7.0 g (53%) of needles: mp 161–162°, lit.[27] 162°; nmr ($CDCl_3$) δ 7.30 (s, 5 H), 4.11 (s, 2 H), 2.65 (s, 4 H) ppm; ν_{max}^{KBr} 2920, 2850, 1720, 1555, 1490, 1419, 1305, 1148, 765, and 713 cm^{-1}.

N-Benzylsuccinimide.—This compound was prepared according to the procedure of Argoria.[28]

Chlorination of Benzyl Sulfide with NCS in the Presence of Deuterium Chloride.—A 15-ml round-bottomed flask equipped with magnetic stirrer was charged with 214 mg (1 mmol) of benzyl sulfide in 4.8 ml of carbon tetrachloride. Into this solution kept at 35° was bubbled a stream of dry deuterium chloride at a rate of one bubble every 10 sec. A 134-mg (1 mmol) portion of solid NCS was then added, and the resulting mixture was continuously stirred under deuterium chloride flow. Nmr analyses of the filtrate after 30 min of reaction showed four peaks for the methylene protons at δ 219, 232.5, 236.5, and 250 Hz downfield from TMS. There were no detectable signals at δ 243.8 and 228.85 Hz as evidenced by expanding this area at 50-Hz sweep width.

(27) W. Tagaki, K. Kikukawa, K. Ando, and S. Oae, *Chem. Ind. (London)*, **38**, 1624 (1964).

(28) A. Argoria, J. Barassi, and H. Lumbroso, *Bull. Soc. Chim. Fr.*, 2509 (1963).

Registry No.—Benzyl sulfide, 538-74-9.

Acknowledgment.—We wish to thank the donors of the Petroleum Research Fund of the American Chemical Society for support of this work.

β-Keto Sulfoxides. X. Conversion of Cycloalkanecarboxylic Esters to 1-Cycloalkylpropane-1,2-diones[1]

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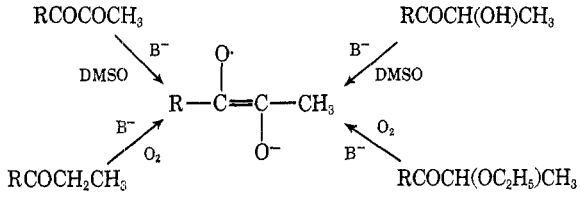
The conversion of cycloalkylcarboxylic esters to cycloalkyl keto sulfoxides ($RCOCH_2SOCH_3$) and hence to α diketones ($RCOCOCH_3$), cycloalkyl ethyl ketones ($RCOCH_2CH_3$), cycloalkyl vinyl ketones [$RCOCH{=}CH_2$, $RCOC(CH_3){=}CH_2$], and α-ethoxy ketones [$RCOCH(OC_2H_5)CH_3$] is described.

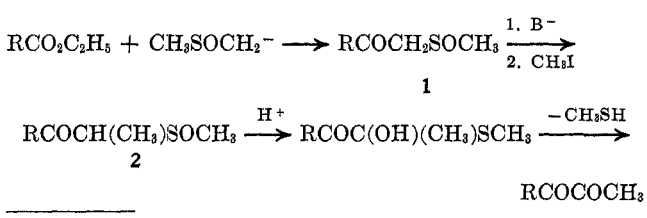
The 1-cycloalkylpropane-1,2-diones, or the corresponding hydroxy ketones, were required for the synthesis of a series of semidione radical anions (Scheme I).[2,3] In addition to the previously known routes to

SCHEME I



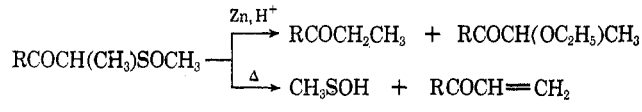
semidiones,[2] we found during the course of this work that the oxidation of α-alkoxy ketones in basic solution was often an excellent method for the preparation of semidiones. We have developed the synthesis of the diketones from the cycloalkanecarboxylic esters *via* the β-keto sulfoxides,[4,5] as shown in Scheme II.[6,7] The alkylated β-keto sulfoxides[8,9] were also reduced[5,6] to yield the ketones ($RCOCH_2CH_3$) and α-ethoxy ketones

SCHEME II



[$RCOCH(OC_2H_5)CH_3$] and pyrolyzed[10] to yield the vinyl ketones (Scheme III).

SCHEME III



Results and Discussion

Condensation of the cycloalkanecarboxylic esters with the methylsulfinyl carbanion presented no particular problems.[4,5] The reaction with cyclohexanecarboxylic ester has been previously reported.[5] Yields ranged from 41% with R = cyclopropyl to 74% with R = cyclopentyl or cyclohexyl. The β-keto sulfoxides (**1**) were converted to the enolate anions with sodium hydride in THF and alkylated with methyl iodide to yield $RCOCH(CH_3)SOCH_3$ (**2**) and $RCOC(CH_3)_2SOCH_3$ (**3**) (**a**–**f**, R): **a**, cyclopropyl; **b**, 1-methylcyclopropyl; **c**, cyclobutyl; **d**, cyclopentyl; **e**, cyclohexyl; **f**, 1-methylcyclobutyl.

The cyclopropyl and cyclobutyl compounds were unique in the ease with which dialkylation occurred. Use of a slight excess of methyl iodide and sodium hydride in the alkylation resulted in a mixture of **2a**–**3a**. In **1a** the second methyl group entered at the position α to both the carbonyl and sulfoxide functions to form **3a** exclusively. The cyclobutyl analog (**1c**) reacts with 2.3 equiv of sodium hydride and methyl iodide to yield a mixture of the dimethyl (**3c**) and trimethyl (**3f**) derivatives. Reaction of **1a** with 3.4 equiv of sodium hydride and methyl iodide yielded only **3a**. We believe the lack of methylation at the methine position of **1a** is due to a stereoelectronic effect which places the methine hydrogen in the nodal plane of the carbonyl group

(1) For part IX, see *J. Org. Chem.*, **35**, 2106 (1970). This work was supported by a grant from the Army Research Office (Durham).

(2) G. A. Russell and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 744 (1964).

(3) G. A. Russell and H. Malkus, *ibid.*, **89**, 160 (1967).

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

(5) E. J. Corey and M. J. Chaykovsky, *ibid.*, **86**, 1639 (1964); **87**, 1345 (1965).

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

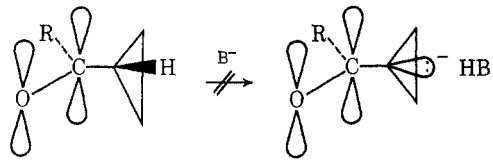
(7) T. L. Moore, U. S. Patent 3,409,673 (Dec 22, 1966).

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

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

(10) C. A. Kingsbury and D. J. Cram., *J. Amer. Chem. Soc.*, **82**, 1816 (1960).

thereby effectively blocking conjugation between the carbonyl group and a developing carbanion center.



