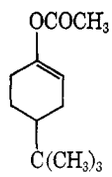
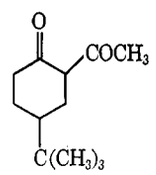
decalone, 150.9 min. The crude product contained **24** (6% yield), **49** (2% yield), **50** (44% yield), **51** (15% yield), and several higher boiling components. The corresponding reaction with 68.8 mg (0.31 mmol) of a silyl enol ether mixture (36% **25**, 59% **26**, and 5% **27**) yielded a crude product containing **24** (3% yield), **49** (7% yield), **50** (18% yield), **51** (32% yield), and several higher boiling peaks. Collected[25] samples of the enol acetate products were identified with authentic samples by comparison of infrared spectra and gas chromatographic retention times. The results of these transformations allow us to conclude that isomers **25** and **50** are stereochemically related as are **26** and **51**.

F. 4-*t*-Butylcyclohexanone Derivatives.—An authentic sample of the enol acetate **52** was available from previous studies.[27]



52



53

After reaction of 18.6 g (89.8 mmol) of the pyrrolidine enamine[27] of 4-*t*-butylcyclohexanone with 20.7 g (203 mmol) of acetic anhydride in 50 ml of dioxane at 25° for 24 hr, the solution was diluted with 10 ml of water, refluxed for 30 min, and concentrated. The residual liquid was partitioned between pentane and water, and the resulting organic phase was washed with aqueous NaCl, dried over Na_2SO_4, concentrated, and distilled in a short-path still (1.0–1.1 mm and 105–132° bath). The crude distillate (14.72 g of pale yellow oil, $n^{26}D$ 1.4942) was fractionally distilled to separate 7.93 g (45%) of the **diketone 53** as a colorless liquid: bp 99–100° (0.9–1.0 mm); $n^{26}D$ 1.4956; ir (CCl_4) 1610 cm^{-1} (broad, enolic β-diketone); uv (95% EtOH) 290 mμ (ε 9840); nmr (CCl_4) δ 1.1–2.6 (*ca.* 7 H multiplet, aliphatic CH), 2.08 (3 H singlet, vinylic or acetyl CH_3), and 0.93 [9 H singlet, $(CH_3)_3C$]; mass spectrum, molecular ion peak at *m/e* 196 with abundant fragment peaks at *m/e* 181, 139, 125, 57, 55, 43, and 41.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.14; H, 10.13.

After reaction for 1 hr of 2.7 mmol of methyllithium with 584.7 mg (2.58 mmol) of the silyl ether **6** in 10 ml of 1,2-dimethoxyethane containing several milligrams of triphenylmethane, the enolate solution was treated with *n*-tetradecane (as an internal standard) and quenched in acetic anhydride. Following the usual isolation procedure, the crude product was analyzed on a column[14] on which the retention times were, for **4**, 9.4 min; **52**, 22.2 min; *n*-tetradecane, 30.7 min; and **53**, 47.0 min. The crude product contained **4** (12% yield), **52** (63% yield), and **53** (12% yield). Collected[14] samples of the enol acetate **52**, and the diketone **53** were identified with authentic samples by comparison of infrared spectra and gas chromatographic retention times.

Registry No.—**5**, 6651-36-1; **6**, 19980-19-9; **9**, 13735-81-4; **10**, 17510-46-2; **12**, 19980-22-4; **13**, 19980-23-5; **15**, 19980-24-6; **16**, 19980-25-7; **18a**, 19980-26-8; **18b**, 6651-40-7; **19a**, 19980-27-9; **19b**, 19980-29-1; **20a**, 19980-30-4; **20b**, 19980-31-5; **22a**, 19980-32-6; **22b**, 19980-33-7; **23a**, 19980-34-8; **23b**, 19980-35-9; **25**, 19980-36-0; **26**, 19980-37-1; **27**, 19980-38-2; **29**, 19980-39-3; **31**, 19980-40-6; **32**, 19980-41-7; **33**, 19980-42-8; **35**, 19980-43-9; **41a**, 19980-44-0; **41c**, 15984-02-8; **42a**, 19980-46-2; **42c**, 15984-03-9; **44**, 19980-48-4; **45**, 19980-49-5; **53**, 19980-50-8.

