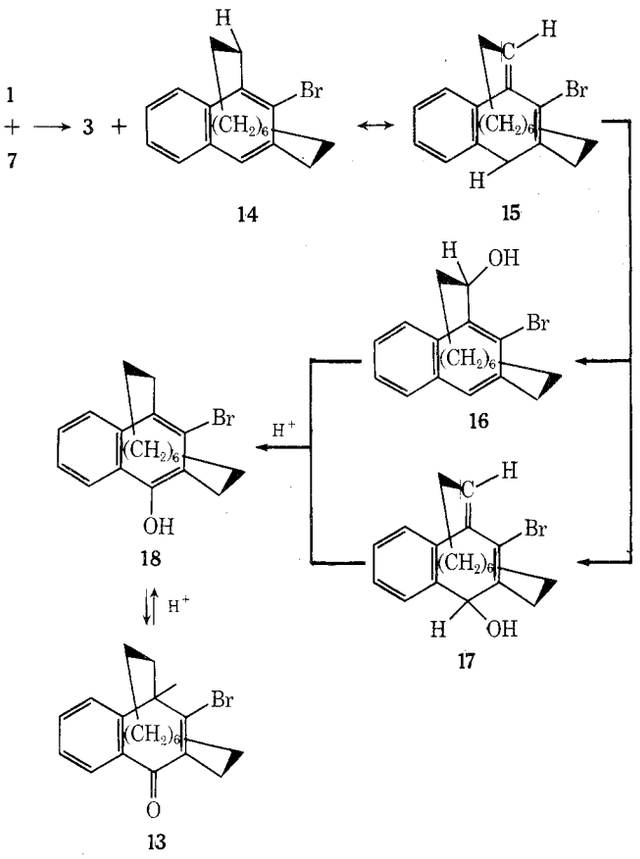
Scheme III



hols **16** and/or **17** could be formed[17] by a normal sequence of reactions from **14** or **15**; the conjugated ketone **13** is assumed to result by prototropic rearrangement of **16** and/or **17** upon acid work-up. That **13** would exist in the keto form rather than the phenolic enol form **18** is interesting and is attributed to relief of strain in the cyclophane system.[14]

Experimental Section

Reaction of 2 with Oxygen. The crude product obtained from **1** (0.75 g)[10] was separated into four bands by preparative chromatography as previously described[10] which were removed with 15% methanol in chloroform to give: (1) leading band, mixture of **1** and **3** (0.240 g); pure **3** (0.107 g, mp 39–40° from ethanol[10]) obtained from trailing edge after rechromatography;[18] (2) yellow oil (0.063 g), mostly **13**; (3) nearly pure **4** (0.101 g; 0.086 g by sublimation, mp 140–142°[10]); (4) alcohols **5** (0.248 g). The yields of **3**, **13**, **4**, and **5** based on consumed **1** were 32.5, 9, 16, and 44%, respectively.

Compound **13**: mp 110–112° from diethyl ether, 0.042 g, yellow solid; high-resolution mass spectral parent ion 360.1089 ($C_{20}H_{25}BrO$); ν 1660 cm^{-1}; pmr δ 7.7 (m, aromatic H, 1.0), 7.6–7.1 (m, aromatic H, 3.0), 3.0 (broad m, ArCH, 1.0), 2.6 (broad m, $=CCH_2$, 2.0), 2.3–0.5 (m, CH_2, 17.5).

Anal. Calcd for $C_{20}H_{25}BrO$: C, 66.48; H, 6.97; Br, 22.12. Found: C, 66.36; H, 7.17; Br, 21.72.

Perdeuteriotetrahydrofuran (98.5% d, E. Merck, Darmstadt) was distilled from $LiAlD_4$ prior to use. Calculations of protio to d_1 species were calculated from mass spectral data as described by Biemann.[19]

Reaction of 2 with *tert*-Butyl Hydroperoxide. A solution of *tert*-butyl hydroperoxide[20] (0.13 g, 1.45 mmol, 99.2% solution[21,22]) in dry (from $LiAlH_4$) tetrahydrofuran (5 ml) was added slowly to a solution of **2** (from **1**,[10] 1.00 g, 2.90 mmol) in dry tetrahydrofuran (15 ml) packed in ice,[15] and the resulting solution was stirred, under nitrogen, for 16 hr while warming to room temperature. The mixture was cooled and 50 ml of 5% aqueous hydrochloric acid was added; the organic material was extracted with ether which was subsequently dried ($MgSO_4$) and concentrated. Chromatography of the oil (0.513 g) obtained from the ether as described above [petroleum ether (bp 60–90°) followed by petroleum ether (bp 30–60°)–5% ether] gave: (1) **3** (1.93 mmol), mp 40–41°,[10] and (2) crude **4** (0.213 g, 98.4% yield; 0.119 g from acetone, 55% yield, mp 138–140°[10]).

