until constant melting point was obtained and were then dried *in vacuo*. Table VIII lists the uncorrected melting points obtained with a Thomas–Hoover Uni-Melt, and literature references for compounds which had been previously reported. Table IX contains data on the new chalcones which were prepared.

Registry No.—1, 22965-98-6; 2, 22965-99-7; 3, 22252-15-9; 4, 22966-01-4; 5, 22252-14-8; 6, 614-47-1; 7, 22966-04-7; 8, 22966-05-8; 9, 22966-06-9; 10, 22966-07-0; 11, 22252-16-0; 12, 22966-09-2; 13, 22966-10-5; 14, 22966-11-6; 15, 22966-12-7; 16, 22966-13-8; 17, 22966-14-9; 18, 22966-15-0; 19, 22966-16-1; 20, 22966-17-2; 21, 2960-55-6; 22, 22966-19-4; 23, 14802-30-3; 24, 13565-44-1; 25, 22966-22-9; 26, 22966-23-0; 27, 22966-24-1; 28, 22966-25-2; 29, 22966-26-3; 30, 13565-37-2; 31, 22946-44-7; 32, 22966-28-5; 33, 13565-39-4; 34, 22966-30-9; 35, 22966-31-6; 36, 22966-32-1; 37, 22966-33-2.

Acknowledgment.—We gratefully acknowledge the Georgia State University Computer Center for computer time on the IBM 7040. We wish to thank Professor Harry P. Hopkins for his helpful discussions.

β-Keto Sulfoxides. VIII. Acid-Catalyzed Reactions of β-Hydroxy Sulfides and the Hydration of Vinyl Sulfides. Synthesis of Ketene Mercaptals, α-Substituted Phenylthioacetic Acids, and α-Substituted Phenylacetaldehydes[1]

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Received June 17, 1969

Secondary benzylic alcoholates adjacent to the thioacetal function [$C_6H_5CH(O^-)CH(SCH_3)_2$] react with thionyl chloride or tosyl chloride to yield a 1,2-di(methylmercapto)ethylene [$C_6H_5C(SCH_3)=CHSCH_3$]. Tertiary benzylic alcohols adjacent to the thioacetal function [$C_6H_5CR(O^-)CH(SCH_3)_2$] react with benzoyl chloride, thionyl chloride, or tosyl chloride to yield the β-styrenyl sulfides ($C_6H_5CR=CHSCH_3$). Hydroboration of β-styrenyl sulfides followed by chromic trioxide oxidation is a convenient synthesis of phenylacetaldehyde and various α-substituted derivatives. Treatment of the anion of the thioacetal of benzilaldehyde with acetyl chloride followed by hydrolysis leads to the formation of α-phenyl-α-(methylmercapto)phenylacetaldehyde. Base-catalyzed eliminations of methanol from α-methoxy thioacetals [$C_6H_5CR(OCH_3)CH(SCH_3)_2$] yields the ketene thioacetals [$C_6H_5CR=C(SCH_3)_2$]. Treatment of the methyl thioacetal of diphenylketene with aqueous acid leads to the formation of α-phenyl-β-(methylmercapto)styrene. Hydration of ketene thioacetals is a convenient route to S-methyl phenylthioacetate and its α-substituted derivatives.

Previous studies have made available a number of β-hydroxy sulfides, including compounds **1–3**.[2,3] It

$C_6H_5CH(OH)CHRSCH_3$
1a, R = H
b, R = CH_3

$C_6H_5CH(OH)C(SCH_3)_3$
3

$C_6H_5CR(OH)CR'(SCH_3)_2$
2a, R = R′ = H
b, R = D; R′ = H
c, R = C_6H_5; R′ = H
d, R = CH_3; R′ = H
e, R = C_2H_5; R′ = H

had been previously established that **1a** is dehydrated under acidic conditions to yield β-(methylmercapto)-styrene, **4a**.[2] The reaction of the α-hydroxy thioacetals **2** under acidic conditions has now been examined in expectation of preparing ketene thioacetals. However, the reaction led instead to either rearrangement products (reaction 1) or to the elimination of the elements CH_3S–OH (reaction 2) to yield the substituted β-styrenyl

$$C_6H_5CH(OH)CH(SCH_3)_2 \xrightarrow{H^+} C_6H_5C(SCH_3)=CHSCH_3 + H_2O \quad (1)$$

$$(C_6H_5)_2C(OH)CH(SCH_3)_2 \xrightarrow{H^+} (C_6H_5)_2C=CHSCH_3 + [CH_3SOH] \quad (2)$$

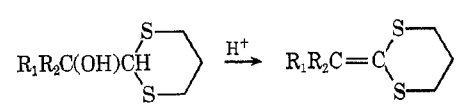
$C_6H_5C(R)=CR'SCH_3$

4a, R = R′ = H
b, R = CH_3S; R′ = H
c, R = Cl; R′ = H
d, R = H; R′ = CH_3
e, R = C_6H_5; R′ = H
f, R = CH_3; R′ = H
g, R = C_2H_5; R′ = H

sulfides **4b–4g**. Rearrangements similar to reaction 1 have been previously observed for some α-halo thioacetals (reaction 3)[4,5] and interpreted in terms of an

$$CH_3CH(Br)CH(SC_2H_5)_2 \longrightarrow CH_3CH(SC_2H_5)=CHSC_2H_5 + HBr \quad (3)$$

episulfonium ion intermediate.[6] When the thioalkyl group of an α-hydroxy thioacetal cannot migrate or be eliminated, the normal catalyzed dehydration is observed, for example, in the β-hydroxy-*m*-dithianes (reaction 4).[7] The methyl ethers or benzoate esters



(4)

(**5**) of α-hydroxy thioacetals will undergo a base-catalyzed elimination to yield the ketene thioacetals **6a–6d**.

$C_6H_5CR(OR')CH(SCH_3)_2$
5a, R = H; R′ = C_6H_5CO
b, R = H; R′ = CH_3
c, R = C_6H_5; R′ = CH_3
d, R = R′ = CH_3
e, R = C_2H_5; R′ = CH_3

$C_6H_5C(R)=C(SCH_3)_2$
6a, R = H
b, R = C_6H_5
c, R = CH_3
d, R = C_2H_5
e, R = OCH_3
f, R = $C_6H_5CO_2$
g, R = SCH_3

(1) This work was supported by a grant from the Army Research Office (Durham). For part VII, see G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **34**, 3624 (1969).

(2) G. A. Russell, E. Sabourin, and G. J. Mikol, *ibid.*, **31**, 2854 (1966).

(3) G. A. Russell and L. A. Ochrymowycz, *ibid.*, **34**, 3618 (1969).

(4) E. Rothstein, *J. Chem. Soc.*, 1553 (1940); E. Rothstein and R. Whitely, *ibid.*, 4012 (1953).

(5) W. E. Parham, J. Heberling and H. Wynberg, *J. Amer. Chem. Soc.*, **77**, 1169 (1955).

(6) K. D. Grundermann, *Angew. Chem. Intern. Ed.*, **2**, 674 (1963).

(7) E. J. Corey and D. Seebach, *Angew. Chem.*, **77**, 1134 (1965).

