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(17) Unpublished results with L. A. Ochrymowycz.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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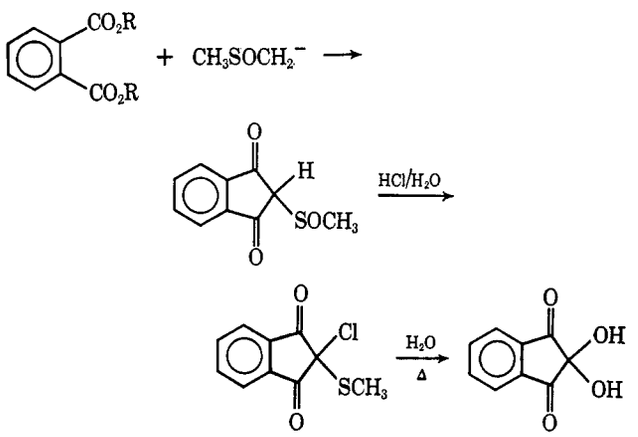
A new condensation reaction between two molecules of the methylsulfonyl carbanion ($CH_3SO_2CH_2^-$) or the methylsulfinyl carbanion ($CH_3SOCH_2^-$) and a variety of 1,2- 1,3- and 1,4-dicarboxylic esters is described. In favorable cases the condensation proceeds to yield an unsaturated monoketo disulfoxide 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

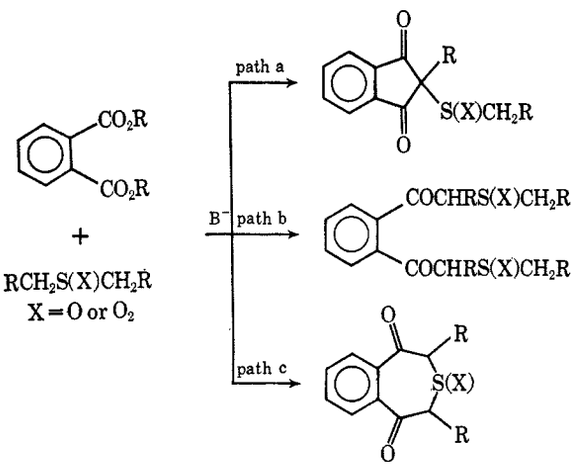
(1) This work was supported by the Army Office of Research (Durham). For part IV, see G. A. Russell and E. J. Sabourin, *J. Org. Chem.*, **34**, 2336 (1967).

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

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

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

SCHEME II



formed carbanion to the ester. We have utilized the reaction between sodium hydride and DMSO or $DMSO_2$ for the irreversible formation of the carbanion.[5] Condensations performed in the presence of "high" concentrations of the carbanions involved the addition of the ester to this carbanion solution.[6]

The dianion of DMSO[7] has also been examined in condensation with diethyl phthalate.

$$CH_3SOCH_3 + 2NaNH_2 \xrightarrow{NH_3} Na^+{}^-CH_2SOCH_2{}^-Na^+ + 2NH_3$$

Results and Discussion

The addition of diethyl phthalate to the irreversibly formed methylsulfinyl carbanion in DMSO solution, or to the dianion of DMSO in liquid ammonia,[7] failed to yield identifiable condensation products even though excellent yields of the indandione can be obtained by the use of the reversibly formed carbanion.[2] The difference in the two sets of experiments is apparently mainly connected with the concentration of the carbanion employed. Thus, the dropwise addition of the irreversibly formed methylsulfinyl carbanion to diethyl phthalate in DMSO solution results in the isolation of 31% 2-chloro-2-methylmercapto-1,3-indandione after acidification with hydrochloric acid. Addition of dimethyl phthalate to the product of the reaction of 2 equiv of sodium amide with each mole of DMSO in hexamethylphosphoramide solution led to the isolation of a low yield (14%) of a new type of condensation product identified as the 2:1 adduct **1a** (Scheme III).

The addition of diethyl phthalate to the preformed carbanion from $DMSO_2$ in THF solution gave rise to a mixture of the 2:1 condensation products, **1b** (10%) and **2** (70%). The formation of a low yield of 1:1 adduct, the indandione, by use of the irreversibly formed methylsulfinyl carbanion in THF solution (potassium *t*-butoxide as base) had been previously observed.[4] Treatment of **1b** with potassium *t*-butoxide in DMSO resulted in complete isomerization to **2**.

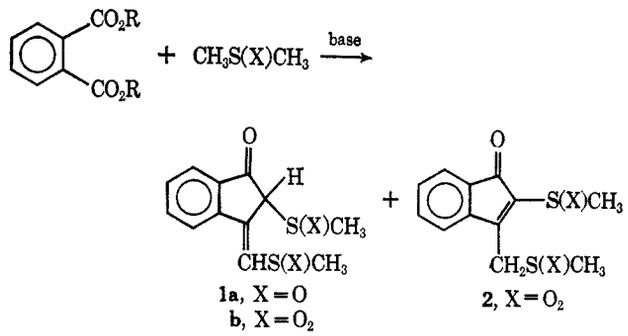
Dimethyl 2,3-naphthalenedicarboxylate underwent a similar series of reactions. Dropwise addition of the irreversibly formed carbanion to the diester resulted in

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

(6) It should be recognized that solvation by the alcohol can also have an appreciable effect on the reactivity of the carbanium.

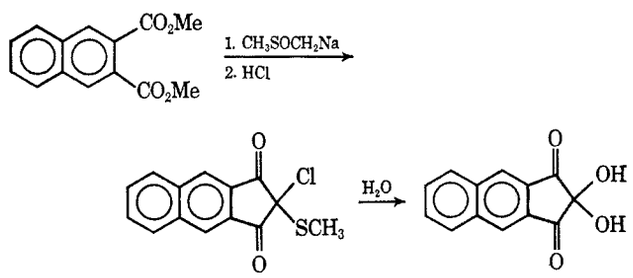
(7) E. M. Kaiser and R. D. Beard, *Tetrahedron Lett.*, 2583 (1968).