Registry No.—**1**, 25097-45-4; **3**, 25097-46-5; **4**, 25097-53-5; **5**, 52358-29-9; **13**, 52358-30-2; *tert*-butyl hydroperoxide, 75-91-2.

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(13) While aryl radicals react with oxygen 10^3 faster than hydrogen abstraction,[11] models show that four bridge hydrogen atoms are in close proximity to the radical site in **6**, and thus are in high concentration relative to molecular oxygen.
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(17) Product **13** could form by related reactions involving abstraction of hydrogen from the other benzylic methylene group.
(18) Leading edge contained 52% of **1** and 48% of **2**; liquid chromatographic analysis [8 ft × ⅛ in. Porasil A, petroleum ether (bp 30–60°); 1 ml/min, six recycles].
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Reactions of *N*-Sulfinylamides with Sulfoxides Bearing Electronegative Substituents

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It has been reported that *N*-sulfinylsulfonamides react with sulfoxides to give sulfimides.[1a,b] In an attempt to get various types of sulfimides for investigation of reactivities, we used sulfoxides containing electron-withdrawing groups on the α carbon. The reaction did not afford the expected substituted sulfimides **7** but led to the rearranged derivatives **3** and their thermal decomposition products **4**.

Reaction of *N*-sulfinyl-*p*-toluenesulfonamide (**1a**) with 2-(methylsulfinyl)acetophenone (**2a**) in refluxing benzene gave 2-(methylthio)-2-(*p*-toluenesulfonamido)acetophenone (**3a**), 2,2-bis(*p*-toluenesulfonamido)acetophenone (**4a**), and 2-methylthioacetophenone (**5a**) in 5, 71, and 11% yields, respectively. The reaction in refluxing ether, however, necessitated prolonged heating and resulted in the formation of **3a** (61%) and **4a** (15%). The structure of **3a**

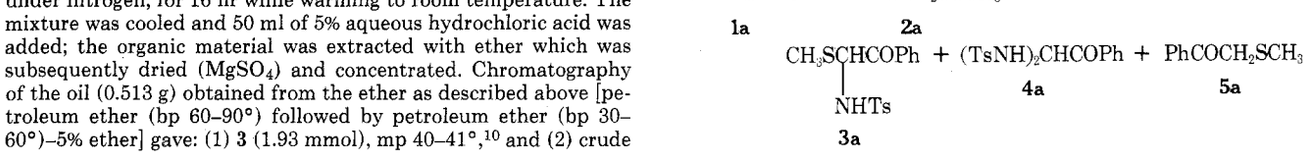


Table I
Reactions of *N*-Sulfinylamides 1a–c with Sulfoxides 2a–f

R^1 in 1	R^2 in 2	Solvent[a]	Temp, °C	Time, hr	Products (yields, %) 3	4	5	6
p-$MeC_6H_4SO_2$	PhCO	B	80	1.5	3a (5)	4a (71)	5a (11)	
p-$MeC_6H_4SO_2$	PhCO	E	35	14.0	3a (61)	4a (15)		
p-$MeC_6H_4SO_2$	*p*-$MeOC_6H_4CO$	B	80	7.0	3b (32)	4b (23)		
p-$MeC_6H_4SO_2$	*p*-$MeOC_6H_4CO$	E	35	14.0	3b (54)			
p-$MeC_6H_4SO_2$	MeOCO	B	80	7.5	3c (3)	4c (66)		
p-$MeC_6H_4SO_2$	*n*-$C_5H_{11}CO$	B	80	5.0		4d (58)		
p-$MeC_6H_4SO_2$	CN	B	80	6.5		4e (61)	5e (4)	6e (53)
p-$MeC_6H_4SO_2$	$C_6H_{11}CO$	B	80	1.5	3f (29)			
$MeSO_2$	PhCO	B	80	9.0	3g (15)	4g (50)		
PhCO	PhCO	B	45–50	5.5	3h (21)		5a (19)	
PhCO	*p*-$MeOC_6H_4CO$	B	40–45	8.0	3i (49)			

[a] B, benzene; E, ether.