The hydration of the vinyl sulfides **4** and the ketene thioacetals **6** has been investigated. The ketene thioacetals are readily hydrated to the S-methylphenylthioacetic acids **7**. The β-styrenyl sulfides **4** are less readily hydrated. However, the application of the hydroboration reaction to **4** followed by oxidation[8] provides a convenient synthesis of the phenylacetaldehydes **8a–8d** and the corresponding β-phenethanols.

$C_6H_5CH(R)COSCH_3$ (**7a**, R = H; **b**, R = CH_3; **c**, R = C_2H_5; **d**, R = SCH_3)

$C_6H_5CH(R)CHO$ (**8a**, R = H; **b**, R = C_6H_5; **c**, R = CH_3; **d**, R = C_2H_5)

$$C_6H_5C(R)=CHSCH_3 \xrightarrow{B_2H_6} \begin{cases} \xrightarrow{CrO_3} C_6H_5CH(R)CHO \\ \xrightarrow{H_2O_2} C_6H_5CH(R)CH_2OH \end{cases} \quad (5)$$

Results and Discussion

1-Phenyl-2,2-di(methylmercapto)ethanol (**2a**) or 1-phenyl-2,2,2-tri(methylmercapto)ethanol (**3**) can be converted to alkoxide anions by sodium hydride in THF solution. The anions undergo methylation with methyl iodide or benzoylation with benzoyl chloride. Treatment of the anion of **2a** with tosyl chloride, or with thionyl chloride in pyridine, led to a product of rearrangement, α,β-di(methylmercapto)styrene (**4b**). The deuterio analog **2b** led to rearrangement with complete loss of deuterium. Compound **3** yielded α,β,β-tri(methylmercapto)styrene (**6g**). These results are easily rationalized by Scheme I.

SCHEME I

$$\mathbf{2a,3} \xrightarrow{B^-} \xrightarrow{YCl} C_6H_5CH(OY)CR(SCH_3)_2 \xrightarrow{-OY^-}$$

$$C_6H_5C(\overset{CH_3}{\overset{|}{S^+}})CR(SCH_3) \longrightarrow C_6H_5CH(SCH_3)-\overset{+}{C}R(SCH_3) \xrightarrow{-H^+} C_6H_5C(SCH_3)=CRSCH_3$$

4b, R = H; **6g**, R = SCH_3

R = H, SCH_3; Y = $C_6H_5SO_2^-$, $ClSO^-$

Heating of **2a** in Pyrex glassware at 80° for 48 hr produced a 99% yield of **4b** as a mixture of *cis* and *trans* isomers that could be completely isomerized to the *trans* isomer by treatment with mineral acids. Pyrolysis of the benzoate ester of **3** at 170° led to **6g** in high yield. Treatment of phenylketene mercaptal (**6a**) with *m*-chloroperbenzoic acid led to the formation of S-methyl-α-(methylmercapto)phenylthioacetic acid (**7d**). No intermediate epoxide could be isolated. Nevertheless, Scheme II seems to be appropriate.

The reaction of **2a** and **3** with acidic reagents gave a variety of products, including rearrangement products analogous to those of Scheme I. Acid-catalyzed cleavage of the methylmercapto function was also an important reaction.[9] Thus, treatment of **2a** with thionyl chloride in methylene chloride gave 40% α-chloro-

SCHEME II

$$C_6H_5CH=C(SCH_3)_2 \xrightarrow{[O]} \mathbf{6a}$$

$$[C_6H_5CH(\overset{O}{\diagdown\diagup})C(SCH_3)_2 \rightleftharpoons C_6H_5CH(\overset{Me}{\overset{|}{S^+}})C(SCH_3)(O^-)] \longrightarrow C_6H_5CH(SCH_3)COSCH_3$$

7d

β-(methylmercapto)styrene (**4c**). Treatment of 1-phenyl-2-(methylmercapto)propanol (**1b**) with hydrogen bromide produced 15% β-methylstyrene oxide and 60% dehydration product, β-methyl-β-methylmercaptostyrene (**4d**). It has previously been reported that methyl orthotrithiomandelate (**3**) is converted by aqueous hydrochloric acid into S-methyl thiomandelate.[3] All of these results are conveniently rationalized by Scheme III.

SCHEME III

(a) $\mathbf{2a} \xrightarrow{SOCl_2} C_6H_5CH(Cl)CH(SCH_3)_2 \xrightarrow{H^+}$

$$C_6H_5CH(Cl)\overset{+}{C}H(SCH_3) \xrightarrow{-H^+} C_6H_5C(Cl)=CH(SCH_3)$$

(b) $C_6H_5CH(OH)CH(SCH_3)CH_3 \xrightarrow{H^+}$

$$C_6H_5CH(OH)\overset{+}{C}HCH_3 \xrightarrow{-H^+} C_6H_5CH(\overset{O}{\diagdown\diagup})CHCH_3$$

(c) $C_6H_5CH(OH)C(SCH_3)_3 \xrightarrow{H^+}$

$$C_6H_5CH(OH)\overset{+}{C}(SCH_3)_2 \xrightarrow{H_2O} [C_6H_5CH(OH)C(OH)(SCH_3)_2] \xrightarrow{-CH_3SH} C_6H_5CH(OH)COSCH_3$$

Reactions of the hydroxy mercaptals **2c–2e** were investigated as routes to the ketene mercaptals. The alkoxide ions can be methylated by methyl iodide.[3] However, reaction of benzoyl chloride or tosyl chloride with the alkoxide anion derived from **2d** led to the formation of 2-(methylmercapto)-1,1-diphenylethylene (**4e**) in 90% and 70% yields. Thionyl chloride in pyridine solution brought about the conversion of **2c** to **4e** as well as the conversion of **2d** and **2e** to **4f** and **4g**, respectively. These results are rationalized in Scheme IV. The reaction of atrolactaldehyde thioacetal with thionyl chloride was performed in the presence of cyclohexene. Under these conditions an appreciable fraction of the methanesulfenyl chloride was converted into *trans*-1-chloro-2-(methylmercapto)cyclohexane (reaction 6). Evidence for a rearranged chloro derivative (Scheme IV) is furnished by the observation that 43% α,α-diphenyl-α-(methylmercapto)acetaldehyde is formed when the reaction product of acetyl chloride and benzilaldehyde thioacetal (**2c**) at 5° is quenched with water. α-Methylmercapto-α-phenylbutyralde-

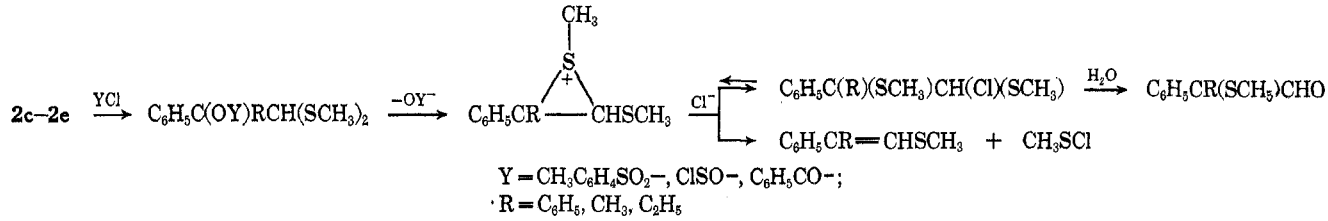
$$C_6H_5C(CH_3)(OH)CH(SCH_3)_2 \xrightarrow{SOCl_2}$$

$$C_6H_5C(CH_3)=CHSCH_3 + [CH_3SCl] \xrightarrow{C_6H_{10}} \text{(Cl, } CH_3S\text{)} \quad (6)$$

