vinyl CH), 1.2–2.5 (10 H, m, aliphatic CH), and four singlets (3 H each, CH_3) at 1.13, 1.06, 1.04, and 0.87; mass spectrum *m/e* (rel intensity) 248 (M^+, 11) 125 (22), 124 (25), 109 (100), 55 (23), 41 (36), and 39 (16).

Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.08; H, 9.64.

A comparable reaction of 0.75 mmol of the unsaturated ketone **15** with an Et_2O solution of 1.5 mmol of $(PhC{\equiv}C)_3CuLi_2$ yielded a crude reaction product which contained[9] $PhC{\equiv}CH$ and the starting ketone **15** accompanied by two minor, higher molecular weight materials and the major product, the previously described diketone **16**, identified by comparison of ir spectra and glpc retention times.

Registry No.—**3**, 21500-57-2; **4**, 20498-05-9; **7**, 21436-26-0; **12**, 14705-56-7; **16**, 21436-17-9.

β-Keto Sulfoxides. VI. Conversion of ω-(Methylsulfinyl)acetophenone into Di- and Tri-ω-(methylmercapto)acetophenone. Synthesis of α-Hydroxy Aldehydes, α-Keto Thio Esters, α-Keto Esters, α-Hydroxy Thio Esters, and α-Hydroxy Esters. The Chemistry of α-Keto Mercaptals[1]

Glen A. Russell and Leo A. Ochrymowycz

Department of Chemistry, Iowa State University, Ames, Iowa 50010

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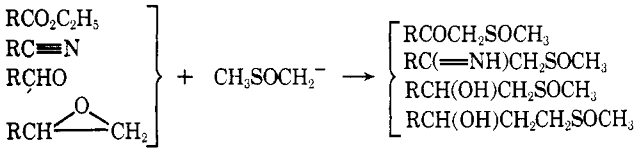
A convenient synthetic conversion of β-keto sulfoxides to α-hydroxy aldehydes involves the sequence, $RCOCH_2SOCH_3 \rightarrow RCOCH(Cl)SCH_3 \rightarrow RCOCH(SCH_3)_2 \rightarrow RCH(OH)CH(SCH_3)_2 \rightarrow RCH(OH)CHO$. Convenient syntheses of mandelaldehyde, atrolactaldehyde, benzilaldehyde, and 2-phenyl-2-ethylglycolaldehyde were developed. The α-chloro β-keto sulfides are readily converted to α-keto acetals. α-Keto mercaptals undergo O-alkylations and O-acylations in the presence of base. Bromination of the α-keto mercaptal followed by hydrolysis yielded S-methyl phenylthioglyoxylate ($C_6H_5COCOSCH_3$). Reaction of phenylglyoxal methyl mercaptal with methanesulfenyl chloride in the presence of base yielded ω,ω,ω-tri(methylmercapto)acetophenone which can also be converted to S-methyl phenylthioglyoxalate. A convenient synthesis of S-methyl thiomandelate is described: $C_6H_5COC(SCH_3)_3 \rightarrow C_6H_5CH(OH)C(SCH_3)_3 \rightarrow C_6H_5CH(OH)COSCH_3$. Bromination of the methyl mercaptal of phenylglyoxal in basic solution in the absence of water leads to *cis*- and *trans*-1,2-dibenzoyl-1,2-di(methylmercapto)ethylene, a product also formed in the pyrolysis of ω-chloro-ω-(methylmercapto)acetophenone.

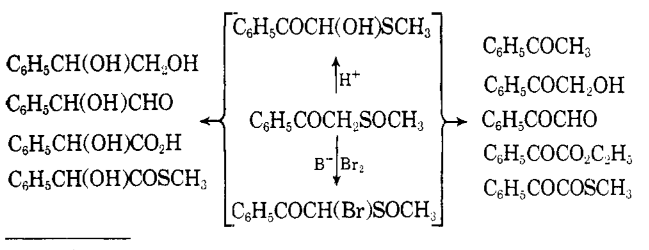
The methylsulfinylcarbanion $(CH_3SOCH_2^-)$[2] reacts readily with a variety of electrophilic centers including esters,[3,4] aldehydes,[4,5] epoxides, and nitriles (Scheme I, also see Experimental Section).

Scheme I



The substituted sulfoxides are potentially important in organic synthesis. β-Keto sulfoxides can be readily converted by the Pummerer rearrangement to α-hydroxy β-keto sulfides.[3] From these materials we have demonstrated practical routes to seven of the nine derivatives shown in Scheme II.[6]

Scheme II



The present investigation was directed toward a convenient synthesis of α-hydroxy aldehydes starting from the β-keto sulfoxides. In addition, new syntheses were developed for α-keto and α-hydroxy esters and thio esters.

Results and Discussion

We initially attempted to prepare mandelaldehyde from the β-hydroxy sulfoxide available from the sodium borohydride reduction of the β-keto sulfoxide (see Scheme III).[7] However, 1-phenyl-2-(methylsulfinyl)ethanol proved to be quite resistant to the Pummerer rearrangement and forcing conditions produced either ω-hydroxyacetophenone or the dehydration product, β-styryl methyl sulfoxide.[7] Treatment of the β-hydroxy sulfoxide with iodine gave only a low yield of the hydroxy aldehyde although the β-keto sulfoxide may be converted to an α-keto aldehyde or α-keto acetal by this procedure.[8]

Scheme III

$$C_6H_5COCH_2SOCH_3 \xrightarrow{NaBH_4} C_6H_5CH(OH)CH_2SOCH_3 \xrightarrow{H_3O^+} [C_6H_5CH(OH)CH(OH)SCH_3 \longrightarrow C_6H_5CH(OH)CHO + CH_3SH]$$

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[1] This work was supported by a grant from the Army Research Office (Durham). For part V see G. A. Russell, E. T. Sabourin, and G. Hamprecht, *J. Org. Chem.*, **34**, 2339 (1969).

[2] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 866 (1962); G. A. Russell, E. G. Janzen, H.-D. Becker, and F. J. Smentowski, *ibid.*, **84**, 2652 (1962).

[3] H.-D. Becker, G. J. Mikol, and G. A. Russell, *ibid.*, **85**, 3410 (1963).

[4] E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1345 (1965).

[5] G. A. Russell and H.-D. Becker, *ibid.*, **85**, 3406 (1963).

[6] G. A. Russell and G. J. Mikol, *ibid.*, **88**, 5498 (1966); see also J. E. Thompson, *J. Org. Chem.*, **32**, 3947 (1967); D. Hodson and G. Holt, *J. Chem. Soc., C*, 1602 (1968).

[7] G. A. Russell, E. Sabourin, and G. J. Mikol, *J. Org. Chem.*, **31**, 2854 (1966).

[8] T. L. Moore, *J. Org. Chem.*, **32**, 2786 (1967).

We thus turned our attention to the synthesis of α-keto and α-hydroxy mercaptals (Scheme IV) since it was apparent from the literature that the α-hydroxy mercaptal could be converted to the α-hydroxy aldehyde.[9-11] Moreover, this route allows a more general synthesis since the ketone can be converted to the alcohol by the addition of a Grignard reagent as well as by simple reduction.