Compound **1a** was reduced by treatment with a fourfold excess of zinc dust in a 3:2 mixture of ethanol–acetic acid by refluxing for 4–5 hr to yield cyclopropyl methyl ketone (62%) and the Pummerer rearrangement product ω-(methylmercapto)-ω-acetoxyacetylcyclopropane (19%). The reduction products of **2a–2e** are summarized in Table I. Table I also lists the pyrolysis products of **2b**, **2d**, **2e**, and **3a–3f** as observed in glpc at 150°.

TABLE I

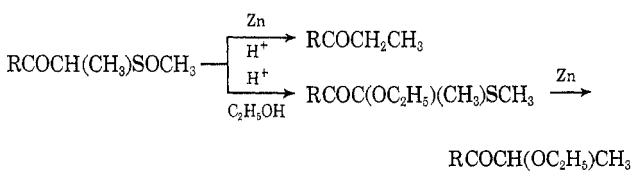
CONVERSION OF β-KETO SULFOXIDES TO KETONES

RCOCH(CH₃)SOCH₃, R	Yield, % RCOCH₂-CH₃[a]	RCOCH-(OC₂H₅)CH₃[a]	RCOCH=CH₂[b]
Cyclopropyl	36	36	
Cyclopropyl	24[c]	54[c,d]	
1-Methylcyclopropyl	53	8	41
Cyclobutyl[e]		37	
Cyclopentyl	33	41	45
Cyclohexyl	36	40	48
RCOC(CH₃)₂SOCH₃, R	**RCOCH-(CH₃)₂**		**RCOC-(CH₃)=CH₂**
Cyclopropyl			51
Cyclobutyl	34[e]		52[f]
1-Methylcyclobutyl			70[f]
Cyclopentyl			51
Cyclohexyl			53

[a] By refluxing 4–5 hr with acetic acid–ethanol in the presence of excess zinc dust. [b] Gas–liquid chromatography using 2-m 15% Carbowax 20M on Chromosorb W column at 150°. [c] Condition *a* with aqueous acetic acid. [d] RCOCH(OH)CH₃. [e] Products isolated by reaction of a mixture of **2c** and **3c**. [f] Conversion of **3f** in a mixture of ~66% **3c** and 34% **3f**.

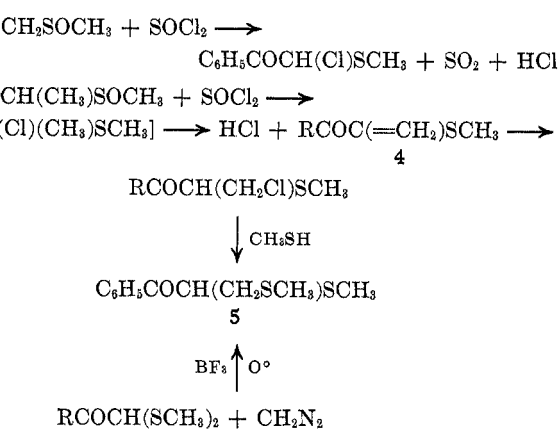
The reduction of the alkylated β-keto sulfoxides appears to involve competing processes to yield the ketone or the Pummerer rearrangement product, Scheme IV.

SCHEME IV



Much more drastic conditions were required to reduce **2** than were encountered in our previous studies with ω-(methylsulfinyl)acetophenone which was easily reduced without ether formation.[6] α substitution generally reduces the ease with which β-keto sulfoxides undergo the Pummerer rearrangement and the yield of the Pummerer rearrangement product.[6,11] Thus treatment of **2a–2e** with thionyl chloride did not yield the α-chloro thio ethers as observed for the unalkylated β-keto sulfoxides.[9,12] Moreover, whereas ω-(methylsulfinyl)acetophenone reacts with thionyl chloride to yield ω-chloro-ω-(methylmercapto)acetophenone,[12] the reaction with the α-methyl derivative yields only the chloromethyl derivative readily characterized as **5**. Apparently, the α-alkyl substituent promotes rearrangement of the α-chloro ketone as shown in Scheme V. Compound **5** was independently synthesized in

SCHEME V



55% yield from the reaction of diazomethane with the methyl mercaptal of phenylglyoxal in ether solution at 0° (boron trifluoride catalysis).

The best yields of isolated diketones were obtained by treatment of the β-keto sulfoxides (**1**) with hydrogen chloride in DMSO solution. Methyl mercaptan was allowed to escape from the reaction flask. Table II

TABLE II

CONVERSION OF β-KETO SULFOXIDES (RCOCH(CH₃)SOCH₃) TO α DIKETONES (RCOCOCH₃)[a]

R	% yield of diketone
Cyclopropyl	37
Cyclobutyl	39
Cyclopentyl	74
Cyclohexyl	63[b]

[a] Isolated by steam distillation from the reaction of 1 g of keto sulfoxide with a mixture of 2 ml of DMSO, 3 ml of concentrated HCl, and 10 ml of water. [b] Isolated by extraction from the reaction product of 3.2 g of the keto sulfoxide with 15 ml of DMSO and 6 ml of concentrated hydrochloric acid.

gives the yields of the observed products. Other techniques for the conversion of β-keto sulfoxides to dicarbonyl compounds involve the reactions of the keto sulfoxide with iodine or acid plus an oxidizing agent.[7,13] The acid will bring about the Pummerer rearrangement and the oxidizing agent will remove the methyl mercaptan from the equilibrium, $RCOCR'(OH)SCH_3 \rightleftarrows RCOCOR' + CH_3SH$. Cupric acetate precipitates $Cu(SCH_3)_2$ and is a very satisfactory reagent for glyoxal preparation.[6,14]

An alternate route to the 1-cyclopropylpropane-1,2-dione was from the α-hydroxy ketone produced by the reduction of the keto sulfoxide in aqueous acetic acid with zinc dust. The hydroxy ketone was oxidized by

(11) G. A. Russell and G. J. Mikol, "Mechanisms of Molecular Migration," Vol. I., B. S. Thyagarajan, Ed., Interscience, 1968, p 157.

(12) G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **35**, 764 (1970).
(13) T. L. Moore, *ibid.*, **32**, 2786 (1967).
(14) G. J. Mikol and G. A. Russell, *Org. Syn.*, **48**, 109 (1968).

cupric sulfate in pyridine to the diketone in a 55% yield.[15] This technique was not extended to the other keto sulfoxides.

The cycloalkyl ethyl ketones could be oxidized to the semidiones in basic solution containing a trace of oxygen (Scheme I). The α-ethoxy derivatives also oxidized to yield the semidione in basic solution. The esr spectra from the α-ethoxy ketones were of particularly high quality, for example, Figure 1 with R = cyclopropyl and 1-methylcyclopropyl. Apparently the process of Scheme VI occurs readily.