SCHEME III

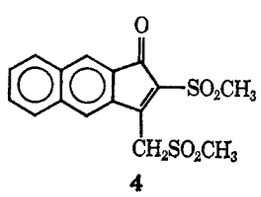


a 59% yield of 2-chloro-2-methylmercapto-1,3-naphthindandione which could be converted into the triketone hydrate **3** in an over-all yield of 45% based on the starting ester (Scheme IV). Addition of the ester to

SCHEME IV

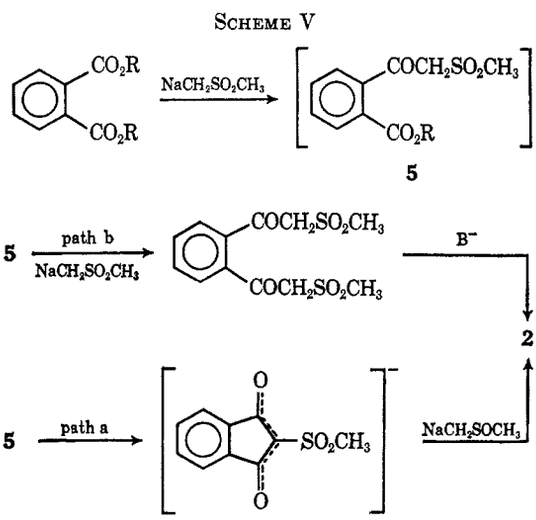


the preformed methylsulfonyl carbanion in THF solution gave an 84% yield of the 2:1 adduct, **4**.

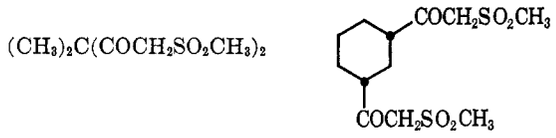


The products of this new condensation reaction appear to result from reaction path b followed by cyclization. However, the alternate formulation *via* addition of the methylsulfonyl carbanion to the product of reaction path a cannot be excluded (Scheme V)

SCHEME V

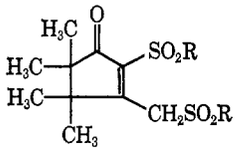


The formation of 2 from reaction path a suffers from the fact that the 2-methylsulfonyl-1,3-indandione is a very strong acid with a $pK_a < 0$.[4] It would thus exist solely in the anionic form in basic solutions and the addition would have to involve the reaction of two negative species. The formation of a low yield of the 2-methylsulfonyl-1,3-indandione when the ester is added to the carbanion generated by equilibrium with potassium *t*-butoxide but the formation of disulfones **1b** and **2** when the ester is added to a higher concentration of the preformed carbanions suggests that intermediate **5** can either cyclize to yield a monosulfone or react with another molecule of the methylsulfonyl carbanion to yield the disulfone which can then cyclize. Under the reaction condition diethyl dimethyl malonate condenses with two molecules of the methylsulfonyl carbanion to yield the disulfone **6**. Thus, when cyclization *via* path a is inhibited by steric considerations, further condensations *via* path b occurs readily. Similarly dimethyl *cis*-1,3-cyclohexanedicarboxylate yielded the disulfone **7**.



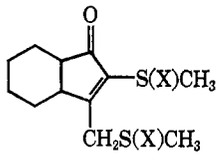
6 **7**

A variety of 1,2-dicarboxylic esters were examined under the conditions that produced **2–4**. Dimethyl succinate underwent self-condensation to yield only 2,5-dicarbomethoxy-1,4-cyclohexanedione when added to the preformed methylsulfonyl carbanion. However, dimethyl tetramethylsuccinate gave a cyclization reaction to yield 34% **8**.



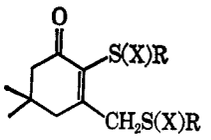
8

Diethyl *cis*-1,2-cyclohexanedicarboxylate reacted with the preformed methylsulfinyl carbanion in THF to yield the disulfoxide **9a** (29%). The analogous reaction with the methylsulfonyl carbanion produced a 93% yield of hexahydro-2-(methylsulfonylmethyl)-Δ^2-inden-1-one (**9b**).



9a, X = O
b, X = O_2

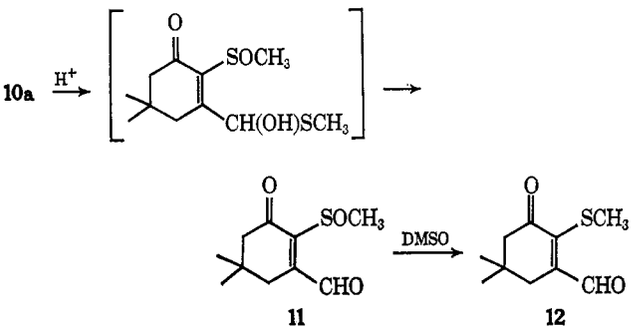
1,3-Dicarboxylic acid diesters underwent condensation with two molecules of DMSO or $DMSO_2$ (addition of the ester to the preformed carbanions). Dimethyl 3,3-dimethylglutarate yielded **10a** and **10b** in yields of 58 and 80%. Phenyl methyl sulfone yielded **10c** in 46% yield. The disulfone **10b** was also obtained (70% yield) when the ester was added to a mixture of



10a, X = O; R = CH_3
b, X = O_2; R = CH_3
c, X = O_2; R = C_6H_5

$DMSO_2$ and potassium *t*-butoxide in THF. Here cyclization *via* path a is apparently quite slow and even a low concentration of methylsulfonyl carbanion will divert the initial condensate to the disulfone. The isolation of **10a** was complicated by a facile rearrangement in the presence of acid. Two aldehydes were produced in DMSO solution with pmr absorption at δ 10.56 and 11.00. Apparently the Pummerer rearrangement[2] is occurring to yield **11** which reacts with DMSO to yield **12** (Scheme VI) which could be isolated in pure form and which had the δ 11.00 pmr absorption.

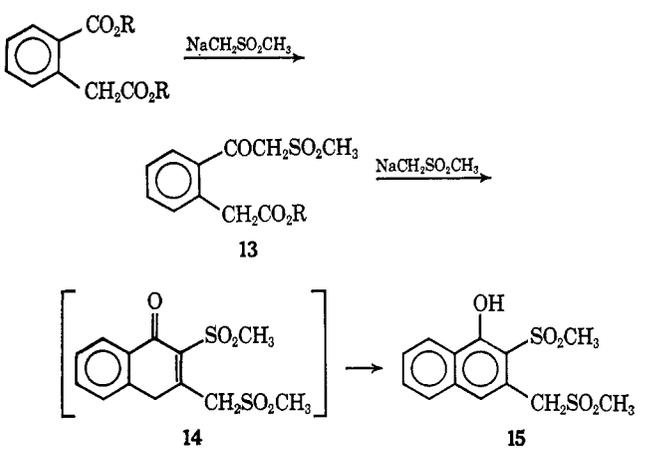
SCHEME VI



11 **12**

Dimethyl homophthalate when added to the preformed methylsulfonyl carbanion yielded **13** (isolated with R = H) and **15** (Scheme VII). Compound **13** is

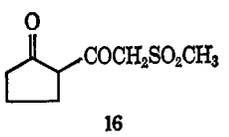
SCHEME VII



13 **14** **15**

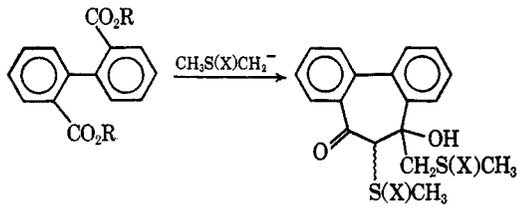
apparently a precursor to **14** and **15** since it was found only in reactions that had proceeded for periods of less than 2 hr. In a 20-hr experiment the yield of **15** was 95%.