Scheme IV

$$C_6H_5COCH_2SOCH_3 \longrightarrow C_6H_5COCH(SR)_2$$

$$C_6H_5COCH(SR)_2 \xrightarrow{NaBH_4} C_6H_5CH(OH)CH(SR)_2$$

$$C_6H_5COCH(SR)_2 \xrightarrow{R'MgX} C_6H_5C(R')(OH)CH(SR)_2$$

$$C_6H_5C(R')(OH)CH(SR)_2 \xrightarrow{I_2} C_6H_5C(R')(OH)CHO$$

Attempts were made to convert phenylglyoxal, or the hemimercaptal ($C_6H_5COCH(OH)SCH_3$), into the keto thio acetal. However, reaction of ethanedithiol proceeded to yield a dimercaptal even when a deficiency of the dithiol was employed (see Experimental Section). With ethylene glycol, phenylglyoxal or its hemimercaptal reacts in a benzene solution of hydrogen chloride to yield only the diacetal.

Reaction 1 appeared to be straightforward. However, we have not been able to demonstrate practicality for this reaction. Yields at best approach the 50% expected for the disproportionation of the hemimercaptal (reaction 2).[12] In part the difficulty lies in the fact that reaction 3 does not proceed readily although anhydrous phenylglyoxal forms the hemimercaptal easily.

$$C_6H_5COCH(OH)SCH_3 + CH_3SH \xrightarrow{H_3O^+} C_6H_5COCH(SCH_3)_2 + H_2O \quad (1)$$

$$2C_6H_5COCH(OH)SCH_3 \xrightarrow{H_3O^+} C_6H_5COCH(SCH_3)_2 + C_6H_5COCH(OH)_2 \quad (2)$$

$$C_6H_5COCH(OH)_2 + CH_3SH \xrightarrow{H_3O^+} C_6H_5COCH(OH)SCH_3 + H_2O \quad (3)$$

The low yield of reaction 1 led to the development of an alternate route to the keto mercaptal. Excellent yields were obtained by treatment of the α-chloro-β-keto sulfide with methyl mercaptan in methylene chloride solution (Scheme V). The chloro keto sulfide in turn was readily available from a Pummerer-type reaction between thionyl chloride and the keto sulfoxide.[13] Moreover, the α-chloro-β-keto sulfide need not be isolated.

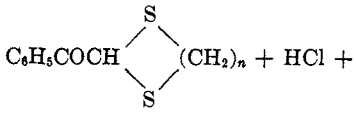
Scheme V

$$C_6H_5COCH_2SOCH_3 + SOCl_2 \longrightarrow C_6H_5COCH(Cl)SCH_3 + SO_2 + HCl \quad (4)$$

$$C_6H_5COCH(Cl)SCH_3 + CH_3SH \xrightarrow{CH_2Cl_2} C_6H_5COCH(SCH_3)_2 + HCl \quad (5)$$

$$C_6H_5COCH(Cl)SCH_3 + CH_3OH \longrightarrow C_6H_5COCH(OCH_3)_2 + HCl + CH_3SH \quad (6)$$

$$C_6H_5COCH(Cl)SCH_3 + HS(CH_2)_nSH \longrightarrow$$



$+ HCl + CH_3SH$ (7)

$n = 2$ or 3

α-Chloro-β-keto sulfides are also a convenient source of keto acetals. For example, reaction 6 occurs in >95% yield.

The keto mercaptal was readily reduced by sodium borohydride and underwent normal addition reactions with methyl, ethyl, and phenyl Grignard reagents (Scheme IV). Isopropyl or *t*-butyl Grignard reagents led to reduction of the carbonyl function.

Conversion of α-hydroxy acetals to α-hydroxy aldehydes is a difficult process. The reaction is reversible and in the presence of acid the α-hydroxy aldehyde readily rearranges to the α-hydroxy ketone.[14,15] α-Hydroxy mercaptals offer the possibility of irreversible hydrolysis by oxidation of the liberated mercaptan[9-11,16,17] or by precipitation of the released mercaptan as a heavy metal salt.[10,17]

Oxidative hydrolysis by bromine has been reported to yield the rearranged α-hydroxy ketones[14,15] or the α-hydroxy aldehyde.[10] In our hands only the rearranged α-hydroxy ketone was found from the brominolysis of the thioacetal of mandelaldehyde (2-hydroxy-2-phenylacetaldehyde).

Weygand and Bestmann report the hydrolysis of α-hydroxy thioacetals under essentially neutral conditions and in the presence of an equal molar mixture of mercuric chloride and cadmium carbonate in refluxing acetone.[10] A long reaction period is required and product separation is difficult.

We have found that a more satisfactory procedure involves the treatment of the hydroxy thioacetal by an equal molar mixture of iodine and sodium bicarbonate in a 1:1 dioxane–water solvent. The reaction appears to involve a 1:1 stoichiometry between iodine and α-hydroxy thioacetal. However, owing to oxidation of the initially formed methyl disulfide, use of 2 mol of iodine increases slightly the yield of α-hydroxy aldehyde (see Table I). An excess of sodium bicarbonate in the dioxane solvent caused the α-hydroxy aldehyde to rearrange to the α-hydroxy ketone.

The yields of α-hydroxy aldehydes and the state of aggregation observed for the isolated product are given in Table I.

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[9] F. Weygand, H. J. Bestmann, and H. Ziemann, *Chem. Ber.*, **91**, 1040 (1958).

[10] F. Weygand, H. J. Bestman, H. Ziemann, and E. Klieger, *ibid.*, **91**, 1043 (1958).

[11] G. B. Gauthier and C. Vaniscotte, *Bull. Soc. Chim. Fr.*, **53**, 30 (1956).

[12] H. Böhme and H. P. Teltz, *Justus Liebigs Ann. Chem.*, **620**, 1 (1959).

[13] F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, **77**, 572 (1955).

[14] J. V. Nef, *Justus Liebigs Ann. Chem.*, **335**, 242 (1904).

[15] W. L. Evans and C. R. Parkinson, *J. Amer. Chem. Soc.*, **35**, 1770 (1913).

[16] E. Pascu, *Chem. Ber.*, **38**, 509 (1905).

[17] K. A. Baxter, G. T. Newbold, and F. S. Spring, *J. Chem. Soc.*, 390 (1947).

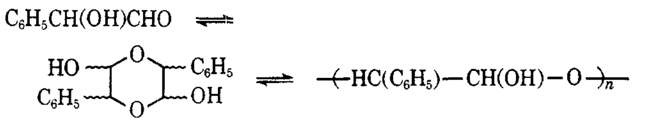
TABLE I

YIELD OF α-HYDROXY ALDEHYDES ($C_6H_5CR(OH)CHO$)

R	Yield, %[a]	Isolated form, mp or bp (Torr), °C	Mol wt[b]	Registry no.
H	88[c]	Mp 135–138	265 (dimer)	21504-13-2
CH_3	94[c]	Mp <27	300 (dimer)	21504-26-7
		Bp 116–120 (0.7)	(monomer[d])	4361-50-6
C_2H_5	80[c]	Bp 65–68 (0.7)	172 (monomer[d])	21504-01-8
C_6H_5	94,[c] 94[e]	Mp 164–166	406 (dimer)	21517-41-9 (*cis*) 21517-42-0 (*trans*)

[a] Isolated by distillation or recrystallization. [b] In tetrahydrofuran by thermoelectric osmometry; Spang Micro Analytical Laboratory, Ann Arbor, Mich. [c] 2 mol of iodine per mol of hydroxy mercaptal. [d] Confirmed by pmr and acid-catalyzed conversion into dimer or polymer. [e] 1 Mol of iodine per mol of hydroxy mercaptal.