SCHEME VI

$$RCOCH(OC_2H_5)CH_3 + B^- \rightleftharpoons RC(O^-)=C(OC_2H_5)CH_3 \xrightarrow{O_2}$$
$$RCOC(OC_2H_5)(CH_3)OO^- \xrightarrow{DMSO} RCOC(OC_2H_5)(CH_3)O^- \longrightarrow$$
$$C_2H_5O^- + RCOCOCH_3 \xrightarrow{DMSO,\ B^-} RC(O\cdot)=C(O^-)CH_3$$

Experimental Section

β-Keto Sulfoxides 1.—A 500-ml three-necked flask with a mechanical stirrer, pressure equalized dropping funnel, a fritted suction tube for removal of solvent, and nitrogen inlet and outlet tubes was employed. Sodium hydride in a mineral oil slurry was placed in the flask and the mineral oil removed by stirring thrice with 20 ml of pentane. Dimethyl sulfoxide was added with 1 drop of an antifoaming agent and the mixture stirred at 63° for 2.5 hr. The cycloalkanecarboxylic ester was added slowly at 10°. After 40-min stirring at 25° the products were poured into 300 ml of ice water. The aqueous solution was extracted twice with 20-ml portions of ether and then acidified to pH 2 while cooled in an ice bath. The solution was extracted with seven 60-ml portions of methylene chloride and the organic extracts washed with 20 ml of 10% aqueous sodium bicarbonate solution. The solution was dried ($MgSO_4$) and evaporated to yield an oil which according to tlc contained only minor impurities The oil was further purified by chromatography with ethyl acetate on silica gel or by distillation.

Ethyl cyclohexanecarboxylate (20 g, 128 mmol) with 260 mmol of sodium hydride and 110 ml of DMSO gave 17.8 g (74%) of **ω-(methylsulfinyl)acetylcyclohexane, 1e**: mp 55–57°, lit. mp 62–63°.[5] Ethyl cyclopentanecarboxylate (30 g, 211 mmol) with 420 mmol of sodium hydride and 160 ml of DMSO gave 27 g (74%) of **ω-(methylsulfinyl)acetylcyclopentane, 1d**: bp 123–125° at 0.5 Torr; ir (CCl_4) 1700 (C=O), 1050 cm^{-1} (SO); mass spectrum (70 eV) *m/e* (rel intensity) 158 (7), 97 (23), 69 (100).

Anal. Calcd for $C_8H_{14}SO_2$ (174): C, 55.14; H, 8.09; S, 18.39. Found: C, 55.28; H, 8.01; S, 18.62.

Ethyl cyclbutanecarboxylate (25.6 g, 200 mmol) with 400 mmol of sodium hydride in 155 ml of DMSO gave 14.1 g (44%) of **ω-(methylsulfinyl)acetylcyclobutane, 1c**: bp 129–130° at 1 Torr; mp 60–62°; ir (KBr) 1697 (C=O), 1025 cm^{-1} (SO); mass spectrum (70 eV) *m/e* (rel intensity) 145 (1.6), 144 (11), 97 (2), 83 (32), 55 (100).

Anal. Calcd for $C_7H_{14}SO_2$ (160): C, 52.47; H, 7.55; S, 20.01. Found: C, 52.44; H, 7.62; S, 20.17.

Ethyl cyclopropanecarboxylate (22.8 g, 200 mmol) with 400 mmol of sodium hydride in 155 ml of DMSO gave 12.1 g (41%) of **ω-(methylsulfinyl)acetylcyclopropane, 1a**: bp 114–115° at 0.5 Torr; ir 1700 (C=O), 1038 cm^{-1} (SO); mass spectrum (70 eV) *m/e* (rel intensity) 130 (15), 69 (100), 41 (58).

Anal. Calcd for $C_6H_{10}SO_2$ (146): C, 49.29; H, 6.89; S, 21.92. Found: C, 49.44; H, 6.89; S, 22.13.

Methyl α-methylcyclopropanecarboxylate was prepared by the reaction of 20 g of methyl methacryate in 40 ml of ether at −15° with the diazomethane prepared from 64 g of Diazald. The pyrazoline was decomposed at 110–120° to give 13.4 g (59%) of the ester, bp 119–120°, lit.[16] bp 123–126°. Reaction of 13.4 g (117 mmol) of the ester with 5.17 g (216 mmol) of sodium hydride in 72 ml of DMSO gave 9.1 g (49%) of **1-(methylsulfinylacetyl)-1-methylcyclopropane, 1b**: bp 105–108° at 0.5 Torr; ir (CCl_4) 1675 (C=O), 1047 cm^{-1} (SO); mass spectrum (70 eV) *m/e* (rel intensity) 160 (1.2), 145 (11), 143 (17), 97 (24), 55 (100).

Anal. Calcd for $C_7H_{12}SO_2$ (160): C, 52.47; H, 7.55. Found: C, 52.25; H, 7.50.

Methylated β-Keto Sulfoxides 2a–2e, 3a–3f.—Sodium hydride was washed free of mineral oil as described previously and dispersed in THF. A solution of the sulfoxide to be alkylated in THF was added to the sodium hydride at 10°. After 30 min methyl iodide was added slowly. The reaction mixture was stirred for 2–4 hr at 25° and then poured into 400 ml of water containing a trace of sodium thiosulfate. The mixture was extracted seven times with 40-ml portions of methylene chloride and dried over $MgSO_4$. Removal of the solvent left oils which were further purified by chromatography with 3:1 chloroform–hexane or ethyl acetate, from silica gel.

α-(Methylsulfinyl)propionylcyclopropane, 2a, was prepared from 9 g of **1a** (61.6 mmol) by reaction with 63 mmol of sodium