(27) H. O. House, B. A. Tefertiller, and H. D. Olmstead, *J. Org. Chem.*, **33**, 935 (1968).

β-Keto Sulfoxides. IV. Conversion into β-Keto Sulfides, Vinyl Ethers, and Enol Acetates[1]

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β-Keto sulfoxides are reduced with sodium metabisulfite to β-keto sulfides. Alkylation of the β-keto sulfide followed by reduction, O methylation, and base-catalyzed elimination in dimethyl sulfoxide solution yields the enol ether. Acylation of the keto sulfides by sodium hydride followed by acetic anhydride gives the enol acetate. Similar treatment of β-keto sulfoxides yields either the enol acetate or the α-acetoxy β-keto sulfide. Reaction of the salt of a β-keto sulfoxide with methanesulfinyl chloride yields a sulfone sulfide rather than the expected disulfoxide. A sulfone sulfide is also produced from the reaction of the enolate anion of acetylacetone or dibenzoylmethane with two molecules of methanesulfinyl chloride. The formation of the sulfone sulfide is pictured as a base-catalyzed modification of the Pummerer reaction.

This paper reports some of our continuing studies of the synthetic utility of β-keto sulfoxides. Such β-keto sulfoxides can be readily prepared by the condensation of esters with the methylsulfinyl carbanion ($CH_3SOCH_2^-$).[2,3] β-Keto sulfoxides will undergo monoalkylation reactions in basic solution.[4,5] In addition a variety of other products still containing one sulfur atom can be formed from the β-keto sulfoxides.[6] We have already described the conversions illustrated in reactions 1–4.[2,4,6] In the present work we describe reactions 5 and 6 and give one illustration of reaction 7.

$$RCO_2R' + CH_3SCOH_2^- \longrightarrow$$

$$RCOCH_2SOCH_3 \xrightarrow[CH_3I]{B^-} RCOCH(CH_3)SOCH_3$$

$$RCOCH_2SOCH_3 \longrightarrow \begin{cases} \xrightarrow{H_3O^+} RCOCH(OH)SCH_3 & (1) \\ \xrightarrow{NaBH_4} RCH(OH)CH_2SOCH_3 & (2) \\ \xrightarrow{LiAlH_4} RCH(OH)CH_2SCH_3 & (3) \\ \xrightarrow{B^-,\ Cl_2} RCOCH(Cl)SOCH_3 & (4) \\ \xrightarrow{Na_2S_2O_5} RCOCH_2SCH_3 & (5) \\ \xrightarrow[CH_3SOCl]{B^-,} RCOCH(SCH_3)SO_2CH_3 & (6) \\ \xrightarrow[(CH_3CO)_2O]{B^-,} RC(O_2CCH_3)=C(CH_3)SOCH_3 & (7) \end{cases}$$

(1) This work was supported by the Army Office of Research (Durham). For part III, see G. A. Russell and G. J. Mikol, *J. Amer. Chem. Soc.*, **88**, 5498 (1966).

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

(3) E. J. Corey and M. J. Chaykovsky, *ibid.*, **86**, 1639 (1964); 1345 (1965).

(4) G. A. Russell and G. J. Mikol, *ibid.*, **88**, 5498 (1966).

(5) P. G. Gassman and G. O. Richmond, *J. Org. Chem.*, **31**, 2355 (1966).

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

We had previously attempted to prepare vinyl ethers from β-hydroxy sulfoxides.[4] However, basic or thermal elimination reaction of β-methoxy sulfoxides yielded the vinyl sulfoxides or the ketone (Scheme I).

