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Reaction of Enol Ethers with Carbenes. X.[1] Ring Opening of 2,2-Dichlorocyclopropyl Phenyl Sulfides[2]

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The ring opening reactions of six known or new 2,2-dichlorocyclopropyl phenyl sulfides have been carried out with potassium *t*-butoxide in *t*-butyl alcohol and with pyridine. The products were enynes, butadienes, allenes and, as minor products, α,β-unsaturated aldehydes containing the phenylmercapto group. Reaction of a mixture of *cis*- and *trans*-1,1-dichloro-2-methyl-3-phenylmercaptocyclopropane (**2**) with pyridine gave unchanged *trans*-isomer. This apparent selectivity is explained on the basis of the steric effects for ring opening.

In recent years the ring opening of *gem*-dichlorocyclopropanes, derived from enol ethers with dichlorocarbene, have been investigated by Parham *et al.*[5] and by Skattebøl,[6] and the subject has been reviewed by Parham and Schweizer.[7] In order to gain additional information on such ring opening reactions, we have prepared the following six *gem*-dichlorocyclopropanes (**1**—**6**) by the reaction of the corresponding α,β-unsaturated sulfides with dichlorocarbene, and have studied their reactions with potassium *t*-butoxide in *t*-butyl alcohol and with pyridine.

The ring opening reactions probably occur by an El elimination process of the type illustrated in Eq. (1) in a manner analogous to that established for the alkoxy analogues.[5-7]

1) Supported in Part by the U. S. Research Office (Durham) (DA-ARO-D-31-124-G-848). Part IX: W. E. Parham, F. M. Parham, J. F. Dooley and M. K. Meilahn, *J. Org. Chem.*, **33**, 3651 (1968).

2) Presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

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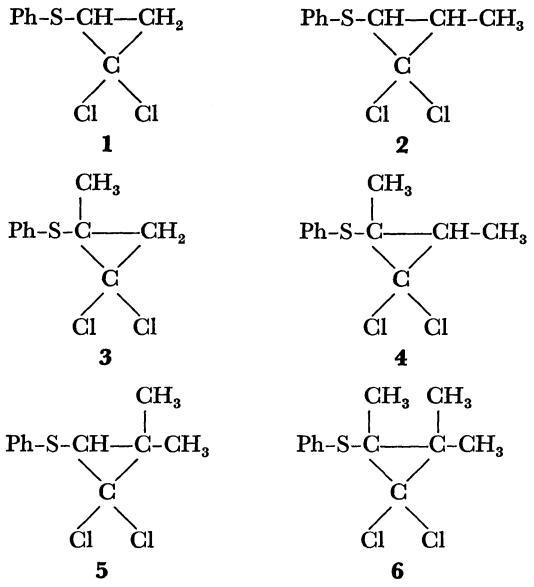
5) W. E. Parham, R. W. Soeder and R. M. Dodson, *J. Amer. Chem. Soc.*, **84**, 1755 (1962).

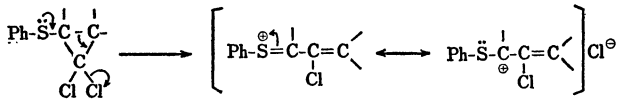
6) L. Skattebøl, *J. Org. Chem.*, **31**, 1554 (1966).

7) For a review, see W. E. Parham and E. E. Schweizer, "Organic Reactions," Vol. 13, p. 55, (1963).



Scheme

In the case of the reaction of **2** with potassium *t*-butoxide in *t*-butyl alcohol, we isolated an α,β-unsaturated aldehyde. Such elimination reaction has been reported.[8] The results of these studies constitute the subject of this report.



(1)

Results

Preparation of α,β-Unsaturated Sulfides (Carbene Acceptors). 1-Methyl-1-phenylmercaptoethylene (**7**),[9] 2-phenylmercapto-2-butene, (**8**), and 3-methyl-2-phenylmercapto-2-butene (**10**) were prepared by distillation of acetone diphenylmercaptol,[10] ethyl methyl ketone diphenylmercaptol, and isopropyl methyl ketone diphenylmercaptol with potassium bisulfate, respectively. 2-Methyl-1-phenylmercapto-1-propene (**9**)[11] was obtained by isomerization of 2-

TABLE 1. SYNTHESES OF α,β-UNSATURATED SULFIDES $Ph\text{-}S\text{-}C(R_1)=C(R_2)\text{-}R_3$

Compd.	R_1	R_2	R_3	Bp, °C/mmHg (lit)	n_D^t (lit.)	Yield, %	Found (Calcd) % C	H	S	
7[a]	CH_3	H	H	81—86/9 (68—69/6)[9a] (50/2)[9b]	n_D^{25} 1.5656	76	71.69 (71.95	6.85 6.71	21.36 21.34	for $C_9H_{10}S$)
8[b]	CH_3	H	CH_3	81—84/3	n_D^{27} 1.5679	94	72.96 (73.12	7.32 7.36		for $C_{10}H_{12}S$)
9	H	CH_3	CH_3	84—86/4 (111—112/9)[11a] (61—64/0.75)[11b]	n_D^{25} 1.5761 (n_D^{25} 1.5782)[11a] (n_D^{20} 1.5792)[11b]	90	72.99 (73.12	7.37 7.36		for $C_{10}H_{12}S$)
10	CH_3	CH_3	CH_3	114—116/7	n_D^{25} 1.5721	68	74.16 (74.10	7.82 7.91		for $C_{11}H_{14}S$)

a) The distillate from acetone diphylmercaptol should be trapped in an alkali solution because product **7** is easily polymerized by acid (thiophenol) which co-distills.
b) Compound **8** is a mixture of *cis* and *trans* isomers.