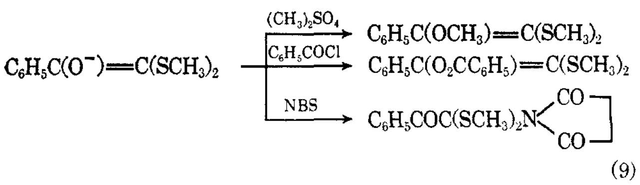
By necessity we were forced to examine the structure of the "α-hydroxy aldehyde" which can exist in the form of a cyclic dimer, 1.[18,19]



1

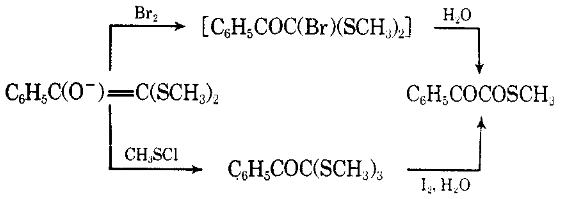
Mandelaldehyde has been reported to be monomeric on the basis of infrared absorption.[10] We found that purified material did not give a carbonyl absorption and showed no aldehyde absorption in pmr. The pmr spectrum was consistent with a diastereomeric mixture of 1,4-dioxanes. The mass spectrum recorded by direct sample inlet (Atlas CH-4) gave a weak peak for the dimer (*m/e* 272) but a much stronger peak for the monomer (*m/e* 136). Benzilaldehyde (2,2-diphenylglycolaldehyde) also was observed to exist only in the dimeric state. However, the mass spectrum gave no peaks with higher mass than the monomer (*m/e* 212). Atrolactaldehyde (2-phenyl-2-methylglycolaldehyde) and 2-phenyl-2-ethylglycolaldehyde both could be isolated as monomers. Upon standing, or more rapidly in the presence of acid, atrolactaldehyde dimerized to the 1,4-dioxane which gave a mass spectrum with a parent peak of *m/e* 300. Both the dimer and monomer have been previously prepared.[20]

Having available α-keto mercaptals that could be prepared in two steps, both proceeding in over 80% yield from an aromatic carboxylic ester, we have investigated some of the other chemistry of these substances. Treatment with sodium hydride in tetrahydrofuran yielded the enolate anion. This anion underwent O-methylation with methyl sulfate and O-benzoylation with benzoyl chloride, but gave a C derivative with N-bromosuccinimide.



(9)

SCHEME VI

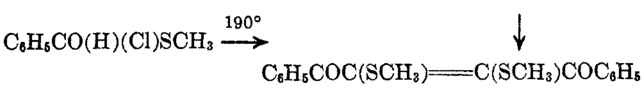


Treatment of the enolate anion with bromine followed rapidly by hydrolysis yielded S-methyl phenylthioglyoxylate (Scheme VI). Reaction of the enolate with methanesulfenyl chloride yielded ω,ω,ω-tri(methylmercapto)acetophenone which underwent oxidative hydrolysis in the presence of iodine to yield the thioglyoxylate ester in excellent yield. The tri(methylmercapto)acetophenone could be reduced to the alcohol and oxidatively hydrolyzed to S-methyl thiomandelate (reaction 10). Treatment of the trimethyl esters of orthotrithiophenylglyoxylic or orthotrithiomandelic acids, $C_6H_5COC(SCH_3)_3$ and $C_6H_5CH(OH)C(SCH_3)_3$, with iodine and bicarbonate ion in the presence of ethanol led directly to ethyl phenylglyoxylate (69%) and ethyl mandelate (59%).

$$C_6H_5COC(SCH_3)_3 \xrightarrow{NaBH_4} C_6H_5CH(OH)C(SCH_3)_3 \xrightarrow[H_2O]{I_2,HCO_3^-} C_6H_5CH(OH)COSCH_3 \qquad (10)$$

When the bromination product of the enolate anion of ω,ω-di(methylmercapto)acetophenone was not immediatedly hydrolyzed, a mixture of *cis*- and *trans*-1,2-dibenzoyl-1,2-di(methylmercapto)ethylene (2) was formed. Compound 2 was also formed when ω-chloro-ω-(methylmercapto)acetophenone was pyrolyzed at 190° in the liquid phase (Scheme VII).

SCHEME VII



2

Attempts to prepare ω,ω,ω-tri(methylmercapto)acetophenone from ω-bromo-ω-(methylsulfinyl)acetophenone were not successful. Treatment with thionyl chloride led to the formation of some ω-bromo-ω-chloro-ω-(methylmercapto)acetophenone, but considerable amounts of ω-chloro-ω-(methylmercapto)acetophenone

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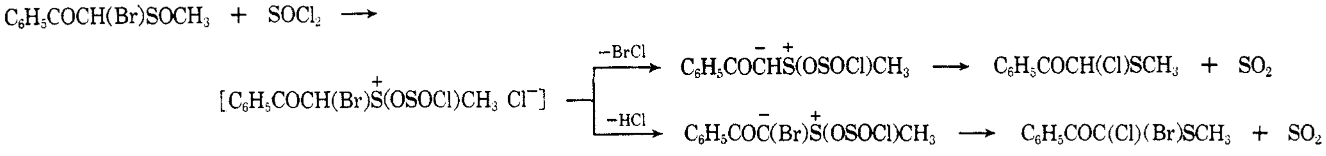
(18) H. Baer and H. Fischer, *J. Biol. Chem.*, **150**, 213 (1943).

(19) C. D. Hurd, *Ann. Rev. Biochem.*, **14**, 107 (1945).

(20) S. Danilov, *Chem. Ber.*, **60**, 2390 (1927); **62**, 2653 (1929).

Scheme VIII



were also formed. Loss of bromine apparently involves a modification of a Pummerer reaction, as in Scheme VIII.[21]

Experimental Section

γ-Hydroxy-γ-phenylpropyl Methyl Sulfoxide.—This compound was prepared by addition of 24.3 ml (~200 mmol) of styrene oxide at −5° to a solution (150 ml) of 200 mmol of sodium hydride dissolved in DMSO under nitrogen. After 4 hr at 25° the reaction mixture was poured into 1 l. of water, acidified with hydrochloric acid to a pH of 4.5. The aqueous solution was extracted with four 125-ml portions of chloroform, dried ($MgSO_4$), and concentrated under water aspirator pressure. The crude oil was chromatographed from silica gel by 30% methylene chloride–70% petroleum distillate-B to yield 15.4 g of product: 60-MHz pmr ($CDCl_3$) δ 2.32 and 2.38 ppm (d, 3 total, $SOC\mathbf{H}_3$, diasteromeric mixture), 4.25 (s, 1, O**H**, deuterium oxide exchanged), 4.7 [t, 1, J = 7 Hz, C(OH)**H**].

Anal. Calcd for $C_{10}H_{14}SO_2$: C, 60.59; H, 7.12; S, 16.15. Found: C, 60.64; H, 7.13; S, 16.08.

Treatment of γ-hydroxy-γ-phenylpropyl methyl sulfoxide with acetic anhydride brought about the Pummerer reaction and the substitution of the acetoxy group in the methyl position to yield **1,5-diacetoxy-5-phenyl-2-thiabutane,** $C_6H_5CH(O_2CCH_3)CH_2CH_2SCH_2O_2CCH_3$, as an oil in 62% yield, mass spectrum (70 eV) m/e 282. The pmr spectrum was consistent with the assigned structure.