SCHEME I

$$RCH(OH)CH_2SOCH_3 \xrightarrow[CH_3I]{B^-}$$

$$RCH(OCH_3)CH_2SOCH_3 \begin{cases} \xrightarrow{B^-} RCH{=}CHSOCH_3 + CH_3OH \\ \xrightarrow{\Delta} RCOCH_3 + CH_3SOH \end{cases}$$

We now have found that the base-catalyzed elimination of β-methoxy sulfides in dimethyl sulfoxide (DMSO) solution yields the vinyl ether. Since the β-keto sulfide can be mono- or dialkylated, a variety of vinyl ethers can be readily prepared from the β-keto sulfide after reduction and etherification.

Results and Discussion

Selective reduction of the sulfoxide group of ω-(methylsulfinyl)acetophenone was achieved by the use of sodium metabisulfite ($Na_2S_2O_5$) in aqueous solution at 90° for 20 hr.[7] In Table I some typical yields of sulfides are given. The reaction is clean and no impurities were detected in the crude products by proton magnetic resonance (pmr).

TABLE I
SODIUM METABISULFITE REDUCTIONS[a]

Substrate	Product	% yield
$C_6H_5COCH_2SOCH_3$	$C_6H_5COCH_2SCH_3$	52
$C_6H_5CH(OH)CH_2SOCH_3$	$C_6H_5CH(OH)CH_2SCH_3$	93
$C_6H_5CH(OCH_3)CH_2SOCH_3$	$C_6H_5CH(OCH_3)CH_2SCH_3$	80
$C_6H_5CH{=}CHSOCH_3$	$C_6H_5CH{=}CHSCH_3$	66
$C_6H_5CH(O_2CCH_3)CH_2SOCH_3$	$C_6H_5CH(O_2CCH_3)CH_2SCH_3$	89

[a] Sodium metabisulfite (10 g) in 25 ml of water/g of sulfoxide, 20 hr at 90°.

The β-methoxy sulfides (**1**) of Table II were prepared from the β-keto sulfides by reduction with sodium borohydride followed by methylation of the sodium salt

TABLE II
PREPARATION OF ENOL ETHERS BY BASE-CATALYZED ELIMINATION OF 1

	Substituents				Yield, %	
Compd	R_1	R_2	R_3	R_4	2	3
1a	C_6H_5	H	H	CH_3	56	16
1b	C_6H_5	CH_3	H	CH_3	43	Nil
1c	C_6H_5	CH_3	CH_3	CH_3	Nil	...
1d	C_6H_5	H	H	C_6H_5	49	15
1e	C_6H_5	CH_3	H	C_6H_5	64	Nil
1f	C_6H_5	CH_3	CH_3	C_6H_5	82	...

of the β-hydroxy sulfide by methyl iodide in tetrahydrofuran (THF) solution. The major elimination product of the β-methoxy sulfides were the vinyl ethers (**2**) accompanied by small amounts of the vinyl sulfides (**3**) when $R_2 = R_3 = H$.

(7) Thianthrone sulfoxide has been selectively reduced by sodium borohydride–sodium hydroxide [A. L. Ternay, Jr., and P. W. Chaser, *J. Org. Chem.*, **32**, 3814 (1967)]. The sodium metabisulfite reduction of methionine sulfoxide has been reported [F. Michael and H. Schmitz, *Chem. Ber.*, **72**, 992 (1939)].

$$\underset{1}{R_1CH(OCH_3)CR_2R_3SR_4} \xrightarrow[70\text{–}75°]{t\text{-BuOK/DMSO}}$$

$$\underset{2}{R_1C(OCH_3){=}CR_2R_3} + \underset{3}{R_1CH{=}CR_2SR_4}$$

Another reaction of the β-keto sulfide that we investigated was the conversion into the enol acetate (reaction 8) **4**.[8] Attempts to prepare **4** from the vinyl sulfoxide (**5**) (readily available by the oxidation of the sulfide **3a**

$$C_6H_5COCH_2SCH_3 \xrightarrow[2.\ (CH_3CO)_2O]{1.\ NaH,\ THF}$$

$$\underset{4}{C_6H_5C(O_2CCH_3){=}CHSCH_3} \quad (8)$$

with sodium periodate[6]) led to the normal Pummerer rearrangement product, **6**. We had expected that **4** might be a product by analogy with the formation of **7** from **5** and thionyl chloride (Scheme II).[6]