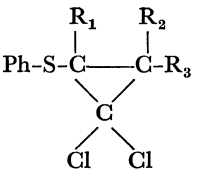
TABLE 2. IR, UV, AND NMR SPECTRA OF THE α,β-UNSATURATED SULFIDES

Compd.	IR (neat), cm^{-1} νC=C	δ=C-H	UV, $\lambda_{max}^{95\%\ EtOH}$ mμ (ε)	NMR (in CCl_4) τ
7	1620	870	244 (6660), 264 (4900)	2.38—2.97 (c,[a] 5, C_6H_5), 4.93, 5.13 (two s, 2, $=CH_2$), 8.06 (s, 3, CH_3)
8	1645	830	247 (7320), 263 (5750)	2.63—3.04 (c, 5, C_6H_5), 3.90—4.43) (m, 1, =CH-), 8.00—8.47 (m, 6, $2CH_3$)
9		810	250 (8150), 266 (7960)	2.66—3.12 (c, 5, C_6H_5), 4.08—4.27 (m, 1, =CH), 8.17 (s, 6, $2CH_3$)
10	1635		249 (10870), 262.5 (sh., 8240)	2.70—3.06 (c, 5, C_6H_5), 8.00, 8.07 8.14 (three s, 9, $3CH_3$)

a) c: complex

8) W. E. Parham and D. G. Weetman, *J. Org. Chem.*, **34**, 56 (1969). *cf.* a) W. E. Parham and J. F. Dooley, *J. Amer. Chem. Soc.*, **89**, 985 (1967); b) W. E. Parham and J. F. Dooley, *J. Org. Chem.*, **33**, 1476 (1968).
9) *cf.* a) N. K. Kulbovskaya, E. P. Grachova and M. F. Shostakovskii, *Zh. Obshch. Khim.*, **30**, 81 (1960); b) R. Kh. Freidlina, A. B. Terentev, and R. G. Petrova, *Dokl. Akad. Nauk SSSR*, **149**, 860 (1963).
10) A. Schönberg and K. Praefcke, *Chem. Ber.*, **100**, 778 (1967).
11) *cf.* a) R. Adams and A. Ferretti, *J. Amer. Chem. Soc.*, **81**, 4927; (1959); b) E. Benzing, US, 3118002 (c 1260—609), Jan. 14, (1964).

Table 3. Syntheses of 2,2-dichlorocyclopropyl phenyl sulfides



Compd.	R_1	R_2	R_3	Bp, °C/mmHg (Mp, °C)	n_D^t	Yield, %	Found (Calcd) % C	H
3	CH_3	H	H	70—73/0.001 (31—33)	n_D^{25} 1.5809	90	51.69 (51.55	4.25 4.32 for $C_{10}H_{10}Cl_2S$)
4[a]	CH_3	H	CH_3	90—92/0.01	n_D^{25} 1.5771	73	53.70 (53.45	4.87 4.89 for $C_{11}H_{12}Cl_2S$)
5	H	CH_3	CH_3	94—95/0.01	n_D^{25} 1.5764	72	53.51 (53.45	4.89 4.89 for $C_{11}H_{12}Cl_2S$)
6	CH_3	CH_3	CH_3	85—87/0.005 (57—58)		74	55.06 (55.18	5.49 5.40 for $C_{12}H_{14}Cl_2S$)

a) Compound **4** is a mixture of *cis* and *trans* isomers.

Table 4. IR, UV, and NMR spectra of the 2,2-dichlorocyclopropyl phenyl sulfides

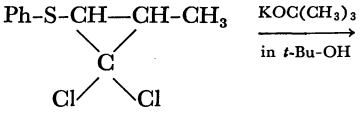
Compd.	UV, $\lambda_{max}^{95\%\ EtOH}$ mμ (ε)	NMR (in CCl_4) τ
3	216(sh., 8200), 238(4880), 254(4590)	2.45—2.98 (c, 5, C_6H_5), 8.20—8.60 (m, 5, CH_3 and CH_2, —s peak at 8.36 due to CH_3, two peaks at 8.42 and 8.46 due to CH_2)
4	216(sh., 7880), 241(sh., 5250), 254(5720)	2.40—2.90 (c, 5, C_6H_5), 8.05—9.00 (m, 7, $2CH_3$ and -CH-, —s at 8.37 due to S-C-CH_3, d(J=2.4Hz) at 8.58 due to CH-CH_3)
5	242(sh,, 7720), 251(8460)	2.40—2.80 (c, 5, C_6H_5), 7.40 (s, 1, CH), 8.48 (s, 3, CH_3), 8.63 (s, 3, CH_3)
6	244(sh., 5940), 254.5 (6700)	2.58—2.82 (c, 5, C_6H_5), 8.46, 8.48 (two s, 6, $C(CH_3)_2$), 8.61 (s, 3, C-CH_3)

methyl-1-phenylmercapto-2-propene[12] with sodium ethoxide using a procedure described by Tarbell *et al.*[13] for phenyl propenyl sulfide from allyl phenyl sulfide. The yields, analytical results and some spectral data of the olefins are summarized in Tables 1 and 2.