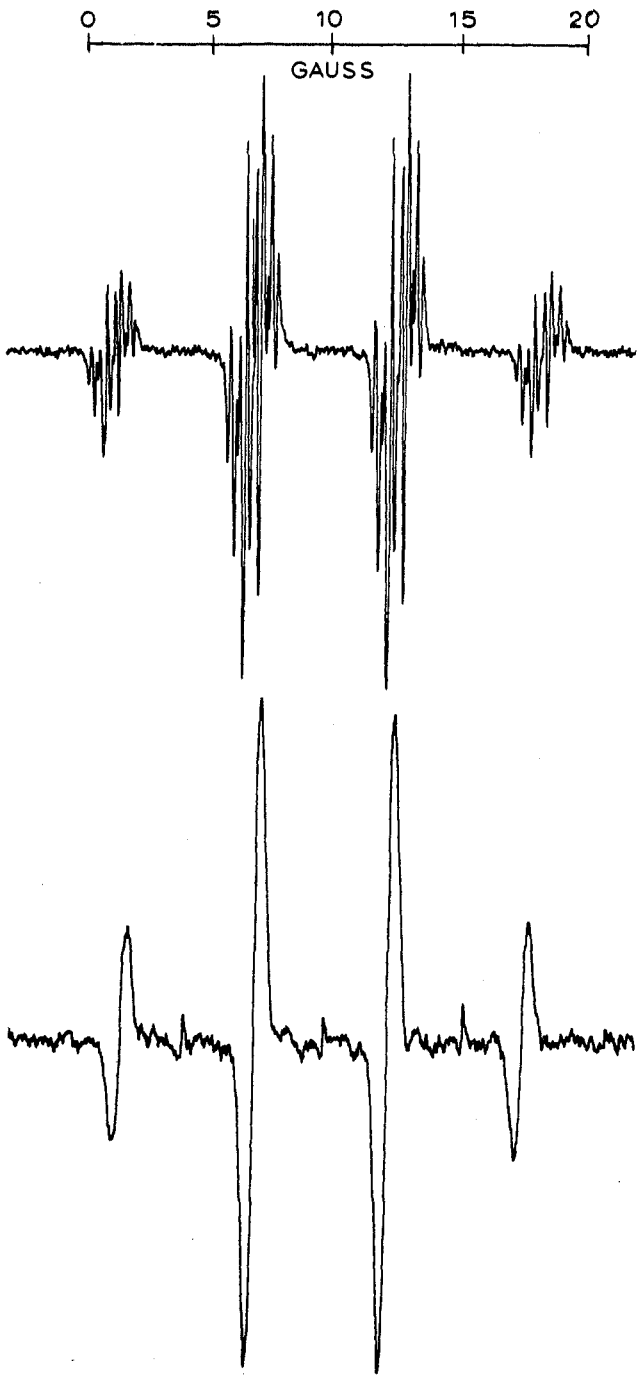


Figure 1.—Top, oxidation, product of 1-ethoxyethyl cyclopropyl ketone in DMSO containing potassium *t*-butoxide; bottom, oxidation product of 1-methylcyclopropyl ethyl ketone in DMSO containing cesium *t*-butoxide.

(15) H. T. Clarke and E. E. Drieger, "Organic Syntheses," Coll. Vol. I, 2nd ed, Wiley, New York, N. Y., 1941, p 87.

(16) S. Siegel, *J. Amer. Chem. Soc.*, **72**, 3815 (1950).

hydride and 65 mmol of methyl iodide. After a 2.5-hr reaction period, 7.1 g (72%) of **2a** was isolated: ir 1683 (C=O), 1042 cm^{-1} (SO); pmr (60 MHz, CCl_4) δ 0.88–1.20 (m, 4.7, CH_2–CH_2), 1.25–1.60 (m, 4, CCH_3), 1.88–2.25 (m, 1, CH), 3.75–4.1 (m, 1, CH–SO), 2.31–2.38 (t, 3.4, CH_3).

1-(Methylsulfinyl)ethyl 1-methylcyclopropyl ketone, 2b, was prepared from 41.5 mmol of **1b** by reaction with 41.6 mmol of sodium hydride and 41.5 mmol of methyl iodide in 55 ml of THF which gave 5.2 g (72%): ir (CCl_4) 1675 (C=O), 1050 cm^{-1} (SO); pmr (60 MHz, CCl_4) δ 0.70–0.95 (m, 2, $-CH_2$–CH_2), 1.15–1.55 (m, 8), 3.86–4.20 (m, 1, CH), 2.38 (d, 3, $SOCH_3$).

α-(Methylsulfinyl)propionylcyclopentane, 2d, was prepared from 8.7 g (50 mmol) of **1d**, 55 mmol of sodium hydride, and 80 mmol of methyl iodide. A 74% yield of **2d** was isolated: ir (CCl_4) 1700 (C=O), 1055 cm^{-1} (SO); pmr (60 MHz, CCl_4) δ 1.4–2.1 (m, 8, $CH_2CH_2CH_2CH_2$), 2.7–3.5 (m, 0.9, CH), 3.80–4.1 (m, 0.75, COCHSO), 1.2–1.53 (q, 3.8, CH_3), 2.29–2.39 (s, 3.8, $SOCH_3$).

α-(Methylsulfinyl)propionylcyclohexane,[9] 2e, was prepared in 79% yield from 40 mmol of **1e**, 43 mmol of sodium hydride, and 67 mmol of methyl iodide in 20 ml of THF.

α-(Methylsulfinyl)isopropyl cyclopropyl ketone, 3a, was prepared in 31% yield from 41.5 mmol of **1a**, 65 mmol of sodium hydride, and 65 mmol of methyl iodide. Chromatography of the product from silica gel using chloroform–hexane as the eluent gave **3a** as the first fraction. A second fraction yielded **2a** in 39% yield. Compound **3a** gave mass spectrum (70 eV) *m/e* (rel intensity) 142 (1.4), 110 (15), 41 (71), 69 (100).

Anal. Calcd for $C_5H_{14}SO_2$ (174); C, 55.14; H, 8.10; S, 18.40. Found: C, 55.13; H, 8.25; S, 18.49.

α-(Methylsulfinyl)propionylcyclobutane (2c), 2-(methylsulfinyl)-2-propyl cyclobutyl ketone (3c), and 2-(methylsulfinyl)-2-propyl 1-methylcyclobutyl ketone (3f) were obtained as mixtures by alkylation. A mixture of ~66% **3c** and ~34% **3f** were obtained by the reaction of 27.4 mmol of **1c** with 63 mmol of sodium hydride and 62 mmol of methyl iodide in 45 ml of THF. Pyrolysis on a glpc Carbowax column yielded a mixture of the two vinyl ketones. Reaction of 41.5 mmol of **1c** with 46 mmol of sodium hydride and 45 mmol of methyl iodide yielded a product that contained approximately equal amounts of **2c** and **3c**. Reduction yielded 1-cyclobutyl-2-ethoxy-1-propanone (from **2c**) and isopropyl cyclobutyl ketone (from **3c**).

Pyrolysis of β-Keto Sulfoxides.—Samples of the β-keto sulfoxides of ~50 mg were passed through a glpc column (2 m) of 20% Carbowax on Chromosorb at 145–170° in an Aerograph Autoprep instrument. The products were collected and identified. Keto sulfoxide **2b** (53 mg) at 180° gave 13.9 mg (41%) of **1-methylcyclopropyl vinyl ketone**: ir (CCl_4) 1678 (C=O), 1612 cm^{-1} (C=C); pmr (60 MHz, CCl_4) δ 0.58–0.84 (m, 2, CH_2–CH_2), 1.02–1.35 (m, 2, CH_2–CH_2), 1.35 (s, 3, CH_3), 5.42–6.46 (m, 3, $CH=CH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 110 (10), 83 (10), 55 (100), 41 (9).

From 57.5 mg of **2d** there was obtained at 180° 17 mg (45%) of **cyclopentyl vinyl ketone**: ir (CCl_4) 1690, 1675 (C=O), 1610 cm^{-1} (C=C); pmr (60 MHz, CCl_4) δ 1.50–1.90 (m, 8, CH_2CH_2-CH_2CH_2), 2.70–3.30 (m, 1, >CH–), 5.56–6.34 (m, 3, $CH=CH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 124 (13), 97 (8), 83 (80), 69 (75), 55 (100), 41 (90).

Anal. Calcd for $C_8H_{12}O$ (124): C, 77.38; H, 9.74. Found: C, 77.25; H, 9.89.