was established as follows. The ir spectrum of **3a** shows N–H and carbonyl absorption bands at 3320 and 1665 cm^{-1}. The frequency of the carbonyl group suggests that **3a** is not phenacylidene (*p*-toluenesulfonamido)methylsulfurane, since the carbonyl group of known phenacylidenemethylphenylsulfurane appears at 1505–1470 cm^{-1}.[2] The nmr spectrum (DMSO-d_6) displays S–CH_3 (s, 3 H), *p*-CH_3 (s, 3 H), methine (d, J = 9.5 Hz, 1 H), phenyl protons (m, 9 H), and N–H (d, J = 9.5 Hz, 1 H) at δ 1.82, 2.35, 6.12, 7.15–8.15, and 8.82, respectively. Reduction of **3a** by Raney Ni in refluxing ethanol yielded a mixture of 2-(*p*-toluenesulfonamido)acetophenone (**9**, 10%) and **4a** (29%).

$$\underset{\text{NHTs}}{\overset{|}{\text{CH}_3\text{SCHCOPh}}} \xrightarrow[\text{ethanol}]{\text{Raney Ni}} \underset{\mathbf{9}}{\text{TsNHCH}_2\text{COPh}}$$

3a

This chemical property and physical data are consistent with the structure **3a.** Structural assignment of **4a** was based on ir data (NH and C=O absorptions at 3250 and 1690 cm^{-1}), nmr data [absorptions for *p*-CH_3 (s, 6 H), methine (t, J = 8.3 Hz, 1 H), aromatic protons (m, 13 H), and NH (d, J = 8.3 Hz, 2 H) at δ 2.32, 6.16, 7.00–8.00, and 8.75], and elemental analysis.

The reactions of **1a** with 2-(methylsulfinyl)-4′-methoxyacetophenone (**2b**), methyl methylsulfinylacetate (**2c**), and (methylsulfinyl)methyl cyclohexyl ketone (**2f**) in refluxing benzene gave the corresponding N-substituted *p*-toluenesulfonamides **3b,c,f** and bisamides **4b,c,** respectively.

The reactions with 1-(methylsulfinyl)-2-heptanone (**2d**) and cyanomethyl methyl sulfoxide (**2e**) led only to the bisamides **4d** and **4e** along with di(methylthio)acetamide (**6e**).

The reactions using *N*-sulfinylmethanesulfonamide (**1b**) and *N*-sulfinylbenzamide (**1c**) gave similar results. These results are summarized in Table I.

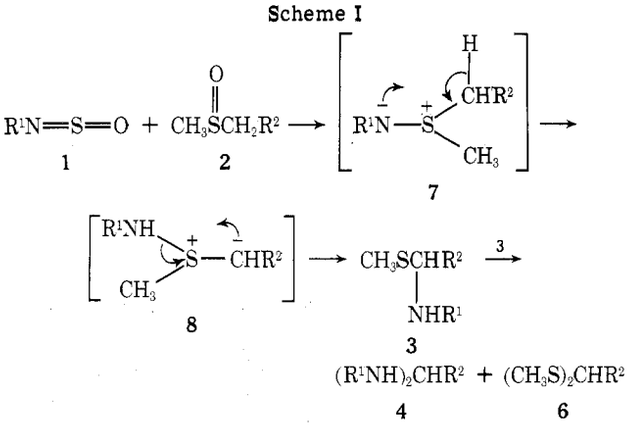
Possible mechanisms for formation of **3** and **4** are shown in Scheme I. Similar results in pyrolysis of *N*-acetyldialkylsulfimides have been reported by Swern, *et al.*[3] In the above reactions, our failure to isolate the expected sulfimides **7** may be due to the methylene group being activated by the electron-withdrawing groups such as the carbonyl (including ester) and cyano groups.

Irradiation of a methanol solution of **3i** with a 500-W

$$\underset{\text{NHCOPh}}{\overset{|}{\text{CH}_3\text{SCHCOC}_6\text{H}_4\text{-}p\text{-OCH}_3}} \xrightarrow{h\nu} \underset{\text{PhCONHCHCOC}_6\text{H}_4\text{-}p\text{-OCH}_3}{\overset{|}{\text{PhCONHCHCOC}_6\text{H}_4\text{-}p\text{-OCH}_3}}$$

3i **10**

Scheme I



high-pressure arc afforded 1,2-di-*p*-anisyl-1,2-dibenzamidoethane (**10**), structural assignment to which could be made with confidence on the basis of its analysis and spectroscopic properties (see Experimental Section), in 27% yield.