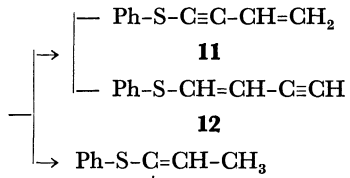
Preparation of 2,2-Dichlorocyclopropyl Phenyl Sulfides. The reactions of **7**, **8**, **9**, and **10** with ethyl trichloroacetate and sodium methoxide in olefin-free petroleum ether gave **3**, **4**, **5**, and **6**, respectively. The yields, analytical results and some spectral data of the 2,2-dichlorocyclopropyl phenyl sulfides are summarized in Tables 3 and 4.

Ring Opening of 1,1-Dichloro-2-phenylmercaptocyclopropane (1). The product of reaction of **1**[14] with potassium *t*-butoxide in *t*-butyl alcohol was an unidentified black tar. The parent cyclopropane **1** was quite stable in hot pyridine (50 hr) and the starting material was recovered in 80% yield.

Ring Opening of 1,1-Dichloro-2-methyl-3-phenylmercaptocyclopropane (2). The reaction of **2**[14] with potassium *t*-butoxide in *t*-butyl alcohol gave a compound assumed to be 1-formyl-1-phenylmercaptopropene (mixture of two geometrical isomers) (**13**), and a mixture[15] of 1-phenylmercaptobut-3-en-1-yne (**11**)[16] and 1-phenylmercaptobut-1-en-3-yne (*cis*- and *trans*-isomers) (**12**) (Eqs. (2) and (3)). Further evidence for the structure of **11** and **12** was obtained by an independent synthesis (50% yield) of the mixture of **11** and **12** by the reactions of 1-chloro-1-

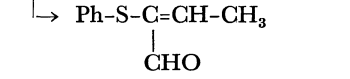


2 (*cis*-, *trans*-)

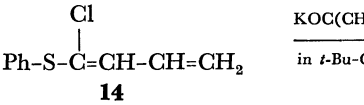


11 (2)

12



13 (3)



14 **11** + **12** (4)

12) W. E. Parham and S. H. Groen, *J. Org. Chem.*, **30**, 728 1965).

13) D. S. Tarbell and M. A. McCall, *J. Amer. Chem. Soc.*, **74**, 55 (1952).

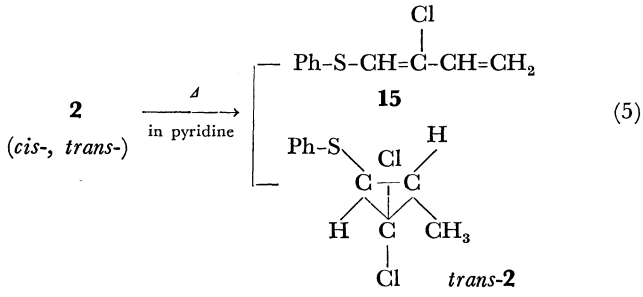
14) W. E. Parham, L. Christensen, S. H. Groen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964).

15) The mixture was not separated by fractional distillation.

16) A. A. Petrov, S. I. Radchenko, K. S. Mingaleva, I. G. Savich, and V. B. Lebedev, *J. Gen. Chem., (USSR)*, **34**, 1911 (1964).

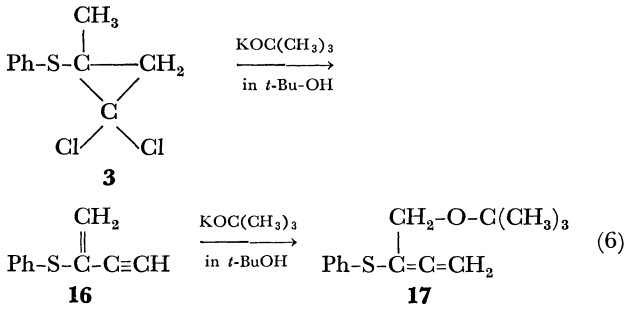
phenylmercaptobuta-1,3-diene (**14**)[17] with potassium *t*-butoxide in *t*-butyl alcohol (Eq. (4)).

The reaction of **2** with a large excess of pyridine under conditions of reflux for 40 hr was studied, and a mixture[15] of 2-chloro-1-phenylmercaptobuta-1,3-diene (**15**) and *trans*-**2** was obtained (Eq. (5)). Butadiene **15** and *trans*-**2** were detected by means of their NMR spectra. Compound **2** (mixture of *cis*- and *trans*-isomers) shows two doublets for S–CH, at τ 7.18 with J=10.0 Hz due to *cis*-isomer and at τ 7.68 with J=7.0 Hz due to *trans*-isomer.[14] The above reaction products showed only a doublet for S-CH due to the *trans*-isomer.



