.38, 5.40, 5.42, 5.44, wt 2.0), C*H*$_3$ (doublet at τ 7.62 nd 7.76, wt 3.2).

Anal. Calcd for C$_{11}$H$_{11}$ClS: C, 62.69; H, 5.26. Found: C, 62.19; H, 5.30.

B.—Impure 1-chloro-1-methylmercapto-4-phenylbutadiene (**26b**): 4.0 g; bp 97–98° (0.01 mm); $n^{22.5}\text{D}$ 1.6665; ν^{neat} 965 cm^{-1} (*trans* CH=CH); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 320 mμ (ϵ 26,000), 272 (sh) (7880), absorption between 220–240 mμ; nmr spectrum[12] (neat), C$_6$*H*$_5$C*H*= (complex, τ 2.70–3.15, wt 6.6), =C*H*C*H*= (complex, τ 3.42–3.83, wt 2.0), C*H*$_3$ (split peak near τ 7.84, wt 3.0), small impurity peaks near τ 4.80, 5.40, 7.40, 8.00, and 9.00. Raney nickel reduction of B (0.9 g) was carried out as described for the carbene reaction products of cinnamyl phenyl sulfide (**24a**). Vapor phase chromatography of the pentane solution showed the presence of *n*-butylbenzene (~81%, derived from **26b**) together with two peaks of unknown identity (together ~8%), *sec*-butylbenzene (~5%, derived from **25b**), and *n*-propylbenzene (~6%, derived from **24b**).

Reduction of the dichlorocarbene reaction mixture of cinnamyl methyl sulfide (**24b**) was carried out, as described for the dichlorocarbene reaction mixture of **24a**, with 2.0 g of the concentrated reaction mixture. Vapor phase chromatography of the pentane solution showed the presence of *n*-propylbenzene (derived from **24b**), *sec*-butylbenzene (derived from **25b**), *n*-butylbenzene (derived from **26b**) in the approximate ratio 26:48:26, respectively, together with a small amount of an unknown compound.

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

[18] The nmr spectrum was taken on a Varian V 4302 at 56.44 Mc (internal standard, tetramethylsilane). Weights were estimates obtained by using a planimeter.

[19] V. Baliah and S. Shanmuganathan, *J. Indian Chem. Soc.*, **35**, 31 (1958).