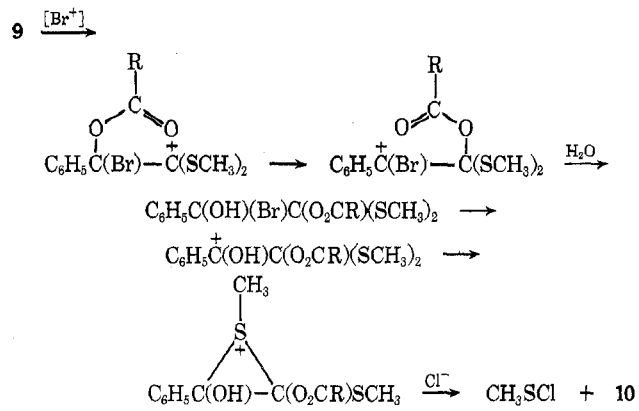
(8) H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **81**, 6434 (1959); H. C. Brown and C. P. Gary, *ibid.*, **83**, 2951 (1961).

(9) For similar reactions of ortho thio esters, see H. C. Volger and J. F. Arens, *Rec. Trav. Chim. Pays-Bas*, **76**, 354 (1957); H. J. Boonstra, L. Brandma, A. Wiegman, and J. F. Arens, *ibid.*, **78**, 252 (1959).

SCHEME IV

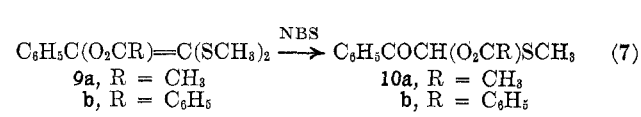


SCHEME V



hyde was prepared in a similar fashion from **2e** in 46% yield.

The enol esters of the thioacetal of phenylglyoxal[3] react with N-bromosuccinimide in aqueous solution to yield a product in which elimination and rearrangement has occurred (reaction 7). Scheme V provides a



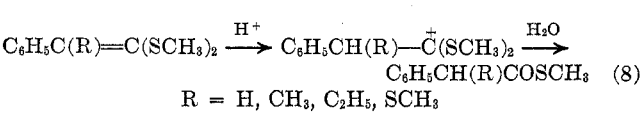
(7)

reasonable rational consistent with Schemes I and IV.

The ketene mercaptals **6a–6d** could be synthesized from the hydroxy mercaptals 2 by the action of strong bases on the O-methyl or O-benzoate derivatives of 2 (*i.e.*, **5a–5e**). β,β-Di(methylmercapto)styrene (**6a**) was prepared in 65% yield by the action of potassium *t*-butoxide in THF on the benzoate ester **5a**, and in 91% yield by the reaction of *n*-butyllithium in ether with **5b**. Compounds **6b–6d** were prepared from **5c–5e** by treatment with butyllithium.

Having available a number of ketene mercaptals **6** as well as styrenyl sulfides **4** from reactions 1 and 2, the authors have investigated the conversion to S-methyl phenylthioacetic acids **7** *via* hydration, and to the phenylacetaldehydes **8** or β-phenethanols [$C_6H_5CH(R)CH_2OH$, **11a**, R = H; **b**, R = C_6H_5; **c**, R = CH_3; **d**, R = C_2H_5] by hydroboration techniques.[8] Table I summarizes the observed yields.

Hydration of the β-(methylmercapto)styrenes occurred with difficulty and yielded the phenylacetaldehydes in low yield (Table I). α,β-Di(methylmercapto)styrene was readily hydrated to yield ω-(methylsulfinyl)acetophenone. Protonation of the ketene mercaptals led to a dithiolium cation for **6a**, **6c**, **6d**, and **6g** (eq 8). However, from **6b** and **6e** products were



(8)

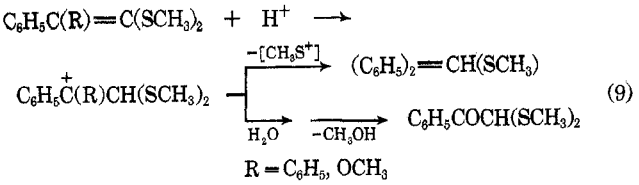
TABLE I[a]

YIELDS OF S-METHYL PHENYLTHIOACETIC ACIDS [$C_6H_5CH(R)COSCH_3$], PHENYLACETALDEHYDES [$C_6H_5CH(R)CHO$], AND β-PHENETHANOLS [$C_6H_5CH(R)CH_2OH$]

R	H	CH_3	C_2H_5	C_6H_5	SCH_3
S-Methyl ester	83[a]	89[a]	80[a]	*b*	72[a]
Aldehyde	50[c], 20[d]	68[c], 25[d]	52,[c] 35[d]	61,[c] 40[d]	*e*
Alcohol	88[f,g]	71[f]	74[f]	80[f]	

[a] Hydration of the ketene mercaptal in 30% aqueous ethanol at ~90°, sulfuric acid catalyst. [b] The major product was 1-thiomethyl-2,2-diphenylethylene (68%). [c] Hydroboration in diglyme followed by 10% excess of CrO_3. [d] Hydration of the β-styrenyl sulfide **4** in 50% ethanol at ~90°, 3 *N* sulfuric acid as catalyst. [e] The only product of hydration of α,β-di(methylmercapto)-styrene was ω-(methylsulfinyl)acetophenone. [f] Hydroboration in diglyme followed by oxidation with basic 30% hydrogen peroxide. [g] Ratio of α- and β-phenethanol, 23:77.

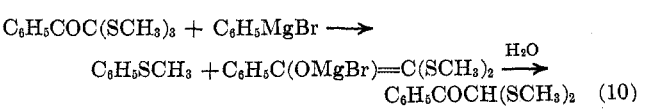
observed that are consistent with protonation at the other carbon atom (eq 9). The products of hydration



(9)

of the ketene mercaptals and α,β-di(methylmercapto)-styrene can be interpreted as yielding a sequence of carbonium ion stabilities: $(C_6H_5)_2\overset{+}{C}CH(SCH_3)_2$, $(C_6H_5)(CH_3O)\overset{+}{C}CH(SCH_3)_2 > (CH_3S)_2\overset{+}{C}CH(R)(C_6H_5)$. On the basis of this stability series it is predicted that α,β,β-tri(methylmercapto)stryene should be protonated to yield the cation $C_6H_5\overset{+}{C}(SCH_3)CH(SCH_3)_2$. The observation that hydration yields the S-methyl phenylthioacetate **7d** perhaps reflects a reversible hydration process and a facile elimination of methylmercaptan from $(C_6H_5)(CH_3S)CHC(OH)(SCH_3)_2$.