Condensation of the methylsulfonyl carbanion with dimethyl adipate yielded only the monosulfone **16**.



16

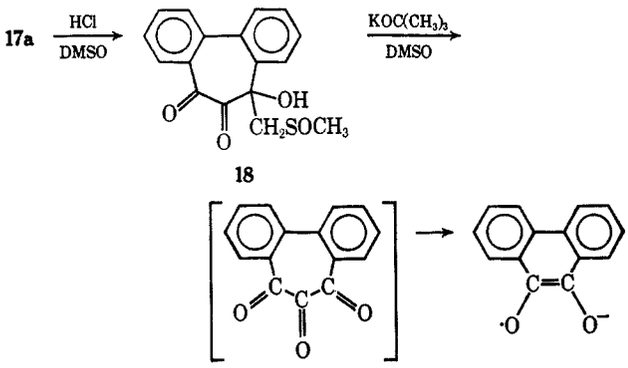
Diethyl diphenate reacted with the methylsulfinyl carbanion to produce **17a**. The disulfoxide was formed from both the carbanion preformed by sodium hydride or the equilibrium concentration generated by potassium *t*-butoxide. Probably the preferred *trans* conformation of the carboxyl groups retards the cyclization of process a and allows disulfoxide formation to occur. The disulfone **17b** could be prepared from the methylsulfonyl carbanion or by oxidation of **17a** was hydrogen peroxide. The resistance of **17a** to dehydration is



17a, X = O
b, X = O_2

noteworthy. Treatment with hydrochloric acid led to the Pummerer rearrangement product **18** which in basic solution yielded the esr spectrum of 9,10-phenanthrene semiquinone[8] (Scheme VIII). Other examples of

SCHEME VIII

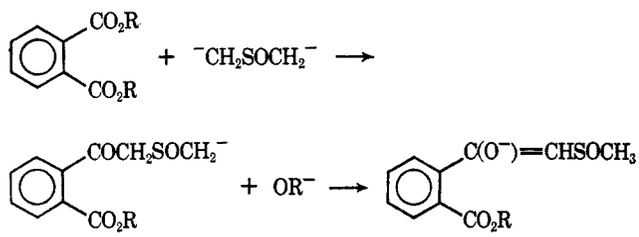


18

triketone decarbonylations under similar conditions are known.[9]

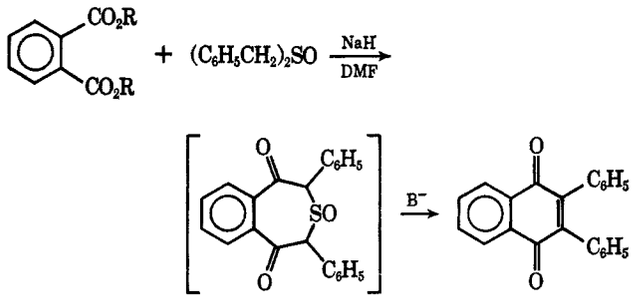
No evidence for the occurrence of process c from reaction of DMSO or $DMSO_2$ with diethyl phthalate had been found,[10] (Scheme IX). Even if the dianion

SCHEME IX



of the sulfone or sulfoxide is employed the acid–base equilibrium is unfavorable. We believe that process c occurred in the reaction of diethyl phthalate with a slurry of sodium hydride and dibenzyl sulfoxide in dimethyl-formamide at 60° (Scheme X). *trans*-Stilbene and a 24% yield of 2,3-diphenyl-1,4-naphthaquinone were isolated. Intermediate **19** is likely to be involved since it is known that dibenzyl sulfoxide is converted into stilbene under the reaction conditions.[11]

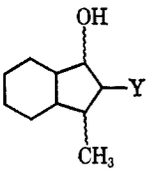
SCHEME X



19

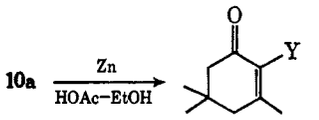
We have attempted to remove the sulfur from the cyclic disulfoxides and disulfones prepared in this work. The sulfoxide linkage is readily cleaved by reduction (*e.g.*, zinc and acid) when it is attached to a saturated carbon α to a carbonyl group.[12] We found that vinylogs ($RCOCH{=}CHCH_2SOCH_3$) are also readily cleaved.

Reduction of **9a** with W-2 Raney nickel[13] in refluxing alcohol gave 70% hexahydro-3-methyl-1-indanone in 5 hr. Larger reaction periods yielded a mixture of the isomeric alcohols (**20a**). The disulfone **9b** was reduced to a mixture of isomers **20b** by Raney nickel in refluxing ethanol.



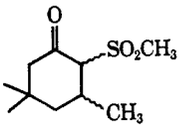
20a, Y = H
b, Y = SO_2CH_3

Reduction of **10a** by zinc in acetic acid–ethanol gave a 30% yield of **21a** accompanied by the sulfide **21b**.



21a, Y = $SOCH_3$
b, Y = SCH_3

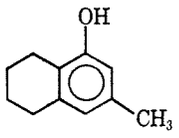
Reduction by aluminum amalgam in aqueous THF[5] gave a mixture of **21a** and **21b**. Refluxing a solution of **10a** in ethanol with Raney nickel gave a 64% yield of the isomeric 3,3,5-trimethylcyclohexanols. The sulfone **10c** could be reduced under similar conditions to yield the trimethylcyclohexanols in 47%. However, the sulfone **10b** was much more resistant to reduction. A reduction of **10b** to **22** in 94% yield was achieved by



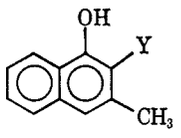
22

(8) M. Adams, M. S. Blois, Jr., and R. H. Sands, *J. Chem. Phys.*, **28**, 775 (1958); G. Vincow and G. K. Fraenkel, *ibid.*, **34**, 1333 (1961).
(9) G. A. Russell and S. A. Weiner, *J. Amer. Chem. Soc.*, **89**, 6623 (1967).
(10) W. E. Truce and F. J. Lotspeick, *ibid.*, **78**, 848 (1956).
(11) T. J. Wallace, H. Pabiner, J. E. Hofmann, and A. Schriesheim, *J. Chem. Soc.*, 1271 (1965).
(12) G. A. Russell and G. J. Mikol, *J. Amer. Chem. Soc.*, **88**, 5498 (1966).
(13) R. Mozingo, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley & Sons, Inc., New York, N. Y., 1955, p 181.

addition of nickel–aluminum alloy to a solution of the sulfone in 10% aqueous sodium hydroxide at 90°.[14] The disulfone **15** was reduced by Raney nickel in refluxing ethanol to 3-methyl-5,6,7,8-tetrahydro-1-naphthol (**23**) in 36% yield. Reduction under the Papa–Schwenk–Whitman conditions yielded a mixture of **24a** and **24b**.