Cyclohexyl vinyl ketone was prepared from 54 mg of **2e** in 48% yield at 145°: ir (CCl_4) 1695, 1675 (C=O), 1610 cm^{-1} (C=C); pmr (60 MHz, CCl_4) δ 1.0–2.0 [m, 10, $(CH_2)_5$], 2.2–2.8 (m, 1, >CH–), 5.5–6.4 (m, 3, $CH=CH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 138 (8), 110 (5), 97 (10), 83 (51), 55 (100).

Anal. Calcd for $C_9H_{14}O$ (138): C, 78.21; H, 10.21. Found: C, 78.09; H, 10.35.

The keto sulfoxide **3a** (50 mg) at 135° gave 16 mg (51%) of **cyclopropyl isopropenyl ketone**: ir (CCl_4) 1665 (C=O), 1627 cm^{-1} (C=C); pmr (60 MHz, CCl_4) δ 0.70–1.15 (m, 4, CH_2CH_2), 2.12–2.52 (m, 1, >CH–), 1.85 [d, 3, $-C(CH_3)=$] 6.00 (s, 1, C=CH), 5.69 (m, 1, C=CH); mass spectrum (70 eV) *m/e* (rel intensity) 110 (14), 69 (100), 41 (56).

Anal. Calcd for $C_7H_{10}O$ (110): C, 76.32; H, 9.15. Found: C, 76.40; H, 9.32.

The mixture of **3c** and **3f** described previously gave about equal amounts of **cyclobutyl isopropenyl ketone** and **1-methylcyclobutyl isopropenyl ketone** when pyrolyzed. Cyclobutyl isopropenyl ketone had ir (CCl_4) 1668 (C=O), 1627 cm^{-1} (C=C); pmr (60 MHz, CCl_4) δ 1.8–2.5 (m, 6, $CH_2CH_2CH_2$), 3.4–3.9 (m, 1, >CH–), 1.81 [d, 3, $C(CH_3)=$], 5.6–5.8 (m, 2, $=CH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 124 (4), 109 (14), 83 (8), 69 (100), 55 (71), 41 (72).

Anal. Calcd for $C_8H_{12}O$ (124): C, 77.38, H, 9.74. Found: C, 77.28; H, 9.90.

1-Methylcyclobutane isopropenyl ketone had ir (CCl_4) 1665 (C=O), 1625 cm^{-1} (C=C); pmr (60 MHz, CCl_4) δ 1.7–2.8 (m, 6, $CH_2CH_2CH_2$), 1.51 (s, 3, $>CCH_3-$), 1.81 [d, 3, $-C(CH_3)=$], 5.53–5.78 (m, 2, $=CH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 138 (2), 123 (7), 95 (11), 70 (12), 69 (100), 68 (11), 41 (95).

Anal. Calcd for $C_9H_{14}O$ (138): C, 78.21; H, 10.21. Found: C, 78.01; H, 10.04.

α-(Methylsulfinyl)isopropyl cyclopentyl ketone (52 mg) gave 18 mg (51%) of **cyclopentyl isopropenyl ketone** at 145°: ir (CCl_4) 1672 (C=O), 1631 cm^{-1} (C=C); pmr (60 MHz, CCl_4) δ 1.5–1.9 [m, 8, $(CH_2)_4$], 3.15–3.54 (m, 1, >CH–), 1.81 [d, 3, $-C(CH_3)=$], 5.68–5.86 (m, 2, $=CH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 138 (11), 110 (7), 97 (22), 69 (100), 55 (8), 41 (73).

α-(Methylsulfinyl)isopropyl cyclohexyl ketone (53 mg) gave 20 mg (53%) of **cyclohexyl isopropenyl ketone** at 145°: ir (CCl_4) 1670 (C=O), 1630 cm^{-1} (C=C); pmr (60 MHz, CCl_4) δ 1.0–2.0 (m, 10, $(CH_2)_5$, 2.73–3.5 (m, 1, >CH–), 2.82 [d, 3, $-C(CH_3)=$], 5.67–5.83 (m, 2, $=CH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 152 (21), 110 (22), 83 (59), 69 (95), 55 (100), 41 (97).

Conversion of 2a and 2c–2e to α Diketones.—The β-keto sulfoxides (1 g) were dissolved in 2 ml of DMSO, 3 ml of concentrated hydrochloric acid, and 10 ml of water. After stirring for 1.5 hr under a stream of nitrogen the mixture was heated to a gentle boil. The nitrogen stream aided in carrying over drops of water and a yellow oil which were collected in a receiver in an ice bath. The distillate was extracted with methylene chloride, which was dried ($MgSO_4$) and concentrated. From 2 g of **2a** there was obtained 520 mg (37%) of **1-cyclopropylpropane-1,2-dione**: bp 43–44° at 12 Torr; ir (CCl_4) 1710, 1690 cm^{-1} (C=O); pmr (60 MHz, CCl_4), δ 0.99–1.10 (m, 4, CH_2CH_2), 2.5–2.9 (m, 1, >CH–), 2.26 (s, 3, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 112 (9.5), 69 (100), 43 (61), 41 (76).

Anal. Calcd for $C_6H_8O_2$ (112): C, 64.27; H, 7.19. Found: C, 64.08; H, 7.29.

From **2c** (2 g, 11.5 mmol) there was obtained 560 mg (39%) of 1-cyclobutylpropane-1,2-dione as a yellow oil: bp 53–54° at 12 Torr; ir 1708 cm^{-1} (C=O); pmr (60 MHz, CCl_4) δ 1.7–2.5 (m, $CH_2CH_2CH_2$), 3.6–4.1 (m, >CH–), 2.25 (s, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 126 (5), 83 (29), 43 (51), 55 (100).

Anal. Calcd for $C_7H_{10}O_2$ (126): C, 66.64; H, 7.99. Found: C, 66.47; H, 8.08.

Compound **2d** (1 g) yielded 0.55 g (74%) of **1-cyclopentylpropane-1,2-dione**: bp 33–35° at 0.6 Torr; ir (CCl_4) 1712 cm^{-1} (C=O); pmr (60 MHz, CCl_4) δ 1.6–2.1 [m, 7.4 $(CH_2)_4$], 3.2–3.7 (m, 1 >CH–), 2.29 (s, 3 CH_3); mass spectrum (70 eV) *m/e* (rel intentisy) 140 (3), 97 (25), 69 (100), 43 (32).

Anal. Calcd for $C_8H_{12}O_2$ (14): C, 68.54; H, 8.62. Found: C, 68.29; H, 8.47.