The synthesis of compounds of the type $C_6H_5C(OH)RC(SCH_3)_3$ with R = methyl, ethyl, and phenyl was attempted because it appeared highly probable that acidic reagents would convert these hydroxy trithioortho esters into ketene mercaptals. However, all attempts to add organomagnesium or organolithium reagents to ω,ω,ω-tri(methylmercapto)acetophenone led to the formation of ω,ω-di(methylmercapto)acetophenone, and in the case of phenylmagnesium bromide, to thioanisole (eq 10).



(10)

CHART I

Use of β-Keto Sulfoxides in Synthesis.—It seems of value to summarize the products that can be derived from β-keto sulfoxides. The conversions of β-keto sulfoxides ($RCOCH_2SOCH_3$) to the three classes of compounds listed in Table II have now been documented.[10,11]

TABLE II

SULFUR FREE PRODUCTS DERIVED FROM β-KETO SULFOXIDES (NUMBER OF REACTION STEPS)

$RCOCH_3$ (1)		
$RCOCH_2OH$ (1)	$RCH(OH)CH_2OH$ (1)	RCH_2CH_2OH (5)
RCOCHO (1)	RCH(OH)CHO (3)	RCH_2CHO (5)
$RCOCO_2H$ (1 or 3)	$RCH(OH)CO_2Et$ (4)	RCH_2CO_2Et (5)

The individual synthetic steps, and certain other useful intermediates,[12] are listed in Chart I. In the first column are listed a number of readily available compounds having the structural unit, R–CO–C–S–CH_3. These substances are converted in high yields and in single step reactions into the intermediates listed in column 2. A wide variety of olefinic substances are mentioned in Chart I. Table III collects these derivatives in a more orderly manner.

TABLE III

OLEFINS SYNTHESIZED FROM β-KETO SULFOXIDES

$RCH=C(SCH_3)_2$	$RCH=CHSCH_3$	$RCH=CHSOCH_3$
$RC(OCH_3)=C(SCH_3)_2$	$RC(Cl)=CHSCH_3$	$RC\equiv CSCH_3$
$RC(SCH_3)=C(SCH_3)_2$	$RC(SCH_3)=CHSCH_3$	$RC(OMe)=CH_2$

The scope of the use of β-keto sulfoxides in organic synthesis is considerably wider than that displayed in Chart I. Thus, β-keto sulfides and β-keto sulfoxides can be alkylated to give $RCOCHR'SCH_3$, $RCOCR_2'SCH_3$, $RCOCHR'SOCH_3$, and $RCOCR_2'SOCH_3$.[10,13] Addition of Grignard reagents to the keto thioacetal allows the synthesis of $RC(R')(OH)CH(SCH_3)_2$ and the derivatives thereof described in Table I. Moreover, β-keto sulfoxides can be alkylated with bromoacetic acid derivatives or undergo Michael addition to acrylate esters to yield after reduction $RCOCH_2CH_2CO_2Et$ and $RCOCH_2CH_2CH_2CO_2Et$.[14,15]

(10) G. A. Russell and G. J. Mikol, *J. Amer. Chem. Soc.*, **88**, 5498 (1966); H. D. Becker, G. J. Mikol, and G. A. Russell, *ibid.*, **85**, 3410 (1963).
(11) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1345 (1965).
(12) G. A. Russell and E. J. Sabourin, *J. Org. Chem.*, **34**, 2336 (1969).
(13) P. G. Gassman and G. O. Richmond, *ibid.*, **31**, 2355 (1966).
(14) G. A. Russell and L. A. Ochrymowycz, *ibid.*, **34**, 3624 (1969).
(15) H. Nozaki, T. Mori, and M. Kawanisi, *Can. J. Chem.*, **46**, 3767 (1968).

Experimental Section

1,2-Di(methylmercapto)-1-phenylethylene (4b) from 2a or 2b.—1,2-Di(methylmercapto)-1-phenylethanol (2a)[3] (10.1 g, 50 mmol) was heated with stirring at 80° in an oil bath for 48 hr, at which time tlc analysis indicated complete conversion of **2a**. The oil was distilled [bp 125–127° (1 Torr)] to yield 9.1 g (93%) of **4b**. A 58:42 mixture of *trans–cis* olefins was indicated by pmr ($CDCl_3$): *trans*-**4b**, δ 2.02, 2.34 (s, 6, SCH_3), 6.37 (s, 1 CH); *cis*-**4b**, δ 2.08, 2.20 (s, 6, SCH_3), 6.27 (s, 1 CH). The olefin mixture could be isomerized to more than 95% *trans* isomer by refluxing in benzene solution containing a trace of hydrogen chloride.

Anal. Calcd for $C_{10}H_{12}S_2$: C, 61.21; H, 6.17; S, 32.62. Found: C, 61.38; H, 6.37; S, 32.66.

Treatment of 5.73 g (26.7 mmol) of **2a** in 30 ml of pyridine with 2.94 g of thionyl chloride resulted in a highly exothermic reaction which refluxed from the heat of reaction for 20 min. After stirring for 1 hr at 25° the mixture was poured into 150 ml of water and 15 ml of concentrated hydrochloric acid was added. The solution was extracted with three 100-ml portions of hexane and the dry ($MgSO_4$) extract concentrated and purified by column chromatography on silica gel with heptane to yield 4.24 g (81%) of **4b** in a *trans/cis* ratio of 70:30. The deuterio-alcohol **2b** was prepared by sodium borohydride-d_4 reduction of ω,ω-di(methylmercapto)acetophenone[3] in D_2O solution. The olefins prepared by thionyl chloride–pyridine treatment were in the 70:30 ratio of *trans/cis*-**4b**, which was shown by pmr and mass spectrum to be free of deuterium.

β-(Methylmercapto)-α-chlorostyrene (4c) from 2a.—To 7.6 g (52 mmol) of **2a** in 100 ml of methylene chloride at 0° there was added 7.15 g of thionyl chloride, with stirring. After 2 hr at 25° the solvent was removed under vacuum to leave a red residue, which was dissolved in chloroform, washed with a saturated aqueous sodium bicarbonate solution, dried ($MgSO_4$), and concentrated. Chromatography on silica gel with petroleum ether as the eluent yielded 4.2 g of **4c** identical with material prepared previously.[2]

β-Methyl-β-(methylmercapto)styrene (4d) from Reaction of Hydrogen Bromide with 1b.—1-Phenyl-2-(methylmercapto)propanol (**1b**) was prepared from ω-(methylsulfinyl)acetophenone by methylation[11] and reduction with first sodium borohydride,[2] and then sodium metabisulfite.[12] A solution of hydrogen bromide in benzene was prepared by extraction of 30 ml of 48% hydrobromic acid by 250 ml of benzene. Compound **1b** (8.83 g, 48.5 mmol) was dissolved in the benzene solution of hydrogen bromide and refluxed for 5 hr in a flask equipped with a Dean–Stark trap to collect the water of dehydration. Removal of the solvent gave a yellow oil that was chromatographed on a 3.5 × 40 cm silica gel column. Elution with hexane yielded 4.75 g (60%) of **4d**. Elution with ethyl acetate (5%)–hexane (15%) yielded 1.03 g (15%) of β-methylstyrene oxide and 1.39 g of unreacted **1b**.