Oxidation of γ-hydroxy-γ-phenylpropyl methyl sulfoxide[7] yielded 60% of the **γ-hydroxy-γ-phenylpropyl methyl sulfone** as an oil: pmr ($CDCl_3$) δ 2.82 (s, 3, $SO_2C\mathbf{H}_3$), 4.84 [t, 1, J = 6.8 Hz, C(OH)**H**], 2.96 (s, 1, O**H**, deuterium oxide exchanged).

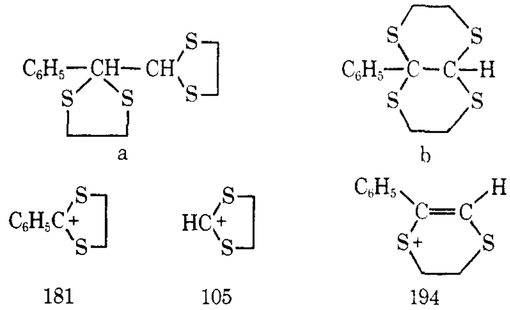
Anal. Calcd for $C_{10}H_{14}SO_3$: C, 56.07; H, 6.59; S, 14.94. Found: C, 56.39; H, 6.56; S, 14.93.

Condensation of Benzonitrile and Methylsulfinyl Carbanion.—The condensation product, ω-(methylsulfinyl)acetophenone imine [$C_6H_5C(=NH)CH_2SOCH_3$], was hydrolyzed to the ketone prior to isolation. Treatment of benzonitrile with the sodium salt of methylsulfinylcarbanion yielded only tar. However, when lithium iodide was present the condensation proceeded normally.[22] To 250 ml of DMSO solution, in which 250 mmol of sodium hydride had been dissolved, was added 65 g of anhydrous lithium iodide. After 1 hr of equilibration, 200 mmol (20.6 g) of benzonitrile was added (dropwise) at 0°. The blue reaction mixture was poured into 500 ml of ice–water, acidified to pH 3 with hydrochloric acid, and extracted with three portions of 200 ml of chloroform. After drying ($MgSO_4$) and concentration the residue crystallized from ether to yield 19.0 g of ω-(methylsulfinyl)-acetophenone (52%), mp 86°.

Ethanedithiol Dimercaptal of Phenylglyoxal.—The methyl hemimercaptal of phenylglyoxal (6.0 g) was dispersed in 60 ml of 85% phosphoric acid. Ethane-1,2-dithiol (6.1 ml) was added and the solution stirred at 50° for 18 hr. The solution was poured into 300 ml of 0.5 N sodium hydroxide and extracted with two 100-ml portions of chloroform. The chloroform extract was washed with water, dried ($MgSO_4$), concentrated, and crystallized from chloroform (30%)-ethanol (70%) to give 8.8 g of product (77%), mp 178°.

Anal. Calcd for $C_{12}H_{14}S_4$: C, 50.35; H, 4.93; S, 44.72. Found: C, 50.38; H, 5.07; S, 44.59.

The mass spectrum [(70 eV) m/e (rel intensity) 286 (66), 194 (100), 181 (29), 166 (15), 121 (59), 105 (9); metastable peaks at 142.0 (194 → 166) and 131.6 (286 → 194)] does not uniquely distinguish between structures a and b.

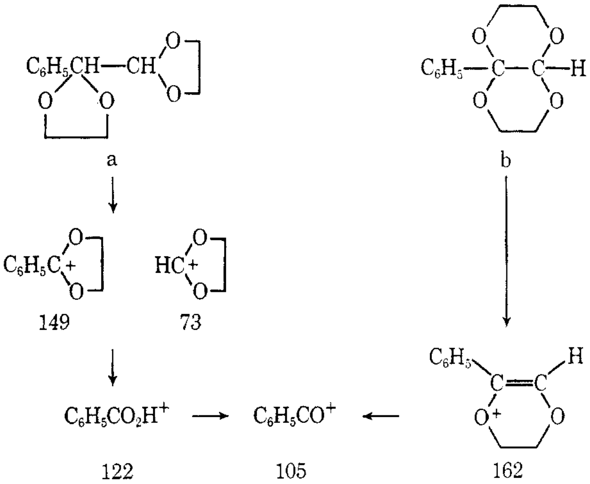


Structure a is more consistent with the ions m/e 105 and 181; however, the predominant ion m/e 194 supports structure b.

Ethylene Glycol Diacetal of Phenylglyoxal.—In a flask equipped with a Dean–Stark trap was placed 200 ml of benzene, 75 mmol of the methyl hemimercaptal of phenylglyoxal, 1 equiv of ethylene glycol, and 20 g of powdered mercuric chloride. The reaction mixture was dehydrated under reflux for 18 hr. The solution was filtered free of inorganic salt and concentrated to a yellow oily residue. The oily residue was dissolved in 200 ml of ether, extracted with 200 ml of saturated aqueous sodium bicarbonate, dried ($MgSO_4$), and concentrated to a semisolid residue that was recrystallized from tetrahydrofuran-water (1:1) mixture to yield 19.8 g (58.5%) of white crystals, mp 113°, of the bisacetal.

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.03; H, 6.42.

The mass spectrum [(70 eV) m/e (rel intensity) 222 (12), 194 (3), 162 (1), 149 (11), 123 (45), 122 (9), 105 (100), 77 (48), 73 (8); metastable peaks at 169.0, 112.9, 100.0, 90.4, 68.1, 56.4, 50.9] seems to clearly indicate a preference for structure a over b. Unfortunately the predominant ion (m/e 105) is derived from both the fragments of m/e 149 and 162.



ω-Chloro-ω-(methylmercapto)acetophenone.—To 48.6 g (266 mmol) of ω-(methylsulfinyl)acetophenone[3] in 250 ml of methylene chloride at 0° was added 19.5 ml of thionyl chloride (275 mmol) over a 5-min period. The reaction flask was swept with a stream of dry nitrogen and stirred for 4 hr to complete the elimination of sulfur dioxide and hydrogen chloride. A 10-ml aliquot was withdrawn and diluted to 25 ml with methylene chloride. This solution was filtered through a bed (1:1) of magnesium sulfate and sodium bicarbonate, concentrated, and distilled in a short-path still to yield 0.73 g of material: bp 105–108° (2 Torr); pmr (CCl_4) δ 6.40 [s, 1, $C\mathbf{H}(Cl)SCH_3$], 2.18 (s, 3, $SC\mathbf{H}_3$). The prod-

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[21] G. A. Russell and G. J. Mikol, "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Interscience Publishers Inc., New York, N. Y., 1968, p 157.

[22] See also R. G. Barnhart, Jr., and W. E. McEwen, *J. Amer. Chem. Soc.*, **89**, 7009 (1967).

uct decomposed slowly at room temperature but could be stored for 3 months at −10° with little decomposition.

Conversion of ω-Chloro-ω-(methylmercapto)acetophenone into the Methyl Mercaptal of Phenylglyoxal.—A solution of 260 mmol of ω-chloro-ω-(methylmercapto)acetophenone in 250 ml of methylene chloride was prepared as previously described. The flask was equipped with a Dry Ice–carbon tetrachloride condenser. To the solution at 0° was added 50 g of methyl mercaptan over a period of 20 min. The solution was stirred and swept with a stream of nitrogen to remove the hydrogen chloride formed. After 1 hr the solution was allowed to reflux at approximately room temperature for 2.5 hr. The solvent was removed by water aspirator vacuum to give a solid that crystallized from petroleum distillate-B to yield 52.0 g of the mercaptal, mp 67° (94%). Recrystallization from ethanol raised the melting point to 69°.