Keto sulfoxide **2e** (3.22 g) was stirred in a mixture of 15 ml of DMSO and 6 ml of concentrated hydrochloric acid for 24 hr at 25° and allowed to stand for another 12 hr. The mixture was diluted with 60 ml of water and extracted thrice with 10 ml portions of chloroform. Drying ($MgSO_4$) and removal of solvent gave a yellow oil. Column chromatography on silica gel with chloroform as the eluent separated the diketone and another product from more polar compounds. A 2nd chromatograph with ethyl acetate as the eluent gave 1.54 g (63%) of **1-cyclohexylpropane-1,2-dione**: bp 26–28° at 0.5 Torr; ir (CCl_4) 1710 cm^{-1} (C=O); pmr (60 MHz, CCl_4) δ 1.1–2.0 [m, 9.6 $(CH_2)_5$], 2.75–3.30 (m, 1, >CH–), 2.25 (s, 3, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 154 (1), 111 (10), 83 (51), 43 (46), 41 (100).

Anal. Calcd for $C_9H_{14}O_2$ (154): C, 70.09; H, 9.14. Found: C, 70.22; H, 9.23.

Methyl Hemimercaptal of 1-Cyclohexylpropane-1,2-dione by Pummerer Rearrangement of 2e.—Compound **2e** (0.80 g) was stirred for 24 hr at 25° in a mixture of 1.8 g of DMSO, 11 ml of water, and 1.6 ml of concentrated hydrochloric acid. The solution was extracted with 30 ml of methylene chloride. Drying and removal of the solvent left 0.75 g (94%) of the hemimercaptal as a yellow oil: ir (CCl_4) 3400 (OH), 1703 cm^{-1} (C=O); pmr

(60 MHz, CCl_4) δ 1.1–2.0 (m, 13.5, C_6H_{11}, CH_3), 1.71 (s, CH_3), 2.28 (m, 3, SCH_3), 5.30 (s, 1, OH).

ω-(Methylmercapto)-ω-(acetoxy)acetylcyclopropane.—This compound was prepared from the anion of **1a** prepared from 3.40 g (23.3 mmol) of **1a** in 40 ml of THF by reaction with 25 mmol of sodium hydride. At 60° a solution of 1.98 g (25 mmol) of pyridine and 1.89 g (24 mmol) of acetyl chloride in 30 ml of methylene chloride was added rapidly. The reaction mixture was allowed refluxed for 3 hr and allowed to stand for 48 hr. It was then diluted with 150 ml of methylene chloride, poured into 100 ml of water, and extracted with 10% aqueous sulfuric acid. The methylene chloride solution was washed with water and dried over $MgSO_4$ and the solvent evaporated. Chromatography from silica gel with 3:1 chloroform–hexane yielded 3.7 g (84%) of the Pummerer rearrangement product: ir (CCl_4) 1755 (ester C=O), 1708 (cyclopropyl carbonyl), 1218 cm^{-1} (ester); pmr (60 MHz, CCl_4) δ 0.84–1.20 (m, 4, CH_2CH_2), 1.9–2.4 (m, 1, >CH–), 2.03, 2.13 (s, 3, CH_3), 5.98 [s, 1, $-CH(SCH_3)(O_2CCH_3)$]; mass spectrum (70 eV), *m/e* (rel intensity) 188 (2), 145 (6), 130 (8), 69 (90), 47 (13), 43 (100), 41 (49).

Anal. Calcd for $C_8H_{12}SO_3$ (188): C, 51.04; H, 6.43; S, 17.03. Found: C, 50.88; H, 6.46; S, 17.15.

1-Phenyl-2-(methylmercapto)-3-chloropropanone.[17]—ω-Methyl-ω-(methylsulfinyl)acetophenone (9.75 g, 50 mmol) was dissolved in 200 ml of CH_2Cl_2 at 0° under nitrogen. Thionyl chloride (6 g, 50 mmole) was added and the reaction mixture allowed to warm to room temperature. After 2 hr the solvent was removed under vacuum to yield 10.9 g of a yellow oil containing (by pmr) approximately 85% 1-phenyl-2-methyl-3-chloropropane (SCH_3, δ 1.96) and 10% ω-methyl-ω-(methylmercapto)acetophenone.

1-Phenyl-2,3-di(methylmercapto)propanone.[17]—The crude 1-phenyl-2-(methylmercapto)-3-chloropropanone prepared from 1.96 g of ω-methyl-ω-(methylsulfinyl)acetophenone was treated in CH_2Cl_2 with 15 ml of methylmercaptan and 0.75 ml of triethylamine. The reaction was allowed to stir for 3 hr under nitrogen, the solvent evaporated, and the crude residue taken up in 100 ml of ether, washed with dilute aqueous sodium bicarbonate, dried, and concentrated to yield a yellow semisolid residue. Chromatography on 20 × 60 cm plates coated with Merck PF_{254} with $CaSO_4$ binder (80%) Merck silica gel H (20%), with elution by 1:1 cyclohexane–cyclopentane yielded 0.14 g (7.7%) of 1-phenyl-2-(methylmercapto)propanone and 1.87 g (83%) of 1-phenyl-2,3-di(methylmercapto)propanone: mp 44–45° from pentane; pmr (60 MHz, $CDCl_3$) δ 1.97, 2.13 (s, 3, SCH_3), an ABX multiplet with A = 2.87, B = 3.26, X = 4.41 (m, 3, $CHCH_2$, J_{AX} = 6.9, J_{BX} = 8.1, J_{AB} = 13.5 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 226 (50), 179 (90), 163 (15), 121 (75), 105 (100).

Anal. Calcd for $C_{11}H_{14}OS_2$ (226): C, 58.40; H, 6.24; S, 28.29. Found: C, 58.36; H, 6.23; S, 28.25.

Reduction of β-Keto Sulfoxides 1a, 2a–2d, 3a–3c.—Amalgamated aluminum foil in aqueous THF, or zinc powder in ethanol–acetic acid failed to reduce **1e** in 1.5 hr at 25°. Keto sulfoxide **1a** (1.83 g, 12.5 mmol) in 12 ml of ethanol was added to 7.8 ml of glacial acetic acid and 4.05 g (62 mg atom) of zinc. After 4 hr of refluxing, 0.65 g (62%) of **cyclopropyl methyl ketone**, bp 106–111°, was obtained. The distillation residue (0.44 g) was **ω-(methylmercapto)-ω-acetoxyacetylcyclopropane** (19%). Treatment of 2.5 g (15.6 mmol) of **2a** in 25 ml of refluxing solvent for 5 hr with 5.1 g (78 mg atom) of zinc powder gave a product that glpc showed to consist of 550 mg (36%) of **cyclopropyl ethyl ketone** and 805 mg (36%) of **α-ethoxyethyl cyclopropyl ketone.** Samples of cyclopropyl ethyl ketone isolated by glpc had ir (CCl_4) 1695 cm^{-1} (C=O); pmr (60 MHz, CCl_4) δ 0.60–0.96 (m, 4, CH_2CH_2), 1.6–2.1 (m, 1, >CH–), 2.3–2.7 (q, 2, CH_2CH_3), 0.9–1.15 (m, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 98 (10), 69 (100), 57 (7.5), 43 (6), 41 (50). α-Ethoxyethyl cyclopropyl ketone gave a semicarbazone, mp 142–143°. The ketone had ir (CCl_4) 1695 (C=O), 1107 cm^{-1} (ether); pmr (60 MHz, CCl_4), δ 0.70–1.0 (m, 4, CH_2CH_2), 1.1–1.3 (m, 6, CH_3), 2.0–2.5 (m, 1, >CH–), 3.6–3.9 (q, 1, $>CHOC_2H_5$), 3.3–3.6 (q, 2, CH_2CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 98 (5.8), 73 (66), 69 (20), 45 (100), 43 (11), 41 (20).