(5)

*Ring Opening of 1,1-Dichloro-2-methyl-2-phenylmercaptocyclopropane (**3**).* The products from the ring opening reaction of **3** with potassium *t*-butoxide in *t*-butyl alcohol were 2-phenylmercaptobut-1-en-3-yne (**16**) (20% yield) and 4-*t*-butoxy-3-phenylmercaptobuta-1,2-diene (**17**) (20% yield) contaminated with a trace amount of a compound containing aldehyde group (the aldehyde group was only detected by IR and NMR spectra: ν_{max} 1670 cm^{-1}; two doublets at τ −0.13, −0.03 (J=6 Hz), and at τ 0.23, 0.33 (J=6 Hz)). Compound **17** was a secondary product derived from **16**. These results are shown in Eq. (6).



(6)

In order to prove the structure of **17**, the reaction of **17** with Raney nickel (W-2) in ethyl alcohol was performed. Benzene and *n*-butyl *t*-butyl ether (**18**)[18] were identified as reduction products. On the other hand, the products from the reduction of **17** with hydrogen in the presence of Raney nickel (W-2) at room temperature were *sec*-butyl phenyl sulfide (**19**)[19] and *t*-butyl 2-phenylmercaptobutyl ether (**20**).

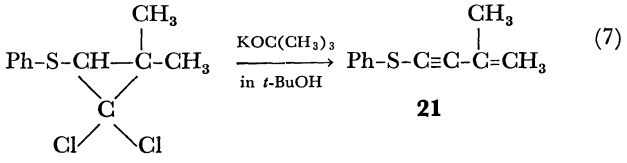
The isolated **16**[20] was converted into **17** (34% yield) by reaction with potassium *t*-butoxide in *t*-butyl alcohol.

When a solution of **3** in pyridine was refluxed for 70 hr, only black tar was obtained.

*Ring Opening of 1,1-Dichloro-2,3-dimethyl-2-phenylmercaptocyclopropane (**4**).* The products of reaction of **4** (mixture of *cis*- and *trans*-isomers) with potassium *t*-butoxide in *t*-butyl alcohol consisted of a considerable amount of black tar and very unstable enyne derivatives (IR, 3290, 2230, 2110, 920, and 800 cm^{-1}). The derivatives turned dark brown in contact with air, and polymerized. The reaction of **4** with hot pyridine was also studied. A large amount of black tar and a small amount of an unidentified liquid were obtained.

*Ring Opening of 1,1-Dichloro-2,2-dimethyl-3-phenylmercaptocyclopropane (**5**).* The product from the ring opening reaction of **5** using potassium *t*-butoxide was 3-methyl-1-phenylmercaptobut-3-en-1-yne (**21**) (60% yield) (Eq. (7)). The structure of **21** was confirmed by its independent synthesis by dehydrohalogenation of 1-chloro-3-methyl-1-phenylmercaptobuta-1,3-diene (**22**)[12] (Eq. (8)).

The ring opening reaction of **5** with pyridine was carried out, and 2-chloro-3-methyl-1-phenylmercaptobuta-1,3-diene (**23**)[21] (48% yield) was isolated. Compound **23** was easily converted into **21** by refluxing with a solution of potassium *t*-butoxide in *t*-butyl alcohol (50% yield) (Eq. (9)).



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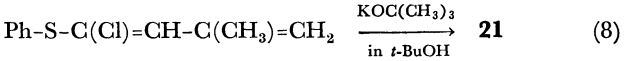

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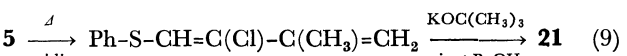
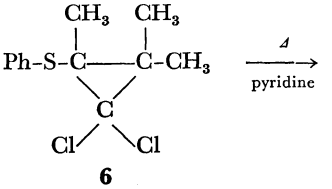


(9)

*Ring Opening of 1,1-Dichloro-2,3,3-trimethyl-2-phenylmercaptocyclopropane (**6**).* Attempts to effect ring opening of **6** with alkoxides (potassium *t*-butoxide in *t*-butyl alcohol, sodium ethoxide in ethyl alcohol and sodium methoxide in methyl alcohol) failed, and starting material **6** was recovered in high yield in every case. When hot pyridine was used as a base and a solvent, a product[21] assumed to be 3-chloro-2-methyl-4-phenylmercaptopenta-1,3-diene (**24**) or 3-chloro-4-methyl-2-phenylmercaptopenta-1,3-diene (**25**) was obtained in 70% yield (Eq. (10)).