Conversion of ω-Chloro-ω-(methylmercapto)acetophenone into the Methyl Acetal of Phenylglyoxal.—ω-(Methylsulfinyl)acetophenone (2.25 g, 13 mmol) was converted to ω-chloro-ω-(methylmercapto)acetophenone in 50 ml of methylene chloride with 0.95 ml (1 equiv) of thionyl chloride. The reaction mixture was swept with nitrogen for 30 min to eliminate acidic fumes. Anhydrous methanol (80 ml) was added and the reaction mixture was allowed to stir for 30 min under a stream of nitrogen. The solvents were removed by vacuum evaporation at 70° to yield 2.15 g of a yellow oil. The pmr analysis of the oil indicated pure acetal. Distillation yielded 1.98 g of material, bp 60–62° (0.3 Torr), identical with that described by Moore:[8] pmr ($CDCl_3$) δ 3.42 (s, 6), 5.18 (s, 1), 7.28–7.55 (m, 3), 7.95–8.20 (m, 2).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.81; H, 6.63.

2-Benzoyl-*m*-dithiane.—ω-(Methylsulfinyl)acetophenone (3.64 g, 20 mmol) was converted into ω-chloro-ω-(methylmercapto)-acetophenone by 1.45 ml of thionyl chloride in 200 ml of methylene chloride. To this reaction product was added 1.40 g (14 mmol) of 1,3-propanediol. The reaction mixture was swept with nitrogen for 3 hr, the solvent evaporated, and the residue chromatographed as a silica gel column. The material was eluted by hexane (95%)–ethyl acetate (5%). The separation was followed by tlc. The fractions containing the major component were concentrated and the product crystallized from hexane–ethyl acetate to give 1.5 g (51% based on dithiol) of the *m*-dithiane: mp 80–83°; pmr ($CDCl_3$) δ 1.90–2.30 (m, 2), 2.35–2.85 (m, 2), 3.20–3.60 (m, 2), 5.19 (s, 1), 7.25–7.60 (m, 3), 7.80–8.05 (m, 2); mass spectrum (70 eV) *m/e* (rel intensity) 224 (22), 119 (100), 105 (85).

Anal. Calcd for $C_{11}H_{12}OS_2$ (224.21): C, 58.92; H, 5.40; S, 28.54. Found: C, 58.66; H, 5.25; S, 28.77.

2-Benzoyl-1,3-dithiolane.—The same procedure as reported for 2-benzoyl-*m*-dithiane was employed. Elution and crystallization of the product with hexane (70%)–ethyl acetate (30%) yielded 76% of product (based on ethylenedithiol), mp 136–139°. Recrystallization from chloroform gave mp 138.5–139.5°; pmr ($CDCl_3$) δ 2.95 (broad s, 1.6), 2.12 (broad s, 2.4), 5.43 (s, 1), 7.25–7.60 (m, 3), 7.85–8.15 (m, 2); mass spectrum (70 eV), *m/e* (rel intensity) 210 (trace), 209 (29), 166 (35), 165 (30), 137 (20), 105 (100), 93 (5), m* 130 (209 → 165), 113.1 (166 → 137), 66.5 (166 → 105), 56.5 (105 → 77).

Anal. Calcd for $C_{10}H_{10}OS_2$ (210.18): C, 57.14; H, 4.80; S, 30.45. Found: C, 56.99; H, 5.01; S, 30.26.

1-Phenyl-2,2-di(methylmercapto)ethanol.—The methyl mercaptal of phenylglyoxal (50 mmol) was reduced by stirring for 6 hr at room temperature with 1.4 g of sodium borohydride dissolved in 200 ml of water. The aqueous solution was neutralized with an excess of ammonium chloride and extracted with three 200-ml portions of ether and dried ($MgSO_4$); the ether extract was concentrated to yield 10.65 g of an oil that distilled at 78–80° (0.2 Torr): pmr ($CDCl_3$) δ 1.88 and 1.98 (d, 6, SCH_3), 3.36 (s, 1, OH), 3.65 and 4.55 [q, 2, J_{AB} = 9 Hz, C(OH)HCH].

Anal. Calcd for $C_{10}H_{14}OS_2$: C, 56.07; H, 6.59; S, 29.88. Found: C, 55.99; H, 6.73; S, 29.88.

1,1-Di(methylmercapto)-2-phenyl-2-propanol.—To methylmagnesium iodide prepared from 1.7 g of magnesium and 21.3 g of methyl iodide in 200 ml of ether was added 10.6 g (50 mmol) of the methyl mercaptal of phenylglyoxal. The product was isolated as a pale yellow oil after neutralization with ammonium chloride and further extraction with ether, bp 130–133° (0.7 Torr) (69%) or by column chromatography on silica gel (with hexane (95%)–ethyl acetate (5%) to yield 93% of product: pmr ($CDCl_3$) δ 1.78 and 1.95 (d, 6, SCH_3), 1.64 [s, 3, C(OH)CH_3], 3.30 (s, 1, OH), 3.72 [s, 1, CH(SCH_3)$_2$].

Anal. Calcd for $C_{11}H_{16}OS_2$: C, 57.88; H, 7.07; S, 28.04. Found: C, 57.48; H, 7.04; S, 28.28.

1,1-Di(methylmercapto)-2-phenyl-2-butanol.—The Grignard reaction following the procedure described for 1,1-di(methylmercapto)-2-phenyl-2-propanol yielded a product isolated as an oil in 89% yield by chromatography and 71% by distillation at 137–138° (0.7 Torr): pmr ($CDCl_3$) δ 2.08 and 0.78 (q, t, 5 total, J = 7.5 Hz, CH_2CH_3), 3.16 (s, 1, OH), 3.79 [s, 1, CH-(SCH_3)$_2$].

Anal. Calcd for $C_{12}H_{18}OS_2$: C, 59.49; H, 7.49; S, 26.42. Found: C, 59.27; H, 7.48; S, 26.41.

1,1-Diphenyl-2,2-di(methylmercapto)ethanol.—Addition of 50 mmol of methyl mercaptan of phenylglyoxal to 70 mmol of phenylmagnesium bromide yielded the product as an oil (86%) by chromatography on silica gel [hexane (95%)–ethyl acetate (5%)] and by distillation at 155–158° at 0.7 Torr (66%); pmr ($CDCl_3$) δ 1.81 (s, 6 SCH_3), 3.53 (s, 1, OH), 4.22 [s, 1, CH-(SCH_3)$_2$].

Anal. Calcd for $C_{16}H_{18}OS_2$: C, 66.19; H, 6.25; S, 22.05. Found: C, 66.42; H, 6.23; S, 21.93.

Mandelaldehyde.—To 80 ml of dioxane solution containing 6.42 g (30 mmol) of 1-phenyl-2,2-di(methylmercapto)ethanol was added 80 ml of water, 9.8 g of iodine (38.5 mmol) and 2.9 g of sodium bicarbonate. After stirring for 3 hr at 25°, a second portion of iodine (5.1 g, 20 mmol) and sodium bicarbonate (1.5 g) was added. In 1.5 hr the solution was colorless at which time it was diluted with 100 ml of saturated aqueous sodium chloride. Extraction of the solution with four 50-ml portions of chloroform, drying ($MgSO_4$), and evaporation of solvent left an oil that crystallized from petroleum distillate-B to yield 3.60 g of crystals, mp 137–138°, of dimeric mandelaldehyde: the material gave no carbonyl absorption in the infrared; pmr (d_6-DMSO) δ 4.5 and 5.6 (m, 2, CHCH), 3.2, 6.2, and 6.8 (broad singlets, 1 total, OH). The pmr spectrum suggests a mixture of *cis–trans* isomers of the 1,4-dioxane structure.