SCHEME II

$$\underset{5}{C_6H_5CH{=}CHSOCH_3} \begin{cases} \xrightarrow{(CH_3CO)_2O} \not\rightarrow\ 4 \\ \xrightarrow{(CH_3CO)_2O} \underset{6}{C_6H_5CH{=}CHSCH_2(O_2CCH_3)} \\ \xrightarrow{SOCl_2} \underset{7}{C_6H_5C(Cl){=}CHSCH_3} \end{cases}$$

When the salt of a β-keto sulfoxide is treated with acetic anhydride either a Pummerer-type rearrangement (reaction 9) or O acylation (reaction 10) occurs.

$$RCOCH_2SOCH_3 \xrightarrow[2.\ (CH_3CO)_2O]{1.\ NaH,\ THF} RCOCH(O_2CCH_3)SCH_3 \quad (9)$$

8a, R = phenyl
b, R = cyclohexyl

$$C_6H_5COCH(CH_3)SOCH_3 \xrightarrow[2.\ (CH_3CO)_2O]{1.\ NaH,\ THF}$$

$$\underset{9}{C_6H_5C(O_2CCH_3){=}C(CH_3)SOCH_3} \quad (10)$$

a and intermediate **10** (Scheme III).[9] Apparently

SCHEME III

$$RCOCH_2SOCH_3 \begin{cases} \xrightarrow[\text{path } a]{(CH_3CO)_2O} [RCOCH_2S(O_2CCH_3)CH_3]^+ \xrightarrow{-H^+} \\ \xrightarrow[\text{path } b]{\text{NaH, THF}} RCO\bar{C}HSOCH_3 \end{cases} \underset{10}{[RCO\bar{C}H\overset{+}{S}(O_2CCH_3)CH_3][CH_3CO_2^-]} \xrightarrow{(CH_3CO)_2O} 8$$

The classical Pummerer rearrangement occurs *via* path intermediate **10** can be formed by path b as well. Path b represents a base-catalyzed analog Pummerer reaction. Since monoalkylated β-keto sulfoxides are not prone to undergo the Pummerer reaction[2,4] the formation of **8** and **9** from the respective β-keto sulfoxides can be rationalized.

Methanesulfinyl chloride was found to react with β-keto sulfoxides in a manner similar to acetic anhydride or acetyl chloride.[10] In the absence of base the

(8) β-Keto sulfones also give O acylation [N. M. Carroll and W. I. O'Sullivan, *J. Org. Chem.*, **30**, 2830 (1965).

(9) G. A. Russell and G. J. Mikol, "Mechanisms of Molecular Migrations," B. S. Thyagarajan, Ed., Vol. I, Interscience Publishers, New York, N.Y., 1968, p 157.

(10) F. G. Bordwell and B. M. Pitts, *J. Amer. Chem. Soc.*, **77**, 574 (1955).

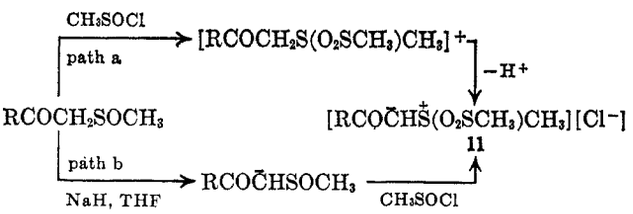
α-chloro-β-keto sulfide (reaction 11) resulted, while the reaction in the presence of base yielded the sulfonyl fulfide (reaction 12). It seems reasonable that the

$$C_6H_5COCH_2SOCH_3 + CH_3SOCl \longrightarrow C_6H_5COCH(Cl)SCH_3 \quad (11)$$

$$C_6H_5COCH_2SOCH_3 \xrightarrow[2.\ CH_3SOCl]{1.\ NaH,\ THF} C_6H_5COCH(SO_2CH_3)SCH_3 \quad (12)$$

products of reactions 11 and 12 could result from the common intermediate shown in Scheme IV. In the