The β-methyl-β-(methylmercapto)styrene was identical with a sample prepared by the potassium *t*-butoxide elimination of methanol from 1-phenyl-4-methoxy-2-(methylmercapto)propane:[12] pmr (60 MHz, $CDCl_3$), δ 2.04 (d, 3, CH_3, J = 1 Hz), 2.26 (s, 3, SCH_3), 6.75 (q, 1, –CH=, J = 1 Hz), 7.2–7.5 (m, 51 C_6H_5). The β-methylstyrene oxide was a mixture of *cis* and *trans* isomers (by pmr). Reduction in 95% ethanol by sodium borohydride yielded 1-phenylpropanol.

1-(Methylmercapto)-2,2-diphenylethylene (4e) from 2c.—Alcohol **2c** (6.15 g, 21.2 mmol) was dissolved in 50 ml of pyridine, and 1.8 ml of thionyl chloride was added dropwise at 0° with stirring. After 2 hr the reaction mixture was poured into 200 ml of saturated aqueous sodium bicarbonate solution and extracted with three 100-ml portions of chloroform. The chloroform extract was dried ($MgSO_4$) and the concentrated residue chromatographed on silica gel with petroleum ether to yield 3.4 g (72%) of **4e** which was recrystallized from pentane: mp 70° (lit.[16] 70.0–71.5°); pmr (60 MHz, $CDCl_3$) δ 2.23 (s, 3, SCH_3), 6.37 (s, 1, –CH=).

Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.24; S, 14.26. Found: C, 79.64; H, 6.33; S, 14.42.

Treatment of **2c** (7.0 g, 24 mmol) with 1 equiv of sodium hydride in 200 ml of THF followed by 4.6 g of tosyl chloride in 60 ml of THF at room temperature yielded after 1 hr 3.9 g (71%) of **4e** isolated as described above. Refluxing with a benzene solution of hydrogen bromide for 10 hr (as described under the preparation of **4d**) gave a 63% yield of **4e** and a 31% yield of benzil from **2c**.

α-(Methylmercapto)-α,α-diphenylacetaldehyde from 2c.—Alcohol **2c** (8.85 g, 30.5 mmol) was converted to the alkoxide with 1 equiv of sodium hydride in 100 ml of THF. At −5° 1 equiv of acetyl chloride was added. After 30 min at −5° the solution was filtered and diluted with 30 ml of water. After refluxing for 15 min the solvent was removed under vacuum and the residue dissolved in ether. The ether solution was washed with three 100-ml portions of 1 *N* sodium hydroxide, dried ($MgSO_4$), concentrated, and chromatographed on silica gel with hexane as the eluent. The styrene **4d** was isolated (1.4 g, 20%) as well as 2.65 g of starting **2c**. The major component eluted after the styrene but before **2c** was α-(methylmercapto)-α,α-diphenylacetaldehyde, which could be recrystallized from petroleum ether (95%)–ether (5%) to give mp 70–71°; ir (CCl_4) 1720 cm^{-1} (C=O); pmr (60 MHz, $CDCl_3$) δ 1.75 (s, 3, SCH_3) 9.44 (s, 1, CHO).

Anal. Calcd for $C_{15}H_4OS$: C, 74.36; H, 5.83; S, 13.20. Found: C, 74.47; H, 5.91; S, 13.35.

α-Methyl-β-(methylmercapto)styrene (4f) from 2d.—Alcohol **2d** (4.55 g, 20 mmol) was treated with 1 equiv of thionyl chloride in pyridine in a fashion identical with that described for conversion of **2c** to **4e**. By chromatography (silica gel with hexane eluent) 2.74 g (83.5%) of a *cis–trans* mixture of **4f** was obtained. Pmr indicated the mixture to contain approximately 90% of the isomer in which the S-methyl and the phenyl group are *cis* to each other. The *cis* and *trans* isomers give quartets of pmr peaks (60 MHz) at δ 6.4 and 5.88, respectively. The pure *cis* isomer was obtained by crystallization from pentane: mp 29–30°; pmr (60 MHz, $CDCl_3$) δ 2.05 (d, 3, CH_3, J = 0.4 Hz); 2.16 (s, 3, SCH_3), 6.21 (q, 1, =CH–, J = 0.4 Hz); 7.0–7.4 (m, 5, C_6H_5).

Anal. Calcd for $C_{10}H_{10}S$: C, 73.14; H, 7.37; S, 19.49. Found: 73.09; H, 7.44; S, 19.65.

Methanesulfenyl chloride was detected in the reaction of **2d** with thionyl chloride in a methylene chloride solution by the isolation of the 1:1 adduct with cyclohexene. To 2.49 g (10.9 mmol) of **2d** in 50 ml of methylene chloride at 0° there was added 0.9 ml of cyclohexene (~10.9 mmol) and 0.80 ml of thionyl chloride. After stirring for 2 hr at 0° the solvent was removed under vacuum at ~10°. The residue was developed with four elutions of pentane on a 20 × 0.3 cm preparative tlc plate prepared by using a mixture of Merck silica gel P_{254} ($CaSO_4$) (80%) and Merck silica gel H (20%).[17] The chromatogram contained two major components of R_f ~0.35 and 0.8. The band with R_f 0.35 was eluted with chloroform to yield 1.55 g (86.5%) of **4f**. The band with R_f 0.8 was eluted with chloroform to yield 1.18 g (66%) of a yellow oil identical with an authentic sample of *trans*-1-(methylmercapto)-2-chlorocyclohexene prepared by the direct addition of methanesulfenyl chloride to cyclohexene, by ir, pmr, and mass spectrum.

α-Ethyl-β-(methylmercapto)styrene (4g) from 2e.—The alcohol **2e** (4.83 g, 20 mmol) was treated with thionyl chloride in pyridine in a manner similar to that employed for the conversion of **2c** **4e**. Chromatography yielded 2.76 g (78%) of **4g**, bp 70–72° (0.2 Torr). Pmr indicated a mixture of isomers in which the phenyl and S-methyl groups were *cis* (80%) or *trans* (20%) to each other pmr (60 MHz, $CDCl_3$): *cis* isomer, δ 2.25 (s, SCH_3), 1.04 and 2.60 (t and q, CH_2CH_3, J = 7.5 Hz), 6.07 (s, =CH–); *trans* isomer, δ 2.12 (s, SCH_3), 5.82 (t, =CH–, J = 0.4 Hz).

Anal. Calcd for $C_{11}H_{14}S$: C, 74.13; H, 7.92; S, 17.96. Found: C, 73.91; H, 7.85; S, 17.90.

α-(Methylmercapto)-α-phenylbutyraldehyde from 2e.—The alcohol (**2e**) was treated in a manner similar to that described for the preparation of α-(methylmercapto)-α,α-diphenylacetaldehyde from **2c**. From 9.66 g (40 mmol) of **2e** there was isolated 2.70 g (38%) of **4g** and 3.63 g (46%) of the butyraldehyde: bp 112–114° (0.25 Torr); pmr (60 MHz, $CDCl_3$) δ 1.73 (s, 3, SCH_3), 0.75 and 1.90 (t and q, 5, CH_2CH_3, J = 7.2 Hz).