23



24a, Y = H
b, Y = SO_2CH_3

A number of condensations were attempted with dimethyl 1,8-naphthalenedicarboxylate, diethyl maleate, diethyl 2,3-dimethyl-maleate, diethyl oxalate, and diethyl carbonate. No isoluble condensation products were found with either the methylsulfonyl or the methylsulfinyl carbanions.

Experimental Section

Methylsulfinyl Carbanion.—Solutions of the methylsulfinyl carbanion were prepared and allowed to react in a dry, prepurified nitrogen atmosphere. Irreversible formation from sodium hydride and dimethyl sulfoxide was accomplished by the method of Corey and Chaykovsky.[5] Equilibrium solutions were formed from alkali metal alkoxides and DMSO.[2]

Methylsulfonyl Carbanion.—Solutions of the methylsulfonyl carbanion were prepared and allowed to react in a dry, prepurified nitrogen atmosphere in DMSO solution. Preparation was similar to that of the methylsulfinyl carbanion, but dimethyl sulfone was added to the mixture.

2-Chloro-2-(methylmercapto)-1,3-naphthindandione.—To 6.1 g of dimethyl 2,3-naphthalenedicarboxylate (25 mmol) in 50 ml of DMSO was added 50 ml of a DMSO solution of the methylsulfinyl carbanion prepared from 2.4 g of sodium hydride (0.1 mol). The addition was accomplished by a hypodermic over a 1-hr period. Vigorous stirring of the solution was essential. As soon as the addition was completed, the mixture was poured into 100 ml of ice water. The aqueous solution was extracted with ether and then added to 100 ml of 6 *N* hydrochloric acid at 0°. A precipitate of 2-chloro-2-methylmercapto-1,3-naphthindandione of 4.1 g (59%) was recovered by filtration: mp 154–155°; ir (CCl_4) 1718 (C=O), 1751 cm^{-1} (C=O); pmr ($CDCl_3$) δ 2.48 (s, 3), 7.6–7.9 (m, 2), 8.0–8.3 (m, 2), 8.53 (s, 2); mass spectrum (70 eV), *m/e* (rel intensity) 276 (100), 278 (39).

Anal. Calcd for $C_{14}H_9ClO_2S$: C, 60.76; H, 3.28; Cl, 12.81; S, 11.59. Found: C, 60.91; H, 3.46; Cl, 12.70; S, 11.45.

1,2,3-Naphthindantrione Hydrate (3).—To 1.5 g of the dimethyl 2,3-naphthalenedicarboxylate in 50 ml of DMSO at 10° was added dropwise (45 min) 100 ml of a 2 *M* solution of sodium hydride in DMSO. The reaction mixture was stirred for 2 hr before it was poured into 200 ml of concentrated hydrochloric acid at 0° with efficient stirring. After stirring for 9 hr, the hydrochloric acid solution was diluted with 1000 ml of water and extracted twice with 500 ml of ethyl acetate. The solvent was removed under vacuum to leave a dark oil that was boiled in water for 2 hr. The cooled, filtered aqueous solution was extracted with ethyl acetate, the solution was dried with sodium sulfate and the solvent was removed by vacuum. The residue was developed on a silica gel column with a 1:1 mixture of ethyl acetate–petroleum ether (bp 60–90°) distillate to yield 640 mg (45%) of the trione, recrystallized from a mixture of ethyl acetate and ether. The material lost water and turned green at 147° and melted at 282° (lit.[15] mp 279–282°). Both **3** and 2-chloro-2-(methylmercapto)-1,3-naphthindandione give a green color with amino acids.

2-(Methylsulfinyl)-3-(methylsulfinylmethylene)indanone (1a).—DMSO (100 mmol) was added to 205 mmol of sodium amide in 250 ml of liquid ammonia. After 3 hr the ammonia was allowed to evaporate and a mixture of 80 ml of hexamethylphosphoramide (HMPA) and 20 ml of ether was added. A mixture of 19.4 g (100 mmol) of dimethyl phthalate in 20 ml of ether was added slowly to the sodium amide solution at 10°. After stirring for 4 hr at 25° the reaction mixture was poured into 250 ml of ice water and extracted with five 40-ml portions of chloroform to remove the HMPA. The aqueous phase was acidified carefully to a pH of 1 by concentrated hydrochloric acid. Phthalamide was removed by filtration and the filtrate was extracted with six 30-ml portions of chloroform. Drying over magnesium sulfate and removal of the solvent under vacuum left 9.65 g of an oil which could be crystallized from acetonitrile–ether to give 3.75 g of **1a**: mp 141–143°; ir (KBr) 1720 (C=O), 1655, 1630 (C=C), 1042, 1025 cm^{-1} (SO); pmr ($CDCl_3$) δ 7.93–7.29 (m, 4), 7.18 (d, 1), 5.00 (d, 1, exchanged with D_2O), 2.92 (s, 3), 2.54 (s, 3).

Anal. Calcd for $C_{12}H_{12}O_3S_2$: C, 53.70; H, 4.50; S, 23.89. Found: C, 53.52; H, 4.54; S, 23.63.

2-(Methylsulfonyl)-3-(methylsulfonylmethyl)indenone (2).—Diethyl phthalate (5.55 g, 25 mmol) in 50 ml of THF was added to the methylsulfonyl carbanion prepared from 9.4 g of $DMSO_2$ (0.1 mol) and 2.4 g of sodium hydride (0.1 mol) in 50 ml of DMSO. After stirring for 3 hr at 25° the reaction mixture was poured cautiously into 100 ml of ice water, neutralized with dilute hydrochloric acid, and thoroughly extracted with chloroform. Removal of the chloroform under vacuum left 5.2 g of **2** (70%), a yellow solid: mp 175–178° (several recrystallizations from chloroform–methanol raised the melting point to 193–195°); ir (KBr) 1718 (C=O), 1608 (C=C), 1304, 1143 cm^{-1} (SO_2); pmr ($CDCl_3$) δ 3.17 (s, 3), 3.26 (s, 3), 4.98 (s, 2), 7.56 (s, 4); mass spectrum (70 eV), parent peak at *m/e* 300.