SCHEME IV



absence of base, intermediate **11** yields the products of reaction 11 *via* process 11a. In the presence of base the process 12a would occur.

$$11 \xrightarrow{H^+} CH_3SO_2H + [RCOCH{=}SCH_3]^+Cl^- \longrightarrow RCOCH(Cl)SCH_3 \quad (11a)$$

$$11 \longrightarrow CH_3SO_2^- + Cl^- + [RCOCH{=}SCH_3]^+ \longrightarrow RCOCH(O_2SCH_3)SCH_3 \quad (12a)$$

The observation of reaction 12 explains a surprising result that we had observed previously. Compound **12** is a potential precursor for a 1,2,3 triketone.[11] Al-

$$\underset{12}{(RCO)_2CHSOCH_3} \xrightarrow{H^+} RCOCOCOR + CH_3SH$$

though methanesulfonyl chloride reacts readily with the anion of a β diketone to yield a diacyl(methylsulfonyl)-methane,[12] the reaction of methanesulfinyl chloride with the enolate anion of 2,4-pentanedione or bibenzoylmethane led to the sulfonyl sulfides, **13a** and **13b**. The reaction appears to be analogous to reaction 12 and involves a Pummerer-type reaction of intermediate **12**.[12a]

$$(RCO)_3CH^- + CH_3SOCl \longrightarrow (RCO)_2CHSOCH_3 \longrightarrow [(RCO)_2CSOCH_3]^- \xrightarrow{CH_3SOCl} (RCO_2)C(O_2SCH_3)SCH_3$$

13a, R = CH_3
b, R = C_6H_5

Experimental Section

Sodium Metabisulfite Reduction.—The reactants were dissolved in water and heated to approximately 90° with stirring for 24 hr. For every gram of sulfoxide to be reduced, 10 g of sodium metabisulfite and 25 ml of water were used. At the end of the reaction period the mixture was cooled and extracted thoroughly with ether. The extracts were dried over magnesium sulfate and filtered. Removal of the solvent gave the sulfide, usually in a high state of purity. The infrared (ir) and pmr spectra of the reduction products were identical with those of materials previously produced by independent synthesis.[6]

Preparation of β-Methoxy Sulfides.—The analogous β-hydroxy sulfides were O methylated using sodium hydride and methyl iodide in THF as previously described.[6] The β-hydroxy sulfides were prepared from β-keto sulfoxides and sulfides by alkylation,[4,6] followed by either lithium aluminum hydride reduction for sulfoxides[4,6] or sodium borohydride reduction for sulfides.[6] The crude β-methoxy sulfides were allowed to react without extensive purification.

Preparation of Enol Ethers.—The β-methoxy sulfide in DMSO solution (*ca.* 1 g/5 ml) was placed in a flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet and outlet. An excess of potassium *t*-butoxide was added and the temperature raised to 70–75°. The reaction time for phenyl sulfides was 5 hr. For methyl sulfides reaction times of 12–24 hr were required. After reaction the mixture was cooled and poured into ice water. After extraction with ether, the extracts were washed with water and dried over magnesium sulfate. Removal of the solvent gave the crude product from which the enol ether was distilled. The pot residue was chromatographed on silica gel to obtain the unsaturated sulfide if the pmr of the crude product indicated its presence.

α-Methoxystyrene (2a–d) had bp 50–51° (2 mm) [lit.[13] bp 30–32° (0.4 mm)]. The spectra of **3a** were identical with those of material produced by the sodium metabisulfite reduction of ω-(methylsulfinyl)styrene.[6]

α-Methoxy-β-methylstyrene (2b–e) had bp 56–57° (2 mm) [lit.[14] bp 96–98° (19 mm)]. The spectra were consistent with a mixture of *cis* and *trans* isomers: pmr (CCl_4) δ 1.67 and 1.74 (doublets, 3 total, J = 7 Hz), 3.45 and 3.54 (singlets, 3 total), 4.69 and 5.22 (quartets, total 1), 7.0–7.5 (m, 5).