Atrolactaldehyde.—The reaction between 72 mmol of iodine and 40 mmol of 1,1-di(methylmercapto)-2-phenyl-2-propanol was performed in the manner employed for the preparation of mandelaldehyde. Vacuum distillation yielded 94% of the monomeric atrolactaldehyde: bp 116–120° (0.7 Torr); ir (CCl_4) 1719 (C=O); pmr ($CDCl_3$) δ 1.57 (s, 3, CH_3), 4.08 (s, 1, OH), 9.43 (s, 1, CHO).

Addition of 1 drop of concentrated hydrochloric acid followed by vacuation of 2 Torr for 12 hr led to a waxy solid, mp <27°, identified as pure dimer. The infrared (CCl_4) was void of carbonyl absorption; pmr ($CDCl_3$) (60 MHz) δ 1.30 (s, 3, CH_3), 3.42 (broad s, 1, CHOH), δ 3.93 (broad s, 1, OH deuterium oxide exchangeable).

2-Phenyl-2-ethylglycolaldehyde.—Oxidative hydrolysis of the appropriate mercaptal gave an 80% yield of oil: bp 65–68° (0.7 Torr); ir (CCl_4) 1719 (C=O); pmr ($CDCl_3$) δ 9.50 (s, 1, CHO), 4.04 (s, 1, OH), 1.97 and 0.81 (q, t, total 5, J = 7.5 Hz, CH_2CH_3).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.24; H, 7.24.

Treatment with 1 drop of hydrochloric acid and evacuation to 2 Torr resulted in an increased viscosity of the oil. However, a dimer was not formed but rather a mixture of monomeric and polymeric form.

Benzilaldehyde.—The mercaptal (16.4 mmol) was treated with 29 mmol of iodine and a slight excess of sodium bicarbonate in 50% aqueous dioxane as previously described. After 3.5 hr, the solution was diluted with saturated aqueous sodium chloride and extracted with chloroform. Drying ($MgSO_4$) and evaporation of the extract left a yellow oil that crystallized on standing to yield 2.94 g of product (94%), mp 160–162°; recrystallization from methanol gave a colorless product, mp 164–166°. The infrared was void of carbonyl absorption. The molecular weight in THF was found to be 406 indicating the material to be dimeric. The pmr spectrum showed (d_6-DMSO) δ 3.60 (broad s, 1, OH) 5.9 and 5.97 (broad s, 1, CHOH) and indicated a *cis–trans* mixture of 1,4-dioxane isomers.

Anal. Calcd for $C_{14}H_{12}O_2$ (424.48): C, 79.22; H, 5.70. Found: C, 79.19; H, 5.60.

β,β-Di(methylmercapto)-α-methoxystyrene.—To a dispersion of 1.1 g of sodium hydride in 150 ml of THF was added 5.3 g (25 mmol) of the methyl mercaptal of phenylglyoxal. The reaction was maintained under a nitrogen atmosphere. After the conversion of the mercaptal to the sodium salt, 3.25 g of methyl sulfate was added dropwise. The solution was stirred for 2 hr, filtered, and concentrated under vacuum and the residue dissolved in 200 ml of ether. The ether solution was washed twice with 50 ml of water and dried ($MgSO_4$). Removal of ether left a pale yellow oil that showed only one component by pmr and tlc. Distillation at 100° (0.2 Torr) gave 4.8 g (85%) of product: pmr ($CDCl_3$) δ 2.34, (s, 3), 2.09 (s, 3), and 3.40 (s, 3, C**H**$_3$).

Anal. Calcd for $C_{11}H_{14}OS_2$: C, 58.40; H, 6.24; S, 28.29. Found: C, 58.38; H, 6.05; S, 28.28.

β,β-Di(methylmercapto)-α-benzoyloxystyrene.—The sodium salt from 21.2 g (100 mmol) of ω,ω-di(methylmercapto)acetophenone was treated in THF solution with 13.4 ml of benzoyl chloride. After 25 min the solution was filtered and concentrated under vacuum; the residue was dissolved in 200 ml of chloroform and washed with 100 ml of aqueous saturated sodium bicarbonate. Removal of solvent left a yellow oil that crystallized from 95% ethanol to yield 29.4 g (93%) of product, as colorless crystals: mp 75°; pmr ($CDCl_3$) δ 2.19 (s, 3) and 2.28 (s, 3).

Anal. Calcd for $C_{17}H_{16}O_2S_2$: C, 64.55; H, 5.10; S, 20.63. Found: C, 64.66; H, 5.01; S, 20.44.

β,β-Di(methylmercapto)-α-acetoxystyrene.—Reaction of 50 mmol of the enolate of ω,ω-di(methylmercapto)acetophenone with 3.9 ml of acetyl chloride yielded 10.4 g of a nearly colorless oil that distilled at 127–129° (0.35 Torr): pmr ($CDCl_3$) δ 2.13 (s, 3) and 2.30 (s, 3), 2.16 (s, 3).

Anal. Calcd for $C_{12}H_{14}O_2S_2$: C, 56.69; H, 5.55; S, 25.17. Found: C, 56.44; H, 5.71; S, 25.25.

ω,ω-Di(methylmercapto)-ω-succiniminoacetophenone.—The methyl mercaptal of phenylglyoxal (5.3 g, 25 mmol) was converted to the anion with 1 equiv of sodium hydride in 250 ml of THF. To this solution was added 4.45 g of N-bromosuccinimide dispersed in 50 ml of THF at 0°. The reaction mixture was stirred for 3 hr under a nitrogen atmosphere and poured into 300 ml of water and the aqueous solution extracted with four 100-ml portions of ether. The ether extracts were washed, dried ($MgSO_4$), and concentrated to a residue that crystallized from hexane (50%)–ethyl acetate (50%) to give 6.8 g (87.5%) of product: mp 154–155°; pmr ($CDCl_3$) δ 2.08 (s, 6), 2.64 (s, 4), 7.28–7.56 (m, 3), 7.98–8.18 (m, 2); mass spectrum (70 eV) *m/e* (rel intensity) 309 (16), 262 (28), 204 (150), 158 (20), 105 (95).

Anal. Calcd for $C_{14}H_{15}O_3S_2N$ (309.27): C, 54.37; H, 4.89; S, 20.70. Found: C, 54.21; H, 4.81; S, 20.63.

ω,ω,ω-Tri(methylmercapto)acetophenone.—The ester of orthophenyltrithioglyoxylic acid was prepared from triply distilled methanesulfenyl chloride.[23] The methyl mercaptal of phenylglyoxal (42.4 g, 200 mmol) in 220 ml of THF was added to 10 g of sodium hydride suspended in 1 l. of ether. After the evolution of hydrogen had ceased the solution was cooled to 0° and 19 g (230 mmol) of methanesulfenyl chloride in 50 ml of ether added. The reaction mixture was stirred and allowed to come to room temperature and then poured into 500 ml of 0.01 *N* hydrochloric acid. The ether fraction was washed, dried ($MgSO_4$), and concentrated. Distillation yielded 36.8 g (71%) of the desired product: bp 129–130° (0.05 Torr); pmr ($CDCl_3$) δ 2.01 (s, 9), 7.17–7.55 (m, 3), 8.30–8.50 (m, 2).