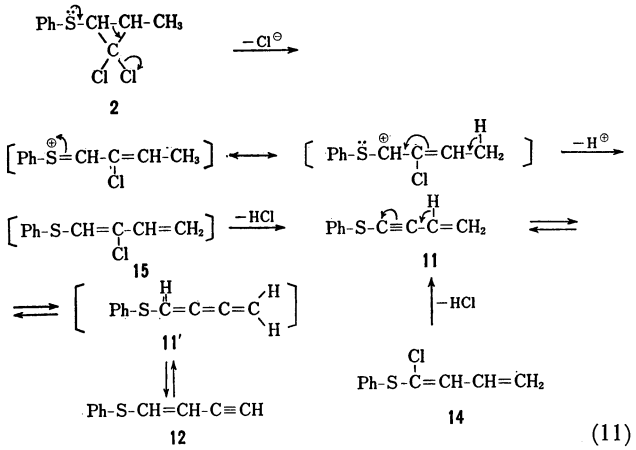


17) W. E. Parham and S. H. Groen, *J. Org. Chem.*, **29**, 2214 (1964).
18) L. Henry, *Rec. Trav. Chim.*, **23**, 329 (1904).
19) W. H. Taylor, *J. Amer. Chem. Soc.*, **58**, 2649 (1936).
20) Compound **16** was unstable, and rapidly turned brown in air.
21) The product appeared to be one compound by its GLPC and NMR spectrum.
22) H. Fischer, "The Chemistry of Alkenes," ed. by Saul Patai, Interscience Publishers, A division of John Wiley and Sons. Inc., New York, N. Y. (1964); p. 1106.

$$\left\{\begin{array}{ll} & \text{Ph-S-C}(CH_3)=C(Cl)-C(CH_3)=CH_2 \quad \mathbf{24} \\ \text{or} & CH_2=C(\text{Ph-S})-C(Cl)=C(CH_3)-CH_3 \quad \mathbf{25} \end{array}\right. \tag{10}$$

Discussion

The accelerating effect of the phenylmercapto group is considered to be a driving force for ring opening

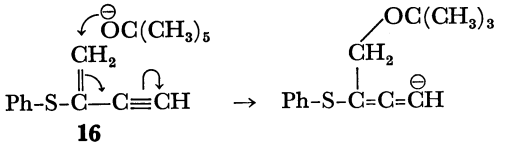


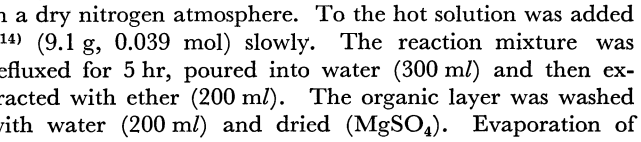
(11)

reaction of these 2,2-dichlorocyclopropyl phenyl sulfides, since the sulfur lone-pair electrons can stabilize the positive charge developed in the transition state or intermediate (Eq. (1)). The formation of **11** and **12** from **2** or **14** by use of potassium *t*-butoxide is explained as shown in Eq. (11). In particular, compound **12** is obtained from an intermediate butatriene (**11'**) by means of retro-propargylic rearrangement[22] in the presence of base. The presumed intermediate **11'** will be derived from **11** by means of prototropic rearrangement.

The ring opening of **2** (mixture of *cis*- and *trans*-isomers) with weak base pyridine led to the mixture of **15** and *trans*-**2** (Eq. (5)). That is, it turned out that *cis*-**2** underwent ring opening more rapidly than *trans*-**2**. As in our previous discussion on the rates of solvolysis of *cis*- and *trans*-1,1-dichloro-2,3-di-*n*-propylcyclopropane,[23] and *cis*- and *trans*-1,1-dichloro-2-ethoxy-3-*n*-propylcyclopropane[24] in the presence of ethanolic silver nitrate, the above experimental results are explained on the basis of steric effects of intermediates (or transition states) derived from the concerted ring opening reactions. Some pertinent arguments for the related preferential formation of only a *trans*-olefin from both *cis*- and *trans*-1,1-dichloro-2-ethoxy-3-methylcyclopropane have been discussed by Skattebøl[6]. Similar steric arguments can account for the stability of **6** in hot *t*-butyl alcohol - potassium *t*-butoxide.

The allene derivative **17** is obtained from **16** by addition of *t*-butoxide ion to **16** as illustrated in Eq. (12).





(12)

Experimental

Infrared spectra were obtained on a Perkin-Elmer 257 or an Unicam SP 200 spectrometer. Ultraviolet spectra were obtained in spectral grade solvents on a Cary spectrophotometer. Nuclear magnetic resonance spectra were mainly obtained on a Varian Associates Model A-60 or T-60 spectrometer using 20% solutions in carbon tetrachloride and tetramethylsilane as an internal standard. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Gas-liquid partition chromatography analyses were determined on a Beckman GC-4 apparatus.

Materials. Most of the α,β-unsaturated sulfides were prepared by distillation of the corresponding ketone diphenylmercaptol with potassium bisulfate (see Tables 1 and 2). 2,2-Dichlorocyclopropyl phenyl sulfides were prepared from the α,β-unsaturated sulfides, sodium methoxide (from a fresh bottle) and ethyl trichloroacetate by a procedure essentially the same as that for the reaction with phenyl propenyl sulfide[14] (see Tables 3 and 4).

Reaction of **2** *with Potassium* t-*Butoxide in* t-*Butyl Alcohol.* Potassium metal (5.9 g, 0.15 g-atom) was dissolved in *t*-butyl alcohol (150 m*l*) heated at the refluxed temperature in a dry nitrogen atmosphere. To the hot solution was added **2**[14] (9.1 g, 0.039 mol) slowly. The reaction mixture was refluxed for 5 hr, poured into water (300 m*l*) and then extracted with ether (200 m*l*). The organic layer was washed with water (200 m*l*) and dried ($MgSO_4$). Evaporation of the dry ether solution afforded a dark oil which gave two fractions on distillation.