Experimental Section[4]

General Procedure. The reactions were run under dry N_2. The temperature was held at the boiling points of benzene or ether until the evolution of sulfur dioxide ceased.

Materials. *N*-Sulfinyl-*p*-toluenesulfonamide,[5] *N*-sulfinylmethanesulfonamide,[5] *N*-sulfinylbenzamide,[6] 2-(methylsulfinyl) acetophenone,[7] 2-(methylsulfinyl)-4′-methoxyacetophenone,[7] 1-(methylsulfinyl)-2-heptanone,[7] (methylsulfinyl)methyl cyclohexyl ketone,[7] and cyanomethyl methyl sulfoxide[8] were prepared according to the established procedures. Methyl methylsulfinylacetate was synthesized by oxidation of methyl methylthioacetate [bp 162–163° (760 mm)], which was prepared from methyl chloroacetate and methyl mercaptan sodium salt, with hydrogen peroxide in 72% yield: bp 103–104° (2.5 mm); $n^{21.5}D$ 1.4840; ir (neat) 1730 (C=O) and 1045 cm^{-1} (SO); nmr (CCl_4) δ 2.77 (s, 3 H, CH_3S=O), 3.73 (s, 2 H, $-CH_2-$), and 3.80 (s, 3 H, $-OCH_3$).

Reaction of *N*-Sulfinyl-*p*-toluenesulfonamide (1a) with 2-(Methylsulfinyl)acetophenone (2a). A solution of **1a** (6.00 g, 27.6 mmol) and **2a** (5.00 g, 27.4 mmol) in 50 ml of dry benzene was refluxed for 1.5 hr. After the solution was allowed to stand at ambient temperature overnight, the resulting crystals (4.0 g) were filtered. The crystals were recrystallized from ethanol to give pure **2,2-bis(*p*-toluenesulfonamido)acetophenone (4a)**: nmr (DMSO-d_6) δ 2.32 (s, 6 H, *p*-CH_3), 6.16 (t, J = 8.3 Hz, 1 H, >CH–), 7.00–8.00 (m, 13 H, aromatic protons), and 8.75 (d, J = 8.3 Hz, 2 H, NH); mass spectrum (70 eV) no molecular ion, *m/e* 212 ($M^+ - TsNH_2 - Ph$), 171 ($TsNH_2$), and 105 ($PhCO^+$).

The filtrate was concentrated to afford a mixture of **4a** and **2-(methylthio)-2-(*p*-toluenesulfonamido)acetophenone (3a)**. Pure samples of individual **4a** (0.50 g) and **3a** (0.50 g, 5%) were isolated by repeated recrystallization of the mixture from ethanol.

Table II
(Methylthio)(substituted amido)methanes 3
$(CH_3S)(R^1NH)CHR^2$

Compd	R^1	R^2	Mp, °C	Ir (Nujol), cm^{-1} ν_{NH}	Ir (Nujol), cm^{-1} $\nu_{C=O}$	Empirical formula[a]
3a	p-$MeC_6H_4SO_2$	PhCO	162–166	3320	1665	$C_{16}H_{17}NO_3S_2$
3b	p-$MeC_6H_4SO_2$	p-$MeOC_6H_4CO$	149–151	3330	1655	$C_{17}H_{19}NO_4S_2$
3c	p-$MeC_6H_4SO_2$	MeOCO	89–90	3240	1725	$C_{11}H_{15}NO_4S_2$
3f	p-$MeC_6H_4SO_2$	$C_6H_{11}CO$	144–145	3270	1665	$C_{16}H_{23}NO_3S_2$
3g	$MeSO_2$	PhCO	135–140	3280	1670	$C_{10}H_{13}NO_3S_2$
3h	PhCO	PhCO	141–142	3360	1670, 1635	$C_{16}H_{15}NO_2S$
3i	PhCO	p-$MeOC_6H_4CO$	155–156	3360	1660, 1635	$C_{17}H_{17}NO_3S$

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds in the table.