Anal. Calcd for $C_{12}H_{12}O_5S_2$ (300.2): C, 48.01; H, 4.03; S, 21.32. Found: C, 47.98, H, 4.05; S, 21.38.

An isomer of **2** identified as **1b** was isolated from the aqueous solution upon standing for 24 hr. Treatment of this material with a DMSO solution of potassium *t*-butoxide for 18 hr yielded a product with an ir spectrum superimposable with that of **2**. The yield of **1b** was 0.77 g (10%): mp 215–217°; ir (KBr) 1736 (C=O), 1608 (C=C), 1304, 1131 cm^{-1} (SO_2); pmr (CF_3CO_2H) δ 3.48 (s, 6), 6.18 (d, 1, *J* = 1.5 Hz), 7.40 (d, 1, *J* = 1.5 Hz), 7.7–8.2 (m, 4); mass spectrum (70 eV) identical with that of **2**.

2-(Methylsulfonyl)-3-(methylsulfonylmethyl)naphthindenone (4).—Dimethyl 2,3-naphthalenedicarboxylate (2.44 g, 10 mmol) in 10 ml of DMSO was added dropwise at 25° to a solution of methylsulfonyl carbanion prepared from 3.8 g of dimethyl sulfone (40 mmol) and 1 g of sodium hydride (40 mmol) in 25 ml of DMSO. After stirring for 3 hr, the mixture was cautiously poured into 200 ml of water and acidified with hydrochloric acid. Filtration of the yellow precipitate formed upon acidification gave 2.94 g (84%) of **4**, mp 225–235° dec. Recrystallization from acetic acid–ethanol gave material with mp 244–246° dec; ir (KBr) 1700 (C=O), 1623 (C=C), 1307, 1136 cm^{-1} (SO_2); pmr (CF_3CO_2H) δ 3.47 (s, 3), 3.52 (s, 3), 5.37 (s, 2), 7.6–8.2 (m, 6).

Anal. Calcd for $C_{16}H_{14}O_5S_2$: C, 54.86; H, 4.03; S, 18.27. Found: C, 54.85; H, 4.06; S, 18.27.

3,3-Dimethyl-1,5-di(methylsulfonyl)-2,4-pentanedione (6).—Diethyl dimethylmalonate (4.7 g, 25 mmol) in 50 ml THF was added to the methylsulfonyl carbanion prepared from 9.4 g of dimethyl sulfone (0.1 mol) and 2.4 g sodium hydride (0.1 mol) in 50 ml of DMSO. The product was isolated as described in the preparation of **2** to yield 1.15 g (16%) of **6**: mp 107–108°; ir (KBr) 1706 (C=O), 1307, 1126 cm^{-1} (SO_2); pmr (CF_3CO_2H) δ 1.57 (s, 6), 3.01 (s, 6), 4.62 (s, 4).

Anal. Calcd for $C_9H_{16}O_6S_2$: C, 38.03; H, 5.67; S, 22.52. Found: C, 38.14; H, 5.66; S, 22.45.

ω,ω-Di(methylsulfonyl)-*cis*-1,3-diacetylcyclohexane (7).—Substitution of 5.0 g of dimethyl *cis*-1,3-cyclohexanedicarboxylate (20 mmol) in the procedure used for the preparation of **2** yielded 5.25 g (65%) of **7** as a white solid, mp 153–155°. Recrystallization from chloroform containing a trace of methanol gave material with mp 157–158°; ir (KBr) 1706 (C=O), 1307, 1127 cm^{-1} (SO_2); pmr (CF_3CO_2H) δ 3.30 (s, 6), 4.57 (s, 4).

Anal. Calcd for $C_{12}H_{20}O_6S_2$: C, 44.44; H, 6.22; S, 19.74. Found: C, 44.37; H, 5.93; S, 19.89.

2-(Methylsulfonyl)-3-(methylsulfonylmethyl)-4,4,5,5-tetramethylcyclopentenone (8).—Substitution of 2.20 g of diethyl tetramethylsuccinate (10 mmol) in the procedure used for the preparation of **2** yielded 1.9 g of a pasty solid. Recrystallization from ethyl acetate and from chloroform–ether mixtures gave 1.03 g (34%) of **8**: mp 179.5–180.0°; ir ($CHCl_3$) 1727 (C=O), 1610

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(C=C), 1311, 1130 cm^{-1} (SO_2); pmr ($CDCl_3$) δ 1.10 (s, 6), 1.20 (s, 6), 3.17 (s, 3) 3.21 (s, 3), 4.82 (s, 2).

Anal. Calcd for $C_{12}H_{20}O_5S_2$: C, 46.75; H, 6.54; S, 20.76. Found: C, 46.70; H, 6.50; S, 20.70.

Hexahydro-2-(methylsulfinyl)-3-(methylsulfinylmethyl)-Δ^2-inden-1-one (9a).—A solution of 5.7 g of diethyl *cis*-1,2-cyclohexanedicarboxylate (25 mmol) in 50 ml of THF was added dropwise to a solution of the methylsulfinyl carbanion prepared from 2.4 g (0.1 mol) of sodium hydride and 50 ml of DMSO. The mixture was stirred for 3 hr at 25°, then poured cautiously into 100 ml of ice water, carefully neutralized with hydrochloric acid, and thoroughly extracted with chloroform. The extracts were dried by magnesium sulfate and the solvent was evaporated to give 2.3 g (29%) of **9a** as a white solid: mp 131–134° (recrystallization from chloroform–ether raised the melting point to 134–137° dec); ir ($CHCl_3$) 1700 (C=O), 1590 (C=C), 1047 cm^{-1} (SO); pmr ($CDCl_3$) broad absorption at δ 1.0–3.0 with methyl singlets at 2.72 and 2.99, total area 16 [the methylene hydrogens adjacent to the sulfoxide group gave an AB pattern at δ 3.98 and 4.90 (J = 12 Hz)].

Anal. Calcd for $C_{12}H_{18}O_3S_2$: C, 52.55; H, 6.62; S, 23.34. Found: C, 52.41; H, 6.65; S, 23.47.