Anal. Calcd for $C_{11}H_{14}OS_3$: C, 51.16; H, 5.47; S, 37.17. Found: C, 51.24; H, 5.67; S, 37.14.

S-Methyl Phenylthioglyoxylate from ω,ω,ω-Tri(methylmercapto)acetophenone.—To the ortho trithio ester (6.4 g, 24.8 mmol) dissolved in 150 ml of ether were added 5 g of sodium bicarbonate, 50 ml of water, and 6.3 g (1 equiv) of iodine. The mixture was stirred under reflux for 7 hr whence the iodine color disappeared. The cooled etheral solution was washed with 100 ml of 0.5% sodium bisulfite, dried ($MgSO_4$), and distilled to yield 4.21 g (94.5%) of S-methyl phenylthioglyoxylate, bp 92–94° (0.1 Torr). The distillate solidified upon standing and was recrystallized from ethanol to yield 3.7 g of needles, mp 39.0–40.5°.

S-Methyl Phenylthioglyoxylate from the Methylmercaptal of Phenylglyoxal.—The mercaptal of phenylglyoxal (5.30 g, 25 mmol) was converted to the enolate anion by 1 equiv of sodium hydride in 250 ml of THF under nitrogen. At 0° 4 g (~1.4 ml) of bromine was injected by syringe directly into the stirred solution followed by the immediate addition of 20 ml of water. After 30 min the reaction mixture was diluted with 300 ml of water and extracted with three 100-ml portions of ether. The ether extracts were dried ($MgSO_4$) and distilled to yield 2.43 g (54%) of the thio ester, bp 91–93° (0.1 Torr).

Ethyl Phenylglyoxylate.—ω,ω,ω-Tri(methylmercapto)acetophenone (4.40 g, 17 mmol) was dissolved in 100 ml of ether to which were added 6.55 g of iodine (1.5 equiv), 35 ml of ethanol, 50 ml of water, and 5.5 g of sodium bicarbonate. After stirring and refluxing for 6 hr, the iodine color disappeared. The cooled ethereal layer was diluted with 100 ml of ether and washed with 100 ml of 0.5% aqueous sodium bisulfite. After drying, distillation yielded 2.05 g (67.5%) of an oil, bp 71–72° (0.1 Torr). In a similar fashion **methyl phenylglyoxylate** was prepared in 52% yield, bp 70–72° (0.3 Torr).

1,2-Di(methylmercapto)-1,2-dibenzoylethylene from the Methyl Mercaptal of Phenylglyoxal.—The mercaptal (4.20 g, 22 mmol) was converted to its anion with 1 equiv of sodium hydride in 220 ml of THF. After the evolution of hydrogen had ceased the reaction product was cooled to 0° and 3.55 g of bromine added dropwise with vigorous stirring over a 5-min period. The reaction product was stirred for 3 hr at 25° and then quenched with 300 ml of water. Extraction with three 100-ml portions of ether yielded an oily residue that crystallized from hexane (95%)–ethyl acetate (5%) to yield 3.10 g of crystals (86%), mp 147–157°. Leaching the crystals with hexane left a crystalline residue that was recrystallized from hexane (50%)–ethyl acetate (50%) to yield 0.54 of crystals, mp 168–171°, assigned the *cis* structure: pmr ($CDCl_3$) δ 1.98 (s); mass spectrum (70 eV) *m/e* (rel intensity) 328 (85), 313 (10), 223 (5), 105 (100), m* 298.1 (328 → 313).

Anal. Calcd for $C_{18}H_{16}O_2S_2$ (328.31): C, 65.85; H, 4.91; S, 19.30. Found: C, 65.94; H, 5.02; S, 19.48.

The material, mp 168–171°, reacted readily with hydrazine in acetic acid[24] to yield the pyridazine: mp 150–152°; mass spectrum (70 eV), *m/e* 324; pmr δ 2.26 (s, 6), 7.3–7.6 (m, 10).

The hexane extract from the original *cis–trans* mixture was concentrated and crystallized to yield 2.30 g of bright yellow crystals: mp 69.0–70.5°; pmr δ 2.13 (s, 3); mass spectrum (70 eV), identical with that of the *cis* isomer. The product of mp 69.0–70.5 was assigned the *trans* structure. It yielded only traces of the pyridazine after refluxing 4 days with hydrazine in acetic acid.

Anal. Calcd for $C_{18}H_{16}O_2S_2$: C, 65.85; H, 4.91; S, 19.30. Found: C, 65.93; H, 5.10; S, 19.47.

1,2-Di(methylmercapto)-1,2-dibenzoylethylene by Pyrolysis of ω-Chloro-ω-(methylmercapto)acetophenone.—The crude product resulting from the reaction of 4.55 g (20 mmol) of ω-(methylsulfinyl)acetophenone with 1 equiv of thionyl chloride was heated in a 100-ml flask equipped with a condenser and swept with nitrogen. After 12 hr at 190–200° the escaping nitrogen was free of acidic vapors. The residue was cooled and dissolved in 100 ml of chloroform. The chloroform solution was washed with aqueous sodium bicarbonate, dried ($MgSO_4$), and concentrated. The residue was crystallized from hexane (50%)–ethyl acetate (50%) to yield 2.94 g (72%) of bright yellow crystals, mp 152–158°, which were fractionated as described previously to give 1.69 of the *cis* isomer, mp 168–170°, and 0.98 g of the *trans* product, mp 66–67°.

Methyl Orthotrithiomandelate.—Methyl orthophenyltrithioglyoxylate (1.58 g) was dissolved in 50 ml of 95% ethanol. To this solution was added 5 ml of water and 0.24 g of sodium borohydride. After 7 hr, the reaction mixture was treated with 100 ml of saturated aqueous ammonium chloride, extracted with three 50-ml portions of ether, and dried ($MgSO_4$) and the solvent removed under vacuum to yield 1.54 g (96%) of the thiomandelate ester: pmr ($CDCl_3$) δ 2.00 (s, 9, SC**H**$_3$), 4.81–4.88 (d, 1, C**H**OH, *J* = 4.2 Hz), 3.47–3.54 (d, 1, CHO**H**, exchanged in D_2O), 7.19–7.68 (m, 5, C$_6$**H**$_5$).

Anal. Calcd for $C_{11}H_{16}OS_3$: C, 50.77; H, 6.20; S, 36.89. Found: C, 50.49; H, 6.42; S, 36.97.

S-Methyl Thiomandelate.—Methyl orthotrithiomandelate (6.5 g, 25 mmol) was dissolved in 200 ml of water containing 5.35 g of ammonium chloride and 1 ml of concentrated hydrochloric acid. The solution was vigorously agitated by an air stream from a gas dispersion tube for 3 hr at 70°. The cooled solution was extracted with two 100-ml portions of ether and washed with 100 ml of saturated aqueous sodium bicarbonate. After drying ($MgSO_4$) the ether was evaporated under vacuum to leave a colorless oil which crystallized upon standing. Recrystallization from ethyl acetate (10%)–hexane (90%) yielded 3.26 g (71.5%)

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[23] Prepared by the method of H. Brintizinger, K. Pfaunstiet, H. Kodderburch, and K. Kling, *Chem. Ber.*, **83**, 87 (1950).