Keto sulfoxide **2b** (2.88 g, 16.5 mmol) after 12 hr at 25° and 4 hr at reflux yielded 1.57 g of an oil that was distilled to give 0.98 g (53%) of **1-methylcyclopropyl ethyl ketone**, bp 68–72° at 36 Torr, and **1-methylcyclopropyl 1-ethoxyethyl ketone** (214 mg, 8%). 1-Methylcyclopropyl ketone had ir 1685 cm^{-1} (C=O); pmr (60 MHz, CCl_4) δ 0.48–0.70 (m, 2, CH_2CH_2), 0.83–1.27 (m, 5, CH_2CH_2, $CHCH_3$), 1.32 (s, 3, $>C(CH_3)-$), 2.20–2.54 (q, 2, CH_2CH_3); mass spectrum (70 eV) *m/e* (rel intensity 112 (11), 83 (42), 57 (20), 55 (100), 41 (7). The α-ethoxy ketone had ir (CCl_4) 1690 (C=O), 111) cm^{-1} (ether); pmr (60 MHz, CCl_4) δ 0.48–0.75 (m, 2, CH_2CH_2), 1.08–1.30 (m, 5, CH_2CH_2 and CH_2CH_3), 1.19 [s, 3, $>C(CH_3)-$], 1.30–1.4, (d, 3, $>CHCH_3$), 3.2–3.6 (q, 2, CH_2CH_3), 3.9–4.2 (q, 1, CH); mass spectrum (70 eV) *m/e* (rel intensity) 110 (3), 83 (16), 73 (71), 55 (29), 45 (100), 41 (5).

A mixture of mono- and dimethylated **1c** (1.8 g, ~10 mmol) yielded 410 mg (34%) of **cyclobutyl isopropyl ketone** and 590 mg (37%) of **α-ethoxy ethyl cyclobutyl ketone.** Cyclobutyl isopropyl ketone had ir (CCl_4) 1704 cm^{-1} (C=O); pmr (60 MHz), CCl_4) δ 1.8–2.6 (m, 7.7, $(CH_2)_3$ and >CH–) 0.97, 1.06 (d, 6, CH_3), 3.0–3.6 (m, 1, cyclobutyl methine); mass spectrum (70 eV) *m/e* (rel intenstiy) 126 (2), 112 (2), 83 (28), 57 (17), 55 (100), 43 (17).

Anal. Calcd for $C_8H_{14}O$ (126): C, 76.14; H, 11.18. Found: C, 76.25; H, 11.24.

The α-ethoxy ketone had ir (CCl_4) 1708 (C=O), 1107 cm^{-1} (ether); pmr (60 MHz, CCl_4) δ 1.06–1.29 (m, 6, CH_3), 1.8–2.3 [m, 6, $CH_2)_3$], 3.3–3.7 (m, 1, >CH–), 3.2–3.56 (q, 2, CH_2CH_3), 3.5–3.9 (q, 1, $CHCH_3$); mass spectrum (70 eV) *m/e* (rel intensity) 112 (4), 73 (85), 55 (25), 45 (100), 43 (7).

Reduction of **2d** (2.95 g, 15.7 mmol) yielded 660 mg (33%) of **ethyl cyclopentyl ketone**, bp 72–80° at 11 Torr, lit.[18] 174–175° at 760 Torr, and 1.11 g (4%) of **α-ethoxyethyl cyclopentyl ketone**: bp 86–94° at 11 Torr, semicarbazone mp 150–151°; ir (CCl_4) 1710 (C=O), 1107 cm^{-1} (ether); pmr (60 MHz, CCl_4) δ 1.1–1.3 (m, 6, CH_3), 1.5–1.9 [m, 8, $CH_2)_4$], 3.0–3.4 (m, 1, CH–), 3.25–3.6 (q, 2, CH_2CH_3), 3.5–3.9 (q, 1, CH_3CH); mass spectrum (70 eV) *m/e* (rel intensity) 126 (5), 97 (4), 73 (100), 69 (27), 45 (97).

Anal. Calcd for $C_{10}H_{18}O_2$ (170): C, 70.55; H, 10.66. Found: C, 70.35; H, 10.62.

Keto sulfoxide **2e** (2.0 g, 10 mmol) yielded 510 mg (36%) of **cyclohexyl ethyl ketone**, bp 89–92° at 12 Torr, lit. bp 88–89° at 19 Torr, semicarbazone mp 147–149, lit.[19] mp 150–152°, and 740 mg (40%) of **α-ethoxyethyl cyclohexyl ketone**: bp 93–104° at 11 Torr, semicarbazone mp 151–152°; ir (CCl_4) 1709 (C=O), 1112 cm^{-1} (ether): pmr (60 MHz), (CCl_4), 1.08–1.32 (m, 6, CH_3), 1.2–2.0 [m, 10, $(CH_2)_5$], 2.5–2.9 (m, 1, CH–), 3.3–3.6 (q, 2, CH_2CH_3), 3.55–3.92 (q, 1, $CHCH_3$); mass spectrum (70 eV) *m/e* (rel intensity) 140 (3), 111 (2), 109 (2), 83 (14), 73 (100), 55 (15), 45 (84).

The reduction of **2a** (2.04 g 12.7 mmol) in 8.2 ml of acetic acid and 12 ml of water by refluxing with 4.25 g (65 mg-atoms) of zinc powder yielded 296 mg (24%) of **cyclopropyl ethyl ketone** and 782 mg (54%) of **cyclopropyl methyl acyloin**: ir (CCl_4) 3450 (OH), 1690 cm^{-1} (C=O); pmr (60 MHz, CCl_4) δ 0.80–1.18 (m, 4, CH_2CH_2), 1.30, 1.42 (d, 3, $CHCH_3$), 1.75–2.17 (m, 1, >CH–), 3.32 (m, 1, OH), 4.1–4.5 [q, 1, CH(OH)]; mass spectrum (70 eV) *m/e* (rel intensity) 113 (1) 112 (9), 69 (100), 43 (78), 42 (81), 41 (6).