Hexahydro-2-(methylsulfonyl)-3-(methylsulfonylmethyl)-Δ^2-inden-1-one (9b).—Substitution of 5.7 g of diethyl *cis*-1,2-cyclohexanedicarboxylate (25 mmol) in the procedure used for the preparation of **2** gave 6.6 g (93%) of **9b**: mp 141–144° (recrystallization from methanol raised the melting point to 143–144°); pmr ($CDCl_3$) δ 1.0–3.0 (m, 10), 3.12 (s, 3), 3.20 (s, 3), 4.18, 5.40 (AB quartet, 2, J = 12 Hz, $CH_2SO_2CH_3$).

Anal. Calcd for $C_{12}H_{18}O_5O_2$: C, 47.06; H, 5.63; S, 20.90. Found: C, 47.00; H, 5.71; S, 20.83.

5,5-Dimethyl-2-(methylsulfinyl)-3-(methylsulfinylmethyl)-Δ^2-cyclohexenone (10a).—Substitution of 4.7 g of dimethyl 3,3-dimethylglutarate (25 mmol) in the process described for the preparation of **9** resulted in the formation of a yellow oil that produced 3.0 g (46%) of **10a**, mp 68–81° upon trituration with cold ether. An additional 0.8 g of **10a** was isolated from the filtrate by column chromatography. In addition column chromatography yielded 0.3 g of 5,5-dimethyl-2-(methylmercapto)-3-carboxaldehyde-2-cyclohexenone (**12**). The wide melting point range of **10a** could not be improved by recrystallization from chloroform–ether and it is concluded that **10a** was a mixture of the racemic pairs of the two possible diastereomers: ir ($CHCl_3$) 1664 (C=O), 1597 (C=C), 1036 cm^{-1} (SO); pmr ($CDCl_3$) δ 1.11 (s, 6), 2.40 (s, 2), 2.65 (s, 2), 2.75 (s, 3), 2.97, 2.99 (singlets, total intensity 3), 3.6–5.2 (m, 2; analyzed as two AB quartets, 3.70 and 4.78, J = 11.6 Hz, and 4.18 and 5.01, J = 11.0 Hz).

Anal. Calcd for $C_{11}H_{18}O_3S_2$: C, 50.37; H, 6.92; S, 24.90. Found: C, 50.47; H, 7.00; S, 24.68.

Compound **12** was identified by its mass, ir, and pmr spectrum: the mass spectrum gave a parent peak at m/e 198 and, from the intensity of $(M + 2)^+$ = 6% of M^+, it could be concluded that only one sulfur atom was present; ir (CCl_4) 1686 (C=O), 1672 cm^{-1} (C=O); pmr (CCl_4) δ 1.65 (s, 6), 2.40, 2.73 (singlets, total intensity 7), 10.56 (s, 1).

5,5-Dimethyl-2-(methylsulfonyl)-3-(methylsulfonylmethyl)-Δ^2-cyclohexenone (10b).—Substitution of 4.7 g of dimethyl 3,3-dimethylglutarate (25 mmol) in the process described for the preparation of **2** resulted in the formation of 5.9 g (80%) of **10b**: mp 150–162° (recrystallization from chloroform raised the melting point to 174.0–174.5°); ir ($CHCl_3$) 1686 (C=O), 1600 (C=C), 1307, 1131 cm^{-1} (SO_2); pmr ($CDCl_3$) δ 1.09 (s, 6), 2.45 (s, 2), 2.79 (s, 2), 3.08 (s, 3), 3.27 (s, 3), 4.88 (s, 2).

Anal. Calcd for $C_{11}H_{18}O_5S_2$: C, 44.90; H, 6.17; S, 21.76. Found: C, 45.06; H, 6.13; S, 21.78.

Compound **10b** was formed but only in low yield when 25 mmol of sodium hydride and $DMSO_2$ were employed. Use of 0.1 mol of potassium *t*-butoxide and 0.1 mol of $DMSO_2$ gave a 70% yield of **10b**. Use of 0.1 mol of potassium *t*-butoxide and 25 mmol of $DMSO_2$ gave **10b** in 22% yield. Inverse addition of 0.1 mol of the methylsulfonyl carbanion gave **10b** in 31% yield.

5,5-Dimethyl-2-(phenylsulfonyl)-3-(phenylsulfonylmethyl)-Δ^2-cyclohexenone (10c).—Substitution of 4.7 g of dimethyl 3,3-dimethylglutarate (25 mmol) and 15.6 g of phenylmethyl sulfone (0.1 mmol), in the process described for the preparation of **2**, yielded 4.8 g (46%) of **10c**: mp 205–207°; ir ($CHCl_3$) 1686 (C=O), 1590 (C=C), 1311, 1144 cm^{-1} (SO_2); pmr ($CDCl_3$) δ 1.03 (s, 6), 2.27 (s, 2), 2.90 (s, 2), 5.12 (s, 2), 7.4–8.2 (m, 10).

Anal. Calcd for $C_{21}H_{22}O_5S_2$: C, 60.28; H, 5.30; S, 15.30. Found: C, 60.66; H, 5.35; S, 15.10.

2-(Methylsulfonyl)-3-(methylsulfonylmethyl)-1-naphthol (15).—Substitution of 10.4 g of dimethyl homophthalate (50 mmol) and extending the reaction period to 24 hr in the preparation described for **2** yielded 14.9 g (95%) of **15**, mp 194–200°, as a solid upon acidification [recrystallization (CH_3CO_2H) gave mp 200–202°]: ir (KBr) 3450 (OH), 1307, 1261 cm^{-1} (SO_2); pmr (DMSO) δ 3.02 (s, 3), 3.52 (s, 3), 5.25 (s, 2), 10.5–11.5 (s, 1, OH exchangeable with d_6-DMSO), 7.5–8.5 (m, 5); mass spectrum (70 eV), m/e (rel intensity) 3.4 (100), 316 (109.6).

Anal. Calcd for $C_{13}H_{14}O_5S_2$: C, 49.68; H, 4.49; S, 20.36. Found: C, 50.00; H, 4.47; S, 20.58.

If reaction periods of 3 hr are employed for the synthesis of **15**, the yield is lower and **13** (R = H) can be isolated. ***o*-(Methylsulfonylacetyl)phenylacetic acid** crystallizes slowly from the aqueous layer after **15** has been removed by filtration: the mass spectrum gave a molecular ion at 256 and from the $(M + 2)^+$ peak the presence of one sulfur atom was indicated; ir (KBr) 3570–2500 (OH), 1686, 1706 (C=O), 1302, 1236 cm^{-1} (SO_2); pmr of methyl ester ($CDCl_3$), δ 3.12 (s, 3), 3.68 (s, 3), 3.95 (s, 2), 4.57 (s, 2), 7.2–8.0 (m, 4).