A.—Mixture of 1-phenylmercaptobut-3-en-1-yne (**11**)[16] and 1-phenylmercaptobut-1-en-3-yne (*cis*- and *trans*-isomers) (**12**) : 2.9 g (46%); bp 54—65°C/0.005 mmHg; n_D^{25} 1.6205. A sample of the mixture was redistilled through a 10 cm Vigreux column for analysis: bp 50—53°C/0.002 mmHg; n_D^{25} 1.6208; IR (neat), 3280 cm^{-1} (≡C–H), 2160, 2100 (C≡C), 970, 925, (CH=CH_2); UV ($\lambda_{max}^{95\%EtOH}$), 219 mμ (sh., 12700), 228 (sh., 9500), 241 (9700), 250.5 (10100), 261 (10200); NMR (CCl_4), τ 2.52—2.98 (c, 5, C_6H_5), 2.92—3.43 (m, CH=CH), 3.70—4.83 (m, CH=CH_2), 6.66, 7.11 (two d, J=3 and 3 Hz, ≡C–H of *cis*- and *trans*-isomers), total wt of CH=CH, CH=CH_2 and ≡C–H was 3H; MS m/e, 160 (M^+). The ratio of **11** to **12** was about 7 to 4 (NMR spectrum).

Found: C, 74.51; H, 5.47; S, 20.17%. Calcd for $C_{10}H_8S$: C, 74.95; H, 5.03; S, 20.01%.

B.—A compound presumed to be 1-formyl-1-phenylmercaptopropene (two geometrical isomers) (**13**): 0.7 g (10%); bp 79—84°C/0.001 mmHg; n_D^{25} 1.5798; IR (neat), 1675 cm^{-1} (C=O), 820 (trisubstituted olefin); UV ($\lambda_{max}^{95\%EtOH}$), 252 mμ (ε 6520), 295 (15000); NMR (CCl_4), τ 2.26—3.05 (c, 6, C_6H_6 and C=CH–), 0.78 (s, 1, CHO), 8.66, 8.88 (two d, J=6.0 and 7.2 Hz, 3, CH_3).

Found: C, 67.94; H, 6.19%. Calcd for $C_{10}H_{10}OS$: C, 67.38; H, 5.66%.

2,4-Dinitrophenylhydrazone of **13**: Violet crystal, mp 221—222°C (corr) (from acetone).

Found: C, 53.54; H, 3.73; N, 15.43%. Calcd for $C_{16}H_{14}N_4SO_4$: C, 53.62; H, 3.94; N, 15.63%.

Reaction of **14** *with Potassium* t-*Butoxide in* t-*Butyl Alcohol.* To a hot (85—90°C) stirred solution prepared from potassium

23) W. E. Parham and K. S. Yong, *J. Org. Chem.*, **33**, 3947 (1968).
24) W. E. Parham and K. S. Yong, *ibid.*, **35**, 683 (1970).

metal (0.8 g, 0.02 g-atom) and *t*-butyl alcohol (90 ml) was added dropwise **14**[17] (8.9 g, 0.045 mole) in a nitrogen atmosphere. The reaction mixture was refluxed for 5 hr, and the solution was processed essentially as described for the reaction of **2** with potassium *t*-butoxide in *t*-butyl alcohol. A mixture of **11** and **12** was obtained: 3.7 g (51%); bp 62—64°C/0.007 mmHg; n_D^{27} 1.6208. The spectra (IR, UV and NMR) were essentially the same as those of the product derived from **2**.

(Found: C, 74.41; H, 5.31%. Calcd for $C_{10}H_8S$: C, 74.95; H, 5.03%).

*Reaction of **2** with Pyridine.* A mixture of **2** (7.0 g, 0.03 mol. The ratio of *cis*-**2** to *trans*-**2** was approximately 8 to 5—NMR spectrum) and pyridine (50 ml) was refluxed for 40 hr under a nitrogen atmosphere. By distilling the solution a considerable amount of residual black red tar and a mixture[15] of 2-chloro-1-phenylmercaptobuta-1,3-diene (**15**) and *trans*-**2** were obtained: 3.0 g; bp 81—82°C/0.06 mmHg; n_D^{25} 1.6235; IR (neat), 900, 980, 1620 cm^{-1} ($CH{=}CH_2$), 1380, 2920 (CH_3); NMR[25] (CCl_4), τ 2.60—3.10 (c, C_6H_5), 3.56 (s, –S–CH=), 3.60, 3.70, 3.76, 3.86 (J_{AX}=16.0 Hz, J_{BX}=10 Hz, $\underline{H}_X$–C=$CH_A H_B$), 4.56 (d, J_{AX}=16 Hz, H_X–C=$C\underline{H}_A H_B$), 4.94 (d, J_{BX}=10 Hz, H_X–C=$CH_A\underline{H}_B$), 7.68 (d, J(*trans*)=7.0 Hz, S–CH), 8.28—8.52 (m, $\underline{H}C$–CH_3), 8.60 (d, J=3.6 Hz, CH_3). The ratio of **15** to *trans*-**2** was about 1 to 2 (NMR spectrum).