Table III
***N,N'*-Substituted Methylene Bis(substituted amides) 4**
$(R^1NH)_2CHR^2$

Compd	R^1	R^2	Mp, °C	Ir (Nujol), cm^{-1} ν_{NH}	Ir (Nujol), cm^{-1} $\nu_{C=O}$	Empirical formula[a]
4a	p-$MeC_6H_4SO_2$	PhCO	206–208	3250	1690	$C_{22}H_{22}N_2O_5S_2$
4b	p-$MeC_6H_4SO_2$	p-$MeOC_6H_4CO$	176–178	3270	1675	$C_{23}H_{24}N_2O_6S_2$
4c	p-$MeC_6H_4SO_2$	MeOCO	189–190	3270	1745	$C_{17}H_{20}N_2O_6S_2$
4d	p-$MeC_6H_4SO_2$	n-$C_5H_{11}CO$	160–165	3250	1725	$C_{21}H_{28}N_2O_5S_2$
4e	p-$MeC_6H_4SO_2$	CN	156–158	3240		$C_{16}H_{17}N_3O_4S_2$
4f	$MeSO_2$	PhCO	200–205	3200	1680	$C_{10}H_{14}N_2O_5S_2$

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds in the table.

The combined yield of **4a** was 4.50 g (71%). **3a** showed the following physical properties: nmr (DMSO-d_6) δ 1.82 (s, 3 H, $-SCH_3$), 2.35 (s, 3 H, p-CH_3), 6.12 (d, J = 9.5 Hz, 1 H, >CH–), 7.15–8.15 (m, 9 H, phenyl protons), and 8.82 (d, J = 9.5 Hz, 1 H, NH); mass spectrum (70 eV) no molecular ion, m/e 288 ($TsNHCHCOPh^+$), 230 ($M^+ - PhCO$), and 212 ($TsNHCHCO^+$).

The filtrate was combined, concentrated, and chromatographed on alumina using benzene as eluent to give 0.51 g (11%) of 2-(methylthio)acetophenone (**5a**), which was identical with an authentic sample[9] by comparison of ir spectra and the retention time of glpc.

In the reaction using ether as solvent at the refluxing temperature for 14 hr, **3a** and **4a** were obtained in 61 and 15% yields.

Reaction of *N*-Sulfinyl-*p*-toluenesulfonamide (1a) with Cyanomethyl Methyl Sulfoxide (2e). The reaction was carried out at 80° for 6.5 hr using **1a** (6.50 g, 0.03 mol) and **2e** (3.10 g, 0.03 mol) in dry benzene (60 ml). After similar treatment, **2,2-bis(*p*-toluenesulfonamido)acetonitrile** (**4e**), cyanomethyl methyl sulfide (**5e**), and **dimethylthioacetamide** (**6e**) were isolated in 3.50 (61%), 0.20 (4%), and 1.21 g (53%) yields, respectively. The crude product **4e** was recrystallized from benzene–ethanol to give a pure sample: mp 156–158°; nmr (DMSO-d_6) δ 2.36 (s, 6 H, p-CH_3), (t, J = 9 Hz, 1 H, >CH–), 7.15–7.80 (m, 8 H, phenyl protons), and 9.50 (d, J = 9 Hz, 2 H, NH); mass spectrum (70 eV) no molecular ion, m/e 287 ($M^+ - PhCH_3$), 261 ($M^+ - PhCH_3 - CN$), and 224 ($M^+ - Ts$). The structure **5e** was determined by comparison of the ir spectrum and glpc behavior with those of an authentic sample.[8]

The crude product **6e** was recrystallized from benzene to give a pure sample: mp 148.5–149°; ir (Nujol) 3340 and 3230 (NH) and 1645 cm^{-1} (C=O); nmr (DMSO-d_6) δ 2.13 (s, 6 H, SCH_3), 4.39 (s, 1 H, >CH–), 7.00–7.30 (broad, 1 H, NH), and 7.30–7.60 (broad, 1 H, NH); mass spectrum (70 eV) m/e 151 (M^+), 107 ($M^+ - CONH_2$), and 105 ($M^+ - CH_3S + H$).

Anal. Calcd for $C_4H_9NOS_2$: C, 31.79; H, 6.00; N, 9.27. Found: C, 31.89; H, 5.91; N, 9.27.

Reactions of *N*-Sulfinylamides 1a–c with Sulfoxides 2a–f. The reactions were carried out in a similar manner. After similar treatments, the products,[10] **3b,c,f–i** and **4b–d,f**, were obtained by recrystallization. The results are summarized in Table I. Melting points and NH and carbonyl absorptions in the ir spectra of **3** and **4** are shown in Tables II and III.