2-(Methylsulfonylacetyl)cyclopentanone (16).—Substitution of 4.35 g of dimethyl adipate (25 mmol) in the preparation described for **2** yielded 3.45 g (67%) of **16**: mp 90–95° (recrystallization from chloroform raised the melting point to 98–100°); ir ($CHCl_3$) 3570–2500 (OH), 167°, 1706 (C=O), 1613 (C=C), 1316, 1429 cm^{-1} (SO_2); pmr ($CDCl_3$) δ 1.8–2.9 (m, 6), 3.91 (s, 2), 13 (broad singlet exchangeable with D_2O).

Anal. Calcd for $C_8H_{12}O_4S$: C, 47106; H, 5.92; S, 15.67. Found: C, 47.17; H, 5.98; S, 15.80.

The spectroscopic data indicated an appreciable enol content which was supported by a positive ferric chloride test.

3-Hydroxy-2-(methylsulfinyl)-3-(methylsulfinylmethyl)dibenzocycloheptanone (17a).—Substitution of 14.9 g of diethyl diphenate (50 mmol) in the preparation described for **9a** gave 14.3 g (79%) of **17a**, mp 150–177°. The same product was obtained using potassium *t*-butoxide as the base. The melting point of **17a** could not be improved by recrystallization. Thus, **17a** is probably a mixture of the racemic modifications of the possible diastereomers. Compound **17a** was insoluble in numerous solvents: its pmr spectrum was not determined; ir (KBr) 3448 (OH), 1672 (C=O), 1038 cm^{-1} (SO); mass spectrum (70 eV), m/e $(M)^+$ 362, $(M - 18)^+$ 344 (strong).

Anal. Calcd for $C_{18}H_{18}O_4S_2$: C, 59.66; H, 5.01; S, 17.66. Found: C, 59.51; H, 5.13; S, 17.74.

Additional proof of structure for **17a** was furnished by reduction to **3-hydroxy-3-(methylsulfinylmethyl)dibenzocycloheptanone** by zinc dust in acetic acid–ethanol.[12] From 8.7 g of **17a**, 20 g of zinc, and 150 ml of solvent, there was obtained after 3 hr at 25° 5.25 g (87%) of 3-hydroxy-3-(methylsulfinylmethyl)dibenzocycloheptanone: mp 160–168°; ir (KBr) 3175 (OH), 1667 (C=O), 1005 cm^{-1} (SO); pmr ($CDCl_3$) δ 2.32, 2.35 (singlets, total intensity 3), 3.07 (s, 2), 3.3–3.6 (m, 2), 5.41 (s, 1), 7.3–8.1 (m, 8).

Anal. Calcd for $C_{17}H_{16}O_3S$: C, 67.99; H, 5.37; S, 10.66. Found: C, 68.08; H, 5.11; S, 10.62.

Compound **17a** readily underwent the Pummerer rearrangement to yield **3-hydroxy-3-(methylsulfinylmethyl)dibenzo-1,2-cycloheptanedione (18).** In DMSO solution, to 1 g of **17a** in 10 ml of DMSO, was added 3 ml of water and 2 ml of concentrated hydrochloric acid at 25°. After 24 hr, the mixture was added to 25 ml of water and extracted with chloroform. The extract was dried with magnesium sulfate and the solvent was evaporated to yield a yellow paste. Treatment with ether containing a trace of methanol gave an unstable product **18**: mp 170–180°; ir (KBr) 3226 (OH), 1718, 1686 (C=O), 1020 cm^{-1} (SO); pmr (CF_3CO_2H, must be recorded rapidly), δ 2.62 (s, 3), 3.60, 4.02 (AB quartet, 2, J = 14 Hz), 7.5–8.2 (m, 8); esr (DMSO plus potassium *t*-butoxide) 1.68 (4 H), 0.4 (4 H) G; mass spectrum (70 eV), m/e 314.

3-Hydroxy-2-(methylsulfonyl)-3-(methylsulfonylmethyl)dibenzoheptanone (17b).—Substitution of 7.45 g of diethyl diphenate (25 mmol) in the process described for the preparation of **2** gave 9.15 g (92%) of **17b**: mp 173–177° [recrystallization (CH_3CO_2H) gave mp 187–188°]; ir (KBr) 3390 (OH), 1669 (C=O), 1299, 1129 cm^{-1} (SO_2); pmr ($CFCO_2H$) δ 3.22 (s, 6), 4.80 (broad singlet, 3), 7.2–8.0 (m, 8).

Anal. Calcd for $C_{18}H_{18}O_6S_2$: C, 54.82; H, 4.60; S, 16.23. Found: C, 54.70; H, 4.65; S, 16.23.

2,3-Diphenyl-1,4-naphthaquinone.—Dibenzyl sulfoxide (3.5 g, 15 mmol) and 1.5 g of sodium hydride (60 mmol) were stirred in

100 ml of DMF at 70°. Diethyl phthalate (3.4 g, 15 mmol) was added dropwise and the reaction mixture was stirred for 1 hr at 70° and 2 hr at 25°. The reaction mixture was added cautiously to water and the solution was extracted with ether. Removal of the ether left an oil that was chromatographed on an alumina column. A trace of *trans*-stilbene was eluted by hexane. A 1:1 hexane–benzene mixture eluted 1.1 g (24%) of the quinone, mp 132–138°. Recrystallization (CH_3CO_2H) gave mp 139.5–140.5° (lit.[16] mp 139–140°).

Reductions of 9a, 9b, 10a, 10b, 10c, and 15 by Raney Nickel.—Compound **9a** (567 mg) was stirred with 15 g of W-2 Raney nickel in 250 ml of refluxing ethanol for 5 hr. After cooling the mixture was filtered through a sintered-glass funnel and the residue was thoroughly washed with ethanol (caution, the residue is pyrophoric). Vacuum evaporation of the solvent left 221 mg (70%) of **hexahydro-3-methyl-1-indanone**: ir (CCl_4) 1739 cm^{-1} (C=O); pmr (CCl_4) δ 0.8–2.6 (m), 7.02 (d, J = 6.5 Hz). The material formed a 2,4-dinitrophenylhydrazone, mp 151–153° (lit.[17] mp 152–154°).