Registry No.—**1a,** 25183-65-7; **1b,** 25183-66-8; **1c,** 25183-69-1; **1d,** 25183-70-4; **2a,** 25183-71-5; **2b,** 25183-72-6; **2d,** 25183-73-7; **3a,** 25183-74-8; 1-methylcyclopropyl vinyl ketone, 25183-75-9; cyclopentyl vinyl ketone, 25183-76-0; cyclohexyl vinyl ketone, 2177-34-6; cyclopropyl isopropenyl ketone, 4663-37-0; cyclobutyl isopropenyl ketone, 25183-79-3; 1-methylcyclobutyl isopropenyl ketone, 25183-80-6; cyclopentyl isopropenyl ketone, 25183-81-7; cyclohexyl isopropenyl ketone, 25183-82-8; 1-cyclopropylpropane-1,2-dione, 15940-89-3; 1-cyclobutylpropane-1,2-dione, 15940-91-7; 1-cyclopentylpropane-1,2-dione, 15940-93-9; 1-cyclohexylpropane-1,2-dione, 13898-90-3; 1-cyclohexylpropane-1,2-dione methyl hemimercaptol, 25183-87-3; ω-(methylmercapto)-ω-(acetoxy)acetylcyclopropane, 25183-88-4; 1-phenyl-2,3-di(methylmercapto)propanone, 25172-45-6; cyclopropyl methyl ke-

(17) Experiment performed by Dr. L. A. Ochrymowycz.

(18) G. Veron and H. M. Mitchovich, *Bull. Soc. Chim. Fr,* **45** [4], 961 (1929).

(19) H. Meerwein, *Justus Liebigs Ann. Chem.,* **419,** 167 (1919).

tone, 765-43-5; cyclopropyl ethyl ketone, 6704-19-4; cyclopropyl α-ethoxyethyl ketone, 25111-29-9; cyclopropyl α-ethoxyethyl ketone (semicarbazone), 25111-30-2; 1-methylcyclopropyl ethyl ketone, 25111-31-3; 1-methylcyclopropyl 1-ethoxyethyl ketone, 25111-32-4; cyclobutyl isopropyl ketone, 25111-33-5; α-ethoxyethyl cyclobutyl ketone, 25111-34-6; α-ethoxyethyl cyclopentyl ketone, 25111-35-7; cyclohexyl ethyl ketone, 1123-86-0; α-ethoxyethyl cyclohexyl ketone, 25111-37-9; α-ethoxyethyl cyclohexyl ketone (semicarbazone), 25111-38-0; cyclopropyl ethyl acyloin, 25111-39-1.

Organic Disulfides and Related Substances. XXIX. Studies in the Chemistry of Sulfenamides[1a-c]

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A variety of sulfenamides, $R^1SNR^2R^3$, were prepared and generalizations were sought for the chemical and physical properties of the class. Of syntheses studied, the smoothest was through reaction of sulfenyl chlorides with amines or amides. Thermal stability decreased from R^1 = *n*-butyl to 2-acetamidoethyl, suggesting an anchimeric effect in the latter; it decreased also with enhanced basicity of NR^2R^3 [*e.g.*, for $R^1 = AcNH(CH_2)_2$, stability for $R^2 + R^3$ = phthaloyl > $R^2 = R^3$ = alkyl], presumably because of an increased rate of proton transfer. The sulfenamides studied were quite stable to light. In their spectra, the predominant EI fragmentation reactions were C–S and N–S cleavage, with or without hydrogen rearrangement depending upon the nature of R^1, R^2, and R^3; ir and Raman spectra showed no useful characteristic absorption for the S–N bond. In their chemical reactions, sulfenamides with electrophiles characteristically gave products consistent with attack on NR^2R^3, followed by nucleophilic cleavage of the S–N bond (*e.g.*, with an alkyl or sulfonyl halide, carbon disulfide, and an isothiocyanate); however, with isocyanates and electron-deficient alkenes the preferred course seemed to be for elimination reactions, which can be formulated as concerted ones. The general pattern of nucleophilic attack was followed in conversion of sulfenamides by thiols to disulfides. In their biological properties, inactivity of several sulfenamides as antiradiation drugs indicated that NR^2R^3 may not be a promising latentiating group for radioprotective thiols.

Sulfenamides, which have the generalized structure **1** of eq 1, have been known for many years, but we are

$$R^1SCl + HNR^2R^3 \longrightarrow R^1SNR^2R^3 + HCl \quad (1)$$

3 → **1**, **4–17**

$$\downarrow {}^1/_2Cl_2$$

$${}^1/_2R^1SSR^1$$

2

$R^1 = AcNHCH_2CH_2$ (for **2–11**)

4, R^2 = H; R^3 = *p*-$C_6H_4CO_2Me$
5, R^2 = H; R^3 = 2-benzothiazolyl
6, $R^2 = R^3 = C_2H_5$
7, $R^2 + R^3 = (CH_2)_5$
8, $R^2 + R^3 = (CH_2)_2O(CH_2)_2$
9, NR^2R^3 = 1-benzimidazolyl
10, $R^2 + R^3$ = *o*-phthaloyl
11, R^2 = H; R^3 = *p*-$CH_2C_6H_4SO_2$
12, $R^1 = C_2H_5$; $R^2 + R^3 = (CH_2)_5$
13, R^1 = *n*-C_4H_9; $R^2 + R^3 = (CH_2)_5$
14, R^1 = *t*-C_4H_9; $R^2 + R^3 = (CH_2)_5$
15, $R^1 = C_2H_5$; $R^2 = R^3 = C_2H_5$
16, R^1 = *t*-C_4H_9; $R^2 = R^3 = C_2H_5$
17, R^1 = *t*-C_4H_9; R^2 = H; $R^3 = C_6H_5$

unaware of any effort to develop a unified theory of their chemistry.[2] Because of the possibility that the NR^2R^3 function might be an effective latentiating group for medicinally useful thiols,[3] we had occasion to prepare a variety of sulfenamides for testing as antiradiation drugs. Investigation thus became possible of the chemistry of typical sulfenamides in the hope of developing concepts useful for rationalizing and predicting chemical and physical properties of this class of compounds.

Preparation.—As a thiol, 2-acetamidoethanethiol was chosen because both it[3a] and the corresponding amine[3b] afford protection against ionizing radiation. As eq 1 shows, its disulfide (**2**) was converted to the sulfenyl chloride (**3**), which then was allowed to react with amines or amides to give the sulfenamides, **1**. This method was preferred to two others tried. Aminolysis of an acetamidoethanethiolsulfonate ($R^1SO_2SR^1$), which is an equilibrium reaction,[4] gave no pure, isolable sulfenamides; the product ratio was the same after 4 days as after 0.5 hr by tlc. Although this method often succeeds,[4] the properties of the acetamido products are not suited to the usual technique. The sulfenyl thiocyanate route[5] gave poor yields; thus crude **8** was obtained in only 30% yield (*vs.* 86% from **3**) and even then showed a strong –SCN band at 2200 cm^{-1} which could not be removed by washing with water. Furthermore, the preparation of 2-acetamidoethanesulfenyl thiocyanate was difficult because of its solubility properties.

The sulfenyl chloride, **3**, was obtained in quite variable yields, usually about 60%, by chlorinolysis of the disulfide in methylene chloride at temperatures in the range of −40 to −25° (eq 1). A lower temperature did not increase the yield of **3**; for example, **10** was

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