β-(Phenylmercapto)styrene (3d) was identified by oxidation to the known sulfone, mp 73–74° [lit.[15] mp 74.0–74.5°].

α-Methoxy-β,β-dimethylstyrene (2f) had bp 59–60° (2 mm); ir (CCl_4) 1661 cm^{-1} (C=C); pmr (CCl_4) δ 1.60 (s, 3), 1.79 (s, 3), 3.20 (s, 3), 7.21 (s, 3); mass spectrum (70 eV), molecular ion at m/e 162.

The enol ethers hydrolyzed in the presence of aqueous acid to the corresponding ketones.

α-Acetoxy-β-(methylmercapto)styrene (4).—ω-(Methylmercapto)acetophenone[6] (4.15 g, 25 mmol), in 100 ml of THF was added to a well-stirred slurry of 0.60 g of sodium hydride (25 mmol) in 50 ml of THF. After the evolution of hydrogen had ceased, 2.55 g (25 mmol) of acetic anhydride was added dropwise and the mixture was stirred at room temperature for 2 hr, quenched with water, and extracted with chloroform. After the extracts were dried over sodium sulfate, the solvent was removed to give 4.92 g (92%) of **4**: mp 55–56°; ir (CCl_4) 1767 (C=O), 1190 cm^{-1} (C—O); pmr δ 2.23 (s, 3), 2.30 (s, 3), 6.31 (s, 1), 7.26 (s, 5).

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.45; H, 5.81; S, 15.37. Found: C, 63.62; H, 5.82; S, 15.35.

Acetoxymethyl β-Styryl Sulfide (6).—A solution of β-(methylsulfinyl)styrene (**5**, 4.15 g, 25 mmol) in 20 ml of acetic anhydride was heated on a steam bath for 12 hr. The mixture was cooled and added cautiously to a saturated solution of sodium bicarbonate. When the reaction had ceased, the mixture was extracted with chloroform. The extracts were dried over magnesium sulfate. Removal of the solvent distillation under reduced pressure gave **6** (4.78 g, 92%) as a colorless liquid: bp 94–95° (0.08 mm); ir (CCl_4) 1751 (C=O), 1192 cm^{-1} (C—O); pmr δ 1.98 (s, 3), 5.22 (s, 2), 6.53 and 6.77 (AB quartet, 2, J = 15.5 Hz), 7.18 (s, 5).

Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.45; H, 5.81; S, 15.37. Found: C, 63.40; H, 5.84; S, 15.38.

Reaction of Acetic Anhydride with Salts of β-Keto Sulfoxides.—ω-(Methylsulfinyl)acetophenone (9.1 g, 50 mmol) was subjected to the action of 1.2 g of sodium hydride (50 mmol) and 5.1 g of acetic anhydride (50 mmol) according to the procedure employed in the preparation of **4**. Distillation of the isolated product yielded 8.35 g (75%) of **ω-acetoxy-ω-(methylmercapto)acetophenone (8a)**, bp 98–100° (0.1 mm). The product had identical spectral properties with those of **8a** prepared by the Pummerer rearrangement of ω-(methylsulfinyl)acetophenone by acetic anhydride in the presence of pyridine.[2] In a similar manner the cyclohexyl derivative (4.6 g, 25 mmol), when treated with sodium hydride (25 mmol) followed by acetic anhydride (25 mmol), yielded 4.05 g (71%) of **8b**, bp 105–109 (0.5 mm).

Treatment of 4.90 g (25 mmol) of ω-methyl-ω-(methylsulfinyl)-acetophenone[1] with 0.6 g (25 mmol) of sodium hydride followed

(11) H.-D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1896 (1963).

(12) H. Böhme and H. Fischer, *Chem. Ber.*, **76**, 99 (1943).

(12a) NOTE ADDED IN PROOF.—We have now succeeded in preparing **12** by the addition of a solution of the enolate anion to methanesulfinyl chloride. As expected **12** is readily converted into the triketone.

(13) S. I. Miller, *J. Amer. Chem. Soc.*, **78**, 6091 (1956).