[24] G. O. Schenck, *ibid.*, **77**, 741 (1944).

of needles: mp 77–77.5°; pmr ($CDCl_3$) δ 2.17 (s, 3, SCH_3), 4.08 (s, 1, CHOH), 5.13 (s, 1, CHOH, D_2O exchanged), 7.16–7.48 (m, 5, C_6H_5).

Ethyl Mandelate.—Methyl orthotrithiomandelate (4.3 g, 16.5 mmol) was dissolved in 50 ml of 90% ethanol. To this solution was added 2.8 g of sodium bicarbonate and 16.5 mmol of iodine which was added slowly in small portions. After 1 hr at 25° the reaction product was concentrated under vacuum, diluted with 100 ml of water, and extracted twice with 100 ml of ether. The ether solution was dried ($MgSO_4$) and distilled to yield 1.74 g of ethyl mandelate (59%): bp 79–81° (0.25 Torr); pmr ($CDCl_3$) δ 1.13 and 4.24 (t, 3 and q, 2, J = 7.3 Hz, CH_3CH_2), 3.90 (s, 1, CHOH), 5.12 (s, 1, CHOH, D_2O exchanged), 7.17–7.55 (m, 5, C_6H_5).

Reduction of Keto Mercaptals and Acetals.—Reduction of 2-benzoyl-1,3-dithiolane with sodium borohydride in 95% ethanol at 25° yielded 1.83 g (86%) of **2-(α-hydroxybenzyl)-1,3-dithiolane** as an oil.

Anal. Calcd for $C_{10}H_{12}O_2S_2$: C, 56.60; H, 5.70; S, 30.16. Found: C, 56.76; H, 5.82; S, 30.11.

In a similar fashion 2-benzoyl-*m*-dithiane was reduced to **2-(α-hydroxybenzyl)-*m*-dithiane**, mp 70–72°, lit.[25] 70.5–71.6°. Reduction of the methyl acetal of phenylglyoxal by sodium borohydride in water yielded **1-phenyl-2,2-dimethoxyethanol**: bp 75–78° (0.25 Torr); pmr ($CDCl_3$) δ 3.20 (s, 6, OCH_3), 4.24–4.59 (m, 3, D_2O simplifies the spectrum to a q, 2, CH(OH)CH, J = 6.7 Hz), 7.15–7.47 (m, 5, C_6H_5).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.87; H, 7.58.

Registry No.—γ-Hydroxy-γ-phenylpropyl methyl sulfoxide, 21504-02-9; γ-hydroxy-γ-phenylpropyl methyl sulfone, 21504-03-0; ethanedithiol dimercaptal of phenylglyoxal, 21504-27-8; ethylene glycol diacetal of phenylglyoxal, 21504-04-1; ω-chloro-ω-(methylmercapto)acetophenone, 14755-55-6; methyl mercapto of phenylglyoxal, 17565-23-0; methyl acetal of phenylglyoxal, 6956-56-5; 2-benzoyl-*m*-dithiane, 21504-07-4; 2-benzoyl-1,3-dithiolane, 21504-08-5; 1-phenyl-2,2-di(methylmercapto)ethanol, 21504-10-9; 1,1-di(methylmercapto)-2-phenyl-2-propanol, 21504-09-6; 1,1-di(methylmercapto)-2-phenyl-2-butanol, 21504-11-0; 1,1-diphenyl-2,2-di(methylmercapto)ethanol, 21504-12-1; β,β-di(methylmercapto)-α-methoxystyrene, 21504-14-3; β,β-di(methylmercapto)-α-benzoyloxystyrene,2 1504-15-4; β,β-di(methylmercapto)-α-acetoxystyrene, 21504-16-5; ω,ω-di(methylmercapto)-ω-succiniminoacetophenone, 21504-17-6; ω,ω,ω-tri(methylmercapto)acetophenone, 21504-18-7; S-methyl phenylthioglyoxylate, 13603-60-6; ethyl phenylglyoxylate, 1603-79-8; 1,2-di(methylmercapto)-1,2-dibenzoylethylene (*cis*), 21537-94-0; 1,2-di(methylmercapto)-1,2-dibenzoylethylene (*cis*) (pyridazine derivative), 21504-21-2; 1,2-di(methylmercapto)-1,2-dibenzoylethylene (*trans*), 21517-43-1; methyl orthotrithiomandilate, 21504-22-3; S-methyl thiomandelate, 21504-28-9; ethyl mandelate, 774-40-3; 1-phenyl-2,2-dimethoxyethanol, 21504-23-4; ω-(methylsulfinyl)acetophenone, 2813-22-1.

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[25] E. J. Corey and D. Seeback, *Angew. Chem.*, **77**, 1134 (1966).

Notes

β-Keto Sulfoxides. VII. Conversion into γ- and δ-Keto Esters[1]

GLEN A. RUSSELL AND LEO A. OCHRYMOWYCZ

Department of Chemistry, Iowa State University, Ames, Iowa 50010

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A recent report by Nozaki, Mori, and Kawanisi on chain extensions by the use of β-keto sulfoxides[2] prompts us to report some similar observations. The reactions described by Nozaki, Mori, and Kawanisi and extended herein provide convenient three and four carbon chain extensions of aliphatic or aromatic esters (Scheme I).

ω-(Methylsulfinyl)acetophenone readily reacts in basic solution with ethyl bromoacetate and ethyl acrylate to yield γ- and δ-keto esters **2** and **3**. All attempts to carboxylate the enolate anion to form the β-keto ester **1** (*e.g.*, with carbon dioxide, ethyl chloroformate, methylmagnesium carbonate[3]) failed. Ethyl chloroformate gave reaction at the oxygen atom to yield **4**.

$C_6H_5COCH(SOCH_3)(CH_2)_xCO_2C_2H_5$

1, $x = 0$

2, $x = 1$

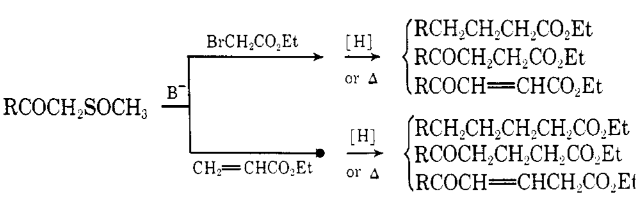
3, $x = 2$

$C_6H_5C(OCO_2C_2H_5){=}CHSOCH_3$

4

Compound **2** is easily reduced to yield ethyl ω-benzoylpropionate. The sulfoxide is easily pyrolyzed to ethyl *trans*-3-benzoylacrylic acid. Compound **3** undergoes similar reactions. Under more vigorous conditions, **3** can be reduced directly to ethyl ω-phenylvalerate.

SCHEME I



When an excess of ethyl acylate is employed in the condensation reaction, a further reaction product (**5**) between **3** and ethyl acrylate is observed in 59% yield.

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[1] For part VI, see G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **34**, 3618 (1969). This work was supported by a grant from the Army Office of Research (Durham).

[2] H. Nozaki, T. Mori, and M. Kawanisi, *Can. J. Chem.*, **46**, 3767 (1968).

[3] M. Stiles, *J. Amer. Chem. Soc.*, **81**, 2598 (1959); E. Szarvary, *Ber.*, **30**, 1836 (1897).