Anal. Calcd for $C_{11}H_{14}OS$: C, 68.02; H, 7.27; S, 16.46. Found: C, 68.19; H, 7.20; S, 16.55.

α,β,β-Tri(methylmercapto)styrene (6g) from 3.—Compound **3**[3] (2.60 g, 10 mmol) was converted to the alkoxide with 1 equiv of sodium hydride in 150 ml of THF. At 0°, 1.2 g of thionyl chloride was added and the reaction stirred for 6 hr at 25°. The reaction was concentrated under vacuum to ~50 ml and diluted with 200 ml of water. The aqueous solution was extracted with

(16) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2075 (1968).

(17) Brinkman Instruments, Inc., Westbury, N. Y.

three 80-ml portions of ether and the dried ethereal extract ($MgSO_4$) concentrated to yield a light yellow oily residue. Chromatography on a 2.5 × 40 cm silica gel column with hexane yielded an oil that crystallized on standing. Recrystallization from pentane gave 1.96 g (81%) of **6g**: mp 59.5–60.9°; pmr (60 MHz, $CDCl_3$) δ 1.82, 2.14, 2.43 (s, 3, SCH_3), 7.05–7.45 (m, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{14}S_3$: C, 54.54; H, 5.83; S, 39.63. Found: C, 54.78; H, 5.97; S, 39.46.

2,2-Di(methylmercapto)-1-phenethyl Benzoate (5a).—Alcohol **2a** (8.93 g, 41.6 mmol) was converted to the alkoxide with 1 equiv of sodium hydride in 200 ml of THF. To this solution was added dropwise 5.75 g of benzoyl chloride at 0°. After stirring for 3 hr at 25°, the solution was filtered and concentrated under vacuum. The residue was dissolved in ether and the ethereal solution washed twice with 0.3 *N* aqueous sodium hydroxide followed by drying ($MgSO_4$). Evaporation of the ether gave an oil which was crystallized from hexane to yield 7.6 g (64%) of crystals: mp 94.0–95.5°; pmr (60 MHz, $CDCl_3$) δ 2.04, 2.10 (s, 3, SCH_3), 4.10 and 6.20 (q, 2, J_{AB} = 9 Hz, >CH–CH<).

Anal. Calcd for $C_{17}H_{18}O_2S_2$: C, 64.14; H, 5.70; S, 20.11. Found: C, 64.29; H, 5.83; S, 19.98.

2,2,2-Tri(methylmercapto)-1-phenethyl Benzoate.—Alcohol **3** (6.20 g, 23.8 mmol) was converted to the alkoxide with 1.2 g of sodium hydride in 100 ml of THF. The reaction was cooled to 0° and 3.5 ml of benzoyl chloride added. After 1 hr of stirring, 20 ml of water was added and the mixture poured into 30 ml of water at 0°. The aqueous solution was extracted with three 100-ml portions of ether and the ether extract washed twice with 0.5 *N* aqueous sodium hydroxide. Drying ($MgSO_4$) and concentration left a colorless oil which did not crystallize. Chromatography from silica gel with ethyl acetate (10%)–cyclohexane (10%)–hexane (80%) yielded 7.4 g (85.6%) of product which could not be distilled under vacuum without pyrolysis: pmr (60 MHz, $CDCl_3$) δ 2.12 (s, 9, SCH_3), 6.37 (s, 1, CH), 7.18–7.80 and 8.00–8.22 (m, 8 and 2, C_6H_5).

Anal. Calcd for $C_{18}H_{20}S_3O_2$: C, 59.33; H, 5.53; S, 26.35. Found: C, 59.56; H, 5.67; S, 26.05.

Pyrolysis of 4.65 g (17 mmol) of 2,2,2-tri(methylmercapto)-1-phenethyl benzoate for 8 hr at 170° (0.3 Torr) in a flask with a reflux condenser led to the formation of a sublimate in the condenser. At the end of the reaction products were washed back into the flask with ~50 ml of chloroform. The reaction mixture was diluted with 200 ml of ether and extracted with 0.2 *N* aqueous sodium hydroxide. The ether extracts were dried ($MgSO_4$) and concentrated under vacuum. Chromatography (silica gel with hexane) yielded 3.1 g (73.8%) of the styrene **6g**, mp 59.0–60.0°, from pentane and 0.89 g (19%) of recovered starting material.

β,β-Di(methylmercapto)styrene (6a).—2,2-Di(methylmercapto)-1-phenethyl benzoate (5.73 g, 20 mmol) was dissolved in 60 ml of THF and added to 3 g of potassium *t*-butoxide suspended in 100 ml of THF. The stirred solution was refluxed for 5 hr. After it cooled, 30 ml of water was added; the solution was concentrated under vacuum before dilution with 200 ml of 0.1 *N* aqueous sodium hydroxide. The aqueous solution was extracted twice with 200 ml of ether, the ethereal extract dried ($MgSO_4$) and concentrated under vacuum to yield a yellow oil that was chromatographed on silica gel by ethyl acetate (3%)–hexane (97%) to yield 2.53 g (64.5%) of **6a** and 1.19 g (28%) of **2a**. The olefin **6a** had bp 94–96° (0.25 Torr); pmr (60 MHz, $CDCl_3$) δ 2.28, 2.32 (s, 3, SCH_3), 6.78 (s, 1, =CH–), 7.10–7.70 (m, 5, C_6H_5).

Anal. Calcd for $C_{10}H_{12}S_2$: C, 6.121; H, 6.17; S, 32.62. Found: C, 61.29; H, 6.22; S, 32.59.

Reactions of β,β-Di(methylmercapto)-α-acetoxystyrene (9a) and β,β-Di(methylmercapto)-α-benzoyloxystyrene (9b) with NBS.—The styrene **9b** (11 g, 35 mmol) was dissolved in 200 ml of 50% aqueous ethanol and 8 g of sodium bicarbonate added. The solution was warmed to 60°; 6.85 g (38.5 mmol) of NBS was added slowly. Each addition resulted in the rapid evolution of carbon dioxide. The reaction was complete in 20 min and was diluted to 300 ml with water and extracted three times with 100-ml portions of ether. The ethereal extract was dried ($MgSO_4$), concentrated, and distilled under vacuum to give 8.1 g (81%) of material, bp 108–110° (0.05 Torr). The oil was crystallized from hexane to give a product, mp 53–55°, which was identical with **ω-benzoyloxy-ω-(methylmercapto)acetophenone (10b)**, independently synthesized from the reaction of the hemimethyl mercaptal of phenylglyoxal with benzoyl chloride in pyridine solution, or by the reaction of benzoyl chloride with the anions of ω-(methylsulfinyl)acetophenone in THF solution:[3] pmr (60 MHz, $CDCl_3$) δ 2.21 (s, 3, SCH_3), 6.22 (s, 1, >CH–), 7.20–7.65 (m, 5, C_6H_5), 8.0–8.2 (m, 5, C_6H_5).

Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.12; H, 4.93; S, 11.18. Found: C, 66.91; H, 4.94; S, 11.37.

Treatment of β,β-di(methylmercapto)-α-acetoxystyrene[3] with NBS in a mixture of water (80%)–dioxane (20%) yielded **ω-methylmercapto-ω-acetoxyacetaphenone (10a)** (51%), bp 110–113° (2 Torr), identical with material described previously.[12]

S-Methyl α-(Methylmercapto)-α-(phenyl)thioacetate (7d).—α,β,β-Tri(methylmercapto)styrene (**6g**, 1.2 g, 4.97 mmol) was suspended in 60 ml of 30% ethanol containing 4.5 ml of concentrated sulfuric acid, and the stirred solution refluxed for 2 hr. After cooling the reaction was diluted with 100 ml of water and extracted twice with 100 ml of ether. The ether extracts were washed with 100 ml of diluted aqueous sodium bicarbonate, dried ($MgSO_4$), and evaporated under vacuum. The residue was chromatographed with hexane on a 1.5 × 25 cm silica gel column to yield a trace of starting material (0.12 g) and 0.76 g (71.6%) of **7d**, crystallized from ethyl acetate–hexane: mp 59°; pmr (60 MHz, $CDCl_3$), δ 2.14, 2.30 (s, 3, SCH_3), 4.66 (s, 1, >CH–), 7.18–7.55 (m, 5, C_6H_5).

Anal. Calcd for $C_{10}H_{12}S_2O$: C, 56.60; H, 5.70; S, 30.16. Found: C, 56.61; H, 5.64; S, 29.94.

Compound **7d** was also prepared from **6a** by reaction with a peracid. The styrene **6a** (4.90 g, 25 mmol) was dissolved in 100 ml of chloroform and cooled to −10°. One equivalent of *m*-chloroperbenzoic acid (83% assay) dissolved in 50 ml of chloroform was poured into the styrene solution and the reaction allowed to stand for 12 hr at −10°. The *m*-chlorobenzoic acid was filtered from the reaction and the chloroform solution washed twice with 100 ml of saturated aqueous sodium bicarbonate, dried ($MgSO_4$) and concentrated under vacuum to yield 5.05 g (95%) of **7d**, mp 59.0–59.5°.

1,1′-Di(methylmercapto)-2-methoxy-2-phenylethane (5b).—Alcohol **2a** (8.0 g, 37 mmol) was converted to the alkoxide with 1 equiv of sodium hydride in 150 ml of THF. To this solution was added 1.3 equiv of methyl iodide (7 g). After 12 hr at 25° the reaction was quenched with 20 ml of methanol and diluted to 200 ml with ether. The ethereal solution was washed with an aqueous ammonium chloride solution, which was in turn extracted with 100 ml of ether. The combined ethereal solutions were dried ($MgSO_4$) and concentrated under vacuum to yield a yellow oil that was distilled to give 7.40 g of colorless **5b** (87.6%): bp 99–100° (0.25 Torr); pmr (60 MHz, $CDCl_3$) δ 2.02, 2.09 (s, 3, SCH_3), 3.76 (s, 3, OCH_3), 3.75–4.47 (AB quartet with δ_A 3.79, δ_B 4.39, J_{AB} = 6 Hz, >CH–CH<), 7.38 (broad s, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{16}OS_2$: C, 57.88; H, 7.07; S, 28.04. Found: C, 57.75; H, 7.07; S, 27.90.

1,1-Di(methylmercapto)-2-methoxy-2,2-diphenylethane (5c).—In a manner similar to that employed for the synthesis of **5b**, 5.25 g (18 mmol) of **2c** was converted to 5.12 g (93%) of **5c**: bp 131–135° (0.25 Torr); pmr (60 MHz, $CDCl_3$) δ 1.76 (s, 6, SCH_3), 2.98 (s, 3, OCH_3), 4.60 (s, 1, >CH–), 7.10–7.50 (m, 10, C_6H_5).

Anal. Calcd for $C_{17}H_{20}OS_2$: C, 67.09; H, 6.62; S, 20.03. Found: C, 66.95; H, 6.75; S, 19.96.

1,1-Di(methylmercapto)-2-methoxy-2-phenylpropane (5d).—In a manner similar to that employed for the synthesis of **5b**, 15.4 g (67.5 mmol) of **2d** was converted to 15.7 g (96.5%) of **5d**: bp 123–125° (0.5 Torr); pmr (60 MHz, $CDCl_3$) δ 1.73, 1.77 (s, 3, SCH_3), 2.11 (s, 3, CH_3), 3.12 (s, 3, OCH_3), 3.73 (s, 1, >CH–), 7.20–7.53 (m, 5, C_6H_5).

Anal. Calcd for $C_{12}H_{18}OS_2$: C, 59.79; H, 7.49; S, 26.42. Found: C, 60.09; H, 7.44; S, 26.66.

1,1-Di(methylmercapto)-2-methoxy-2-phenylbutane (5e).—In a manner similar to that employed for the synthesis of **5b**, 11.2 g of **2e** was converted to 10.1 g (91%) of **5e**: bp 109–112° (0.25 Torr); pmr (60 MHz, $CDCl_3$) δ 1.81, 1.90 (s, 3, SCH_3), 0.93 (t, 3, CH_3, J = 7.3 Hz), 2.18 (q, 2, CH_2, J = 7.3 Hz), 3.20 (s, 3, OCH_3), 3.96 (s, 1, >CH–), 7.18–7.60 (m, 5, C_6H_5).

Anal. Calcd for $C_{13}H_{20}OS_2$: C, 60.92; H, 7.87; S, 24.97. Found: C, 60.90; H, 7.72; S, 24.88.

Conversion of 5b–5e into 6a–6d by Elimination of Methanol.—The α-methoxy mercaptal (~25 mmol) in 150 ml of ether was treated with 1 equiv of *n*-butyllithium by the dropwise addition at 0° of a 1.6 *M* solution of butyllithium in hexane. The reaction was stirred for 1 hr before neutralization by the addition of an excess of solid ammonium chloride and 10 ml of methanol.

After being washed with 100 ml of water the ethereal solution was dried ($MgSO_4$) and concentrated under vacuum. The colorless residue was distilled to yield the pure ketene mercaptal. Thus, **6a** was prepared from **5b** in 91.3% yield.

In a similar fashion **5c** was converted in 84% yield into **1,1-di(methylmercapto)-1,1-diphenylethene (6b)** in 84% yield: mp 83–84°; pmr (60 MHz, $CDCl_3$) δ 2.19 (s, 6, SCH_3), 7.26 (s, 10, C_6H_5).

Anal. Calcd for $C_{16}H_{16}S_2$: C, 70.57; H, 5.92; S, 23.50. Found: C, 70.72; H, 6.20; S, 23.41.