*Reaction of **3** with Potassium* t-*Butoxide in* t-*Butyl Alcohol.* Potassium *t*-butoxide was prepared from potassium (3.90 g, 0.1 g-atom) and *t*-butyl alcohol (100 ml). Compound **3** (7.0 g, 0.03 mol) was added and the solution was heated under reflux and with stirring for 3 hr. Water (300 ml) was added and the products were extracted with 200 ml of petroleum ether (bp 72°C) and dried ($MgSO_4$). Fractionation gave two products (*A* and *B*) and a considerable amount of residual black tar.

A.—2-Phenylmercaptobut-1-en-3-yne (**16**): 0.9 g (19%); bp 48—51°C/0.02 mmHg; n_D^{25} 1.5712; IR (neat), 3290 cm^{-1} (≡C–H), 2120 (C≡C), 1645, 880 ($C{=}CH_2$); UV ($\lambda_{max}^{95\%EtOH}$), 253 mμ (ε 9470), 272 (sh., 5420); NMR (CCl_4), τ 2.42—2.88 (c, 5, C_6H_5), 4.33, 4.56 (two s, 2, CH_2=), 7.16 (s, 1, ≡C–H).

Found: C, 74.97; H, 5.35%. Calcd for $C_{10}H_8S$: C, 74.96; H, 5.03%.

B.—4-*t*-Butoxy-3-phenylmercaptobuta-1,2-diene (**17**): 1.3 g (19%); bp 87—90°C/0.02 mmHg. A sample of this product was redistilled for analysis: bp 78°C/0.002 mmHg; n_D^{25} 1.5581; IR (neat), 1950 cm^{-1} (C=C=C); UV ($\lambda_{max}^{95\%EtOH}$), 246 mμ (ε 10800), 270 (sh., 5120); NMR (CCl_4), τ 2.55—3.04 (c, 5, C_6H_5), 5.20 (t, J=2.4 Hz, 2, $=CH_2$), 6.11 (t, J=2.4 Hz, 2, CH_2), 8.88 (s, 9, *t*-Bu); MS m/e, 234 (M^+).

Found: C, 71.46; H, 7.32%. Calcd for $C_{14}H_{18}SO$: C, 71.75; H, 7.74%.

*Reduction of **17** with Raney Nikel (W-2).* A mixture of **17** (2.1 g, 0.009 mol), Raney nickel (W-2) (15 g) and 95% ethyl alcohol (100 ml) was refluxed for 5 hr. The alcoholic solution was analyzed by glpc (silicone oil, DC-710, 20% on Chromosorb W), and the spectrum showed the presence of two components (other than ethyl alcohol). The compounds were identified (by injection of authentic samples) as benzene and *n*-butyl *t*-butyl ether.[18]

*Reduction of **17** with Hydrogen Gas on Raney Nickel (W-2).* A mixture of **17** (1.1 g, 0.0047 mol), Raney nickel (W-2) (6 g) and methyl alcohol (150 ml) was shaken with hydrogen gas (50 lb) in a hydrogenation apparatus[26] for 28 hr at room temperature. The Raney nickel was filtered and washed with methyl alcohol (100 ml). The combined filtrate was distilled through a 10 cm Vigreux column, and a large portion of methyl alcohol was distilled. Further distillation of the brown residue (0.6 g) gave two products.

A.—*sec*-Butyl phenyl sulfide (**19**); 0.1 g (13%); bp 77—80°C/3 mmHg; n_D^{25} 1.5390; NMR (CCl_4), τ 2.57—3.12 (c, 5, C_6H_5), 6.95 (sextet, J=6.6 Hz, 1, –CH–), 8.11—9.22 (m, 8, CH_2—CH_3 and CH_3).

Found: C, 72.02; H, 8.37%. Calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.49%.

This product was identical with an authentic sample of **19**.[19]

B.—*t*-Butyl 2-phenylmercaptobutyl ether (**20**): 0.4 g (36%); bp 72°C/0.001 mmHg; n_D^{25} 1.5191; IR (neat), 1070 cm^{-1} (C–O–C); UV ($\lambda_{max}^{95\%EtOH}$), 255 mμ (ε 5730); NMR (CCl_4), τ 2.56—3.04 (c, 5, C_6H_5), 6.49—7.18 (m, 3, C–CH_2–CH), 8.07—9.18 (m, 14, C_2H_5 and *t*-Bu, —a sharp peak at 8.88 due to *t*-Bu).

Found: C, 69.89; H, 8.93%. Calcd for $C_{14}H_{22}SO$: C, 70.54; H, 9.30%.

*Preparation of **17** from **16** and Potassium t-Butoxide.* Freshly prepared **16** (12 g, 0.0075 mol) was added to a stirred solution prepared from potassium (0.60 g, 0.015 g-atom) and *t*-butyl alcohol (20 ml) which was maintained in a nitrogen atmosphere. The reaction mixture was refluxed for 2 hr and then poured into water (100 ml), and the resulting mixture was extracted twice with 100 ml portions of ether. The ether solution was dried ($MgSO_4$) and concentrated in a rotatory evaporator. Distillation of the residue gave **17**: 0.6 g (34%); bp 80°C/0.005 mmHg; n_D^{26} 1.5678; IR and NMR spectra were identical with those of **17** obtained by the reaction of **3** with potassium *t*-butoxide in *t*-butyl alcohol.