Treatment of **9b** (2.0 g) with 50 g of Raney nickel in 200 ml of refluxing ethanol in the manner described for **9a** yielded 550 mg of a pasty solid that was eluted from Florisil with chloroform to give 373 mg (25%) of **hexahydro-2-(methylsulfonyl)-3-methyl-1-indanol (20b)**: mp 151°; ir ($CHCl_3$) 3536 (OH), 1290, 1122 cm^{-1} (SO_2); pmr ($CDCl_3$ δ 0.8–2.4 (m, 14 total), 1.18 (d, J = 6.5 Hz), 2.6–2.8 (broad s, 1, exchangeable with D_2O), 2.9–3.2 (m, 4), 3.05 (s), 3.7–4.1 (m, 1).

Anal. Calcd for $C_{11}H_{20}O_3S$: 56.88; H, 8.68; S, 13.78. Found: C, 56.92; H, 8.40; S, 13.49.

Reduction of **10a** (2.0 g) in 200 ml of ethanol by 50 g of Raney nickel according to the procedure given for **9a** yielded 642 mg (64%) of **3,3,5-trimethylcyclohexanol** which solidified upon the addition of a seed crystal of an authentic sample prepared by a two-step reduction (hydrogen over Pd on C followed by $NaBH_4$) of isophorone. The ir spectra of the two samples were superimposable. 3,3,5-Trimethylcyclohexanol was also prepared from **10c** (500 mg) by treatment with 40 g of Raney nickel in 200 ml of refluxing ethanol for 12 hr. The yield of alcohol was 69 mg (47%).

Treatment of **10b** with Raney nickel in ethanol for periods up to 48 hr yielded only mixtures of sulfones. Where 10 g of the nickel–aluminum alloy was added in small portions to 3 g of **10b** in 100 ml of 10% aqueous sodium hydroxide with vigorous stirring, there was obtained after 1 hr 2.09 g (94%) of **2-(methylsulfonyl)-3,5,5-trimethylcyclohexanone (22)**. The ketone was isolated by filtration of the hot solution, followed by neutralization with hydrochloric acid, and extraction with chloroform. After the extracts were dried over magnesium sulfate, the solvent was evaporated to give material with mp 67–70° [recrystallization (ether) gave mp 71–72°]; ir (CCl_4) 1706 (C=O), 1309, 1134 cm^{-1} (SO_2); pmr (CCl_4) δ 1.02 (s, 6) 1.30 (d, 3, J = 6.5 Hz), 1.5–1.7 (m, 2 H), 2.3 (broad s, 2), 2.4–2.9 (m, 1), 2.97 (s, 3), 3.50 (d, 1, J = 10 Hz).

Anal. Calcd for $C_{10}H_{18}O_3S$: C, 55.03; H, 8.31; S, 14.66. Found: C, 55.08; H, 8.30; S, 14.69.

Compound **15** (2.0 g) when treated in the manner described for **9a** yielded 372 mg (36%) of **3-methyl-5,6,7,8-tetrahydro-1-naphthol (23)**: mp 95–96° (from hexane) (lit.[18] mp 98.5°); pmr (CCl_4) δ 1.5–2.0 (m, 4), 2.11 (s, 3), 2.3–2.8 (m, 4), 5.12 (s, 1, exchangeable in D_2O), 6.10 (broad s, 1), 6.33 (broad s, 1); mass spectrum (70 eV), m/e 162.

Treatment of 2.0 g of **15** in the manner previously described for **10b** by 15 g of aluminum–nickel alloy gave 1.55 g of an oil analyzed by pmr to contain 28% **3-methyl-1-naphthol (24a)** and 50% **2-(sulfonylmethyl)-3-methyl-1-naphthol (24b)**. Treatment of the oil with hexane dissolved **24a** and left **24b** as a semisolid mass. Cooling the hexane solution produced crystals of **24a**: mp 88–89° (lit.[18] mp 89.0–89.5°); pmr (CCl_4) δ 2.30 (s, 3), 5.52 (s, 1, exchangeable with D_2O), 6.45 (d, 1, J = 1.5 Hz), 7.1–7.8 (m, 4), 7.9–8 (m, 1). Recrystallization of the hexane-insoluble material from ether yielded **24b**: mp 93.5–94°; ir (CCl_4) 3195 (OH), 1399, 1258 cm^{-1} (SO_2); pmr ($CDCl_3$) δ 2.65 (s, 3), 3.15 (s, 3), 7.0–7.6 (m, 4), 8.2–8.4 (m, 1), 11.05 (s, 1, exchangeable with D_2O).

Anal. Calcd for $C_{12}H_{12}O_3S$: C, 61.01; H, 5.12; S, 13.55. Found: C, 60.96; H, 5.07; S, 13.50.

2-(Methylsulfinyl)-3,5,5-trimethyl-Δ²-cyclohexenone (21a).—Compound **10a** (9.2 g) was reduced with 20 g of zinc dust in 600 ml of acetic acid–ethanol (60:40) for 1 hr.[12] The mixture was filtered, neutralized with sodium bicarbonate, and extracted with benzene. Evaporation of the benzene left 2.2 g (13%) of **21a**: mp 77–78°; ir ($CHCl_3$) 1667 (C=O), 1605 (C=C), 1042 cm^{-1} (SO); pmr ($CDCl_3$) δ 1.05 (s, 6), 2.32, 2.38 (s, total 7), 2.90 (s, 3).

Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.98; H, 8.05; S, 15.98. Found: C, 59.88; H, 8.19; S, 15.89.

If the reduction was continued for a longer period of time a number of side products were formed including **2-(methylmercapto)-3,5,5-trimethyl-Δ³-cyclohexenone (21b)**: bp 82–84° (0.5 mm); pmr ($CDCl_3$) δ 1.02 (s, 6), 2.21 (broad s, 6), 2.35 (broad s, 4). Compound **21b** could be oxidized to **21a** by sodium metaperiodate.

Registry No.—Dimethyl sulfoxide, 67-68-5; dimethyl sulfone, 67-71-0; 2-chloro-2-(methylmercapto)-1,3-naphthindandione, 19916-37-1; 3-hydroxy-3-(methylsulfinylmethyl)dibenzocycloheptanone, 19916-51-9; **1a**, 19916-38-2; **2**, 19916-39-3; **4**, 19955-00-1; **6**, 19916-40-6; **7**, 19933-73-4; **8**, 21647-19-8; **9a**, 19916-41-7; **9b**, 19916-43-9; **10a**, 19916-44-0; **10b**, 19916-45-1; **10c**, 19916-46-2; **13** (R = H), 19916-47-3; **15**, 19916-48-4; **16**, 19916-49-5; **17a**, 19916-50-8; **17b**, 19916-52-0; **18**, 19916-53-1; **20b**, 19916-54-2; **21a**, 19916-55-3; **21b**, 19916-56-4; **22**, 19955-01-2; **24b**, 19916-57-5.

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