α-Methyl-β,β-di(methylmercapto)styrene (6c) was prepared from **5d** in 78.5% yield: bp 97–99° (0.25 Torr); pmr (60 MHz, $CDCl_3$), δ 2.35 (s, 6, SCH_3); 2.13 (s, 3, CH_3), 7.15–7.33 (m, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{14}S_2$: C, 62.84; H, 6.71; S, 30.44. Found: C, 62.78; H, 6.76; H, 30.32.

α-Ethyl-β,β-di(methylmercapto)styrene (6d) was prepared from **5e** in 84.5% yield: bp 94–95° (0.25 Torr); pmr (60 MHz, $CDCl_3$), δ 2.12, 2.33 (s, 3, SCH_3), 0.94 (t, 3, $-CH_3$, J = 9 Hz), 2.78 (q, 2, CH_2, J = 9 Hz), 7.00–7.45 (m, 5, C_6H_5).

Anal. Calcd for $C_{12}H_{16}S_2$: C, 64.27; H, 7.19; S, 28.54. Found: C, 64.21; H, 7.14; S, 28.46.

Hydration of Ketene Mercaptals 6a–6f to Yield Thioacetates 7a–7e.—The ketene mercaptals **6a–6f** (5–15 mmol) were dispersed in 150 ml of 30% aqueous ethanol and 12 ml of concentrated sulfuric added. The solution was stirred on a steam bath for 1 hr. After cooling to room temperature, the reaction mixture was diluted with 200 ml of water and extracted twice with 100 ml of ether. The ethereal extracts were washed with 100 ml of dilute aqueous sodium bicarbonate and dried ($MgSO_4$), and the ether was removed under vacuum. The residue was chromatographed on silica gel with hexane. Compound **6a** yielded 83% **S-methyl phenylthioacetate**, identical with an authentic sample. Compound **6b** gave a mixture of reaction products that could not be separated by column chromatography. Analysis of the mixture by pmr indicated the presence of ~68% 1-(methylmercapto)-2,2-diphenylethylene (**4e**) and traces (~5%) of α-(methylmercapto)-α,α-diphenylacetaldehyde.

Hydration of **6c** gave 88.5% **S-methyl α-phenylthiopropionate (7b)**: bp 83–85° (0.3 Torr); pmr (60 MHz, $CDCl_3$), δ 1.50 (d, 3, CH_3, J = 8 Hz), 2.22 (s, 3, SCH_3), 3.95 (q, 1, >CH–, J = 8 Hz), 7.28 (s, 5, C_6H_5).

Anal. Calcd for $C_{10}H_{12}OS$: C, 66.65; H, 6.71; S, 17.76. Found: C, 66.52; H, 6.91; S, 17.50.

Hydration of **6d** gave 80% **S-methyl α-phenylthiobutyrate (7c)**: bp 76–78° (0.3 Torr); pmr (60 MHz, $CDCl_3$) δ 1.92 (t, 3, CH_3, J = 7 Hz), 2.25 (s, 3, SCH_3), 2.15 (m, 2, CH_2), 3.67 (t, 1, >CH–, J = 9 Hz).

Anal. Calcd for $C_{11}H_{14}OS$: C, 68.02; H, 7.27; S, 16.48. Found: C, 68.21; H, 7.24; S, 16.67.

Hydration of **6e**[3] gave 92% methyl mercaptal of phenylglyoxal that was isolated by column chromatography on silica using hexane (95%)–ethyl acetate (5%) as the eluent.

Hydration of **6f**[3] yielded 71% methyl mercaptal of phenylglyoxal and 22% phenylglyoxal.

Hydroboration and Chromic Acid Oxidation of 4a and 4e–4g to 8a–8d.—The β-styrenyl sulfides (20–30 mmol) were treated at 0° in 30 ml of diglyme with the *in situ* generated diborane from 0.5 g of sodium borohydride and 2.6 ml of boron trifluoride etherate. The reactions were stirred for 4 hr at 0° after which 10 ml of water and 100 ml of ether were added followed by oxidation with a 10% excess of chromium trioxide.[8] The heterogeneous reaction was stirred for 2 hr at 25°, after which 100 ml of water was added and the ethereal layer separated. The aqueous layer was extracted with 100 ml of ether and the combined ethereal extracts washed with 0.1 *N* sodium bicarbonate and dried ($MgSO_4$). After removal of the solvent under vacuum the residue was distilled or chromatographed on silica gel with hexane as the eluent. The isolated yields of aldehydes are given in Table I. It is of interest that the reaction of **4a** produced 14% acetophenone in addition to 50% phenylacetaldehyde.

Hydroboration and Oxidation of 4a and 4e–4g to Phenethanol, 2,2-Diphenethanol, 2-Phenylpropanol, and 2-Phenylbutanol.[8]—The β-styrenyl sulfides (~25 mmol) were treated at 0° in 35 ml of diglyme with the *in situ* generated diborane from 0.62 g of sodium borohydride and 3.39 ml of boron trifluoride etherate. After stirring for 3 hr, the solution was allowed to come to room temperature and excess hydride destroyed by 60 ml of water. A solution of 1.1 g of sodium hydroxide and 4.9 ml of 30% hydrogen peroxide in 40 ml of water was added and the reaction mixture stirred for 10 hr after which 100 ml of water was added and the aqueous solution was extracted twice with 100 ml of ether. The ether extracts were washed with water, dried ($MgSO_4$) and concentrated under vacuum. The residue was distilled or crystallized to yield the alcohols. Pmr of phenethanol from **4a** indicated a ratio of 1 to 2 isomer of 23:77,[18] overall yield of phenethanol, 89%. Olefin **4e** yielded 79% 2,2-diphenethanol, mp 60–62 (lit.[19] mp 61–62°), from pentane (80%)–ethyl acetate (20%). Olefin **4f** yielded 2-phenylpropanol, bp 68–70° (0.7 Torr) [lit.[20] bp 113–114° (14 Torr)], in 71% yield. From **4g** there was obtained 74% 2-phenylbutanol, bp 84–87° (0.7 Torr) [lit.[21] bp 120–121° (14 Torr)].

Registry No.—*cis*-**4b**, 22950-84-1; *trans*-**4b**, 22950-85-2; **4e**, 15096-10-3; *cis*-**4f**, 22950-86-3; *cis*-**4g**, 22950-87-4; *trans*-**4g**, 22950-88-5; **5a**, 22966-55-8; **5b**, 22966-56-9; **5c**, 22966-57-0; **5d**, 22966-58-1; **5e**, 22966-59-2; **6a**, 14063-69-5; **6b**, 22966-61-6; **6c**, 22966-62-7; **6d**, 22966-63-8; **6g**, 22946-45-8; **7b**, 22966-64-9; **7c**, 22966-65-0; **7d**, 22946-46-9; **10b**, 22966-66-1; α-(methylmercapto)-α,α-diphenylacetaldehyde, 22966-67-2; α-(methylmercapto)-α-phenylbutyraldehyde, 22966-68-3; 2,2,2-tri(methylmercapto)-1-phenethyl benzoate, 22966-69-4.

(18) Styrene yields a 20:80 mixture of the 1- and 2-phenethanols: H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **82**, 3222, 3223, 4708 (1960).
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(21) A. Ramart, J. Lucas and G. Amagat, *ibid.*, [10] **8**, 284 (1927).