*Reaction of **5** with Potassium* t-*Butoxide in* t-*Butyl Alcohol.* The reaction of **5** (4.94 g, 0.02 mole) with potassium *t*-butoxide (potassium 2.35 g, 0.06 g-atom; *t*-butyl alcohol 60 ml) was carried out for 3 hr as described for **2**. 3-Methyl-1-phenylmercaptobut-3-en-1-yne (**21**) was obtained: 2.1 g (60%); bp 60—62°C/0.004 mmHg; n_D^{25} 1.6075; IR (neat), 2140, 2170 cm^{-1} (C=C), 900 ($C{=}CH_2$), 2970, 2910, 1375 (CH_3); UV ($\lambda_{max}^{95\%EtOH}$) 218 mμ (sh., ε 14600), 228 (sh., 11500), 241 (11200), 249 (11800), 258 (11600): NMR[25] (CCl_4), τ 2.50—3.08 (c, 5, C_6H_5), 4.72, 4.82 (two s, 2, $=CH_2$), 8.06 (s, 3, CH_3).

Found: C, 75.71; H, 5.94%. Calcd for $C_{11}H_{10}S$: C, 75.82; H, 5.78%.

*Dehydrohalogenation of 1-Chloro-3-methyl-1-phenylmercaptobuta-1,3-diene (**22**).* The reaction of **22**[12] (3.7 g, 0.018 mole) with potassium *t*-butoxide (potassium 1.6 g, 0.04 g-atom; *t*-butyl alcohol 40 ml) was carried out as described for **14** and gave **21**: 2.3 g (73%); bp 62—65°C/0.005 mmHg; n_D^{27} 1.6041. This product was shown to be identical (IR spectrum) with **21** prepared from **5**.

Found: C, 75.55; H, 5.95%. Calcd for $C_{11}H_{10}S$: C, 75.82; H, 5.78%.

*Reaction of **5** with Pyridine.* The reaction of **5** (4.9 g, 0.02 mol) with pyridine (20 ml), carried out for 18 hr as described for **2**, gave 2-chloro-3-methyl-1-phenylmercaptobuta-1,3-diene (**23**): 2.0 g (48%): bp 88—90°C/0.01 mmHg; n_D^{30} 1.6210; IR (neat), 1615, 895 cm^{-1} ($C{=}CH_2$), 2960, 1370 (CH_3); UV ($\lambda_{max}^{95\%EtOH}$) 252 mμ (ε 5380), 268 (4970), 296 (5560), NMR (CCl_4), τ 2.42—2.97 (c, 5, C_6H_5), 3.42 (s, 1, –CH=), 4.56, 4.99 (two s, 2, $=CH_2$), 8.01 (s, 3, CH_3). The glpc (silicone oil, DC-710, 20% on Chromosorb W) of the product **23** showed only a single peak.

25) The NMR spectrum was obtained on a JEOL MH-100 spectrometer.

26) Made by Parr Instrument Co. Inc. (Moline, III., U. S. A.).

Found: C, 62.35; H, 4.99%. Calcd for $C_{11}H_{11}SCl$: C, 62.72; H, 5.26%.

Dehydrogenation of ***23***. The reaction of **23** (1.6 g, 0.008 mol) with potassium *t*-butoxide (potassium 0.6 g, 0.0016 g-atom; *t*-butyl alcohol 20 m*l*), carried out as described for **14**, gave **21**: 0.7 g (50%); bp 60—61°C/0.001 mmHg; n_D^{27} 1.6002. The IR and NMR spectra of this product were identical with those of authentic **21** prepared from **5** or **22**.

Reaction of ***6*** *with Pyridine.* The reaction of **6** (1.3 g, 0.005 mol) with pyridine (10 m*l*) was carried out for 70 hr as described for **2**, and a compound assumed to be 3-chloro-2-methyl-4-phenylmercaptopenta-1,3-diene (**24**) or 3-chloro-4-methyl-2-phenylmercaptopenta-1,3-diene (**25**) was obtained: 0.8 g (71.4%); bp 66—68°C/0.005 mmHg; n_D^{26} 1.5815; IR (neat), 1635, 890 cm^{-1} (C=CH_2), 2920, 1370 (CH_3); UV ($\lambda_{max}^{95\%EtOH}$), 218 mμ (sh., ε 10900), 251 (5470), 270 (sh., 3910); NMR (CCl_4), τ 2.38—2.96 (c, 5, C_6H_5), 4.81 4.91 (two s, 2, CH_2=), 8.00, 8.22 (two s, 6, $2CH_3$). The GLPC (silicone oil, DC-710, 20% on Chromosorb W) of the product showed only a single peak.

Found: C, 63.96; H, 5.74%. Calcd for $C_{12}H_{13}SCl$: C, 64.13; H, 5.84%.