(14) W. M. Lauer and M. A. Spielman, *ibid.*, **53**, 1533 (1931).

(15) M. Balasubramian and V. Baliak, *J. Chem. Soc.*, 1844 (1954).

by 2.55 g (25 mmol) of acetic anhydride yielded 5.55 g of a yellow oil which hydrolyzed readily to yield the starting keto sulfoxide. The spectra of the oil indicated predominant O alkylation: ir ($CHCl_3$) 1770 (C=O), 1200 (C—O), 1047 cm^{-1} (SO).

ω-(Methylmercapto)-ω-(methylsulfonyl)acetophenone.—A solution of 9.1 g (50 mmol) of ω-(methylsulfinyl)acetophenone in 150 ml of THF was added with stirring to a suspension of 1.2 g of sodium hydride (50 mmol) in 25 ml of THF. After the evolution of hydrogen ceased, 5.0 g (51 mmol) of methanesulfinyl chloride[16] was added dropwise. The mixture was stirred for 1 hr and then poured into 300 ml of water. Extraction with chloroform followed by drying over magnesium sulfate and evaporation of the solvent gave 9.15 g (75%) of product: mp 100–111° (recrystallization from chloroform–ether gave mp 115–117°); ir ($CHCl_3$) 1675 (C=O), 1307 and 1110 cm^{-1} (SO_2); pmr ($CDCl_3$) δ 2.47 (s, 3), 3.23 (s, 3), 5.36 (s, 1), 7.4–7.7 (m, 3), 7.9–8.1 (m, 2).

Anal. Calcd for $C_{10}H_{12}O_3S_2$: C, 49.18; H, 4.95; S, 26.21. Found: C, 49.06; H, 4.91; S, 26.15.

Pummerer Rearrangement of ω-(Methylsulfinyl)acetophenone to Yield ω-Chloro-ω-(methylmercapto)acetophenone.—Treatment of 3.64 g (19 mmol) of the keto sulfoxide with 1.86 g (19 mmol) of methanesulfinyl chloride yielded 3.47 g (87%) of ω-chloro-ω-(methylmercapto)acetophenone: bp 108 (2 mm); pmr δ 2.18 (s, 3), 6.40 (s, 1). Identical material was formed by the reaction of the β-keto sulfoxide with thionyl chloride or by the reaction of phenylglyoxal hemimercaptal with thionyl chloride.[17]

(16) I. B. Douglas and D. R. Poole, *J. Org. Chem.*, **32**, 536 (1957); I. B. Douglas and B. S. Farsh, *ibid.*, **33**, 330 (1958).

(17) Unpublished results with L. A. Ochrymowycz.

3-(Methylmercapto)-3-(methylsulfonyl)-2,4-pentanedione (13a).—2,4-Pentanedione (10 g, 0.1 mol) in 100 ml of THF was added dropwise to a suspension of 2.4 g (0.1 mol) of sodium hydride in 25 ml of THF. After the evolution of hydrogen had ceased, 9.8 g (0.1 mol) of methanesulfinyl chloride was added cautiously. The mixture was stirred for 2 hr at 25° before dilution with 400 ml of water. Extraction with chloroform followed by drying over magnesium sulfate and evaporation of the solvent left 11.6 g of a yellow paste which could be recrystallized from chloroform–ether to give 7.0 g of **13a** (62%): mp 102.5–104°; ir 1721 (C=O), 1316 and 1130 cm^{-1} (SO_2); pmr ($CHCl_3$) δ 2.29 (s, 3), 2.41 (s, 6), 3.10 (s, 3).

Anal. Calcd for $C_7H_{12}O_4S_2$: C, 37.50; H, 5.40; S, 28.55. Found: C, 37.35; H, 5.41; S, 28.85.

Dibenzoyl(methylmercapto)(methylsulfonyl)methane (13b).—Substitution of 4.48 g (20 mmol) of dibenzoylmethane, 0.5 g (21 mmol) of sodium hydride, and 2.0 g (20 mmol) of methanesulfinyl chloride in the procedure used for the preparation of **13a** resulted in the formation (1.9 g, 56%) of **13b**: mp 143–144°; ir ($CHCl_3$) 1721 (C=O), 1316 and 1130 cm^{-1} (SO_2); pmr ($CDCl_3$) δ 2.20 (s, 3), 3.21 (s, 3), 7.2–7.6 (m, 6), 7.8–8.2 (m, 4).

Anal. Calcd for $C_{17}H_{16}O_4S_2$: C, 58.62; H, 4.63; S, 18.32. Found: C, 58.33; H, 4.71; S, 18.14.

Registry No.—**4**, 19916-60-0; **6**, 19916-61-1; C_6H_5CO-$CH(SCH_3)SO_2CH_3$, 19916-62-2; **13a**, 19916-63-3; **13b**, 19916-64-4.

β-Keto Sulfoxides. V. Condensation of Dimethyl Sulfoxide and Dimethyl Sulfone with Dibasic Esters[1]

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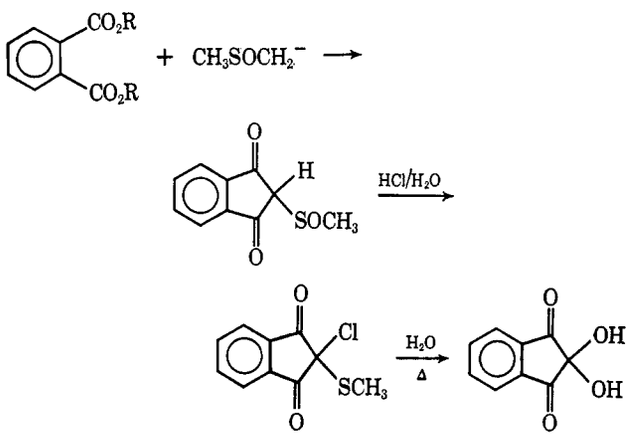
A new condensation reaction between two molecules of the methylsulfonyl carbanion ($CH_3SO_2CH_2^-$) or the methylsulfinyl carbanion ($CH_3SOCH_2^-$) and a variety of 1,2- 1,3- and 1,4-dicarboxylic esters is described. In favorable cases the condensation proceeds to yield an unsaturated monoketo disulfoxide or disulfone containing a new five-, six-, or seven-membered ring. Desulfurization of the disulfoxides and disulfones using Raney nickel has been investigated.

The condensation of esters of phthalic acid with the methylsulfinyl carbanion ($CH_3SOCH_2^-$) have been described.[2,3] 2-(Methylsulfinyl)-1,3-indandione is readily formed when the ester is added to a solution of sodium methoxide in dimethyl sulfoxide (DMSO). The methylsulfinylindandione was readily converted into ninhydrin *via* treatment with hydrochloric acid and hydrolysis of the resulting 2-chloro-2-(methylmercapto)-1,3-indandione (Scheme I). In dimethylformamide solution containing potassium *t*-butoxide a low yield of 2-(methylsulfonyl)-1,3-indandione was obtained from the reaction of ethyl phthalate with dimethyl sulfone ($DMSO_2$).[4]

Two other types of condensation can be imagined in the reaction of a dialkyl sulfoxide or dialkyl sulfone with the ester of a dibasic acid (paths b and c, Scheme II). We herein describe a study of a variety of reaction parameters of the nature of the condensation reaction between esters of dibasic acids and DMSO and $DMSO_2$. Our results are consistent with the expectation that the concentration of the carbanion is important in determining whether the product of process a or process b is formed.

SCHEME I



A "low" concentration of the methylsulfinyl or methylsulfonyl carbanion was presumably involved in the previous work wherein the carbanions were generated by an acid–base equilibrium. In the present work we have also approached a low concentration of the carbanion by the dropwise addition of the irreversibly

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(3) H.-D. Becker, *J. Org. Chem.*, **29**, 1358 (1964).

(4) H.-D. Becker and G. A. Russell, *ibid.*, **28**, 1896 (1963).