Reduction of 3a. A solution of 0.50 g (1.5 mmol) of **3a** in 100 ml of ethanol containing 1 g of Raney Ni was allowed to stir under reflux for 4 hr. The organic layer was separated and allowed to stand overnight. The resulting crystals were filtered, followed by recrystallization from benzene–ethanol to give 40 mg (10%) of pure **2-(*p*-toluenesulfonamido)acetophenone** (**9**): mp 195–197°; ir (Nujol) 3200 (NH), 1670 (C=O), 1345 (SO_2), and 1165 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 2.30 (s, 3 H, p-CH_3), 5.08 (d, J = 7.0 Hz, 1 H, $>CH_aH_b$), 5.70 (d, J = 7.0 Hz, 1 H, $>CH_aH_b$), 7.08 (d, J = 7.0 Hz, 1 H, NH), and 7.30–7.70 (m, 9 H, phenyl protons); mass spectrum (70 eV) m/e 288 ($M^+ - H$), 171 ($TsNH_2^+$), and 105 ($PhCO^+$).

Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.28; H, 5.19; N, 4.84. Found: C, 62.27; H, 5.07; N, 4.92.

The filtrate was concentrated and the resulting crystals were recrystallized from benzene to give pure **4a** (0.20 g, 29%).

Irradiation of 3i. A solution of **3i** (0.55 g, 1.75 mmol) in 20 ml of methanol was irradiated for 20 hr with a 500-W high-pressure mercury arc under nitrogen at room temperature. The resulting precipitate was filtered and recrystallized from benzene–ethanol to give 0.128 g (27%) of **1,2-di-*p*-anisoyl-1,2-dibenzamidoethane** (**10**): mp 209–211°; ir (Nujol) 3280 (NH), 1670 (C=O), and 1630 cm^{-1} (C=O); nmr (DMSO-d_6) δ 3.84 (s, 6 H, OCH_3), 6.10–6.35 (broad, 2 H, >CH–), 6.90–8.15 (m, 18 H, phenyl protons), and 8.90–9.20 (broad, 2 H, NH); mass spectrum (70 eV) m/e 536 (M^+), 415 ($M^+ - PhCONH_2$), 401 ($M^+ - MeOC_6H_4CO$), and 280 ($M^+ - PhCONH_2 - MeOC_6H_4CO$).

Anal. Calcd for $C_{32}H_{28}N_2O_6$: C, 71.63; H, 5.26; N, 5.22. Found: C, 71.28; H, 5.09; N, 5.17.

Registry No.—**1a,** 4104-47-6; **1b,** 40866-96-4; **1c,** 20043-21-4; **2a,** 2813-22-1; **2b,** 2813-23-2; **2c,** 52147-67-8; **2d,** 2863-47-0; **2e,** 52109-49-6; **2f,** 2863-48-1; **3a,** 52109-50-9; **3b,** 52109-51-0; **3c,** 52109-52-1; **3f,** 52147-68-9; **3g,** 52109-53-2; **3h,** 52109-54-3; **3i,** 52109-55-4; **4a,** 52109-56-5; **4b,** 52109-57-6; **4c,** 52109-58-7; **4d,** 52109-59-8; **4e,** 52109-60-1; **4f,** 52109-61-2; **6e,** 5311-18-2; **9,** 30057-92-2; **10,** 1183-24-0; methyl methylthioacetate, 16630-66-3.

Supplementary Material Available. Nmr and mass spectral data of **3b,c,f–i** and **4b–d,f** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3412.

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(10) See paragraph at end of paper regarding supplementary material.

Sulfonation of Unsaturated Compounds. I. Sulfonation of Branched-Chain Ketones with Sulfur Trioxide. A One-Step Synthesis of Tetramethylene Sulfate through a Retro Pinacol-Type Rearrangement

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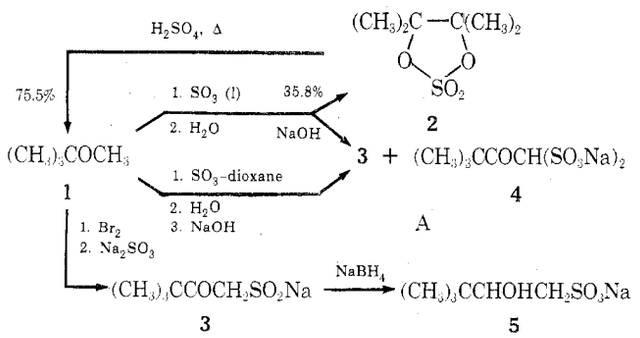
The sulfonation of aldehydes,[1] ketones,[1,2] and carboxylic acids[3] with sulfur trioxide and its adducts[4] is a facile process[4] leading to the corresponding sulfonic acids in which the sulfo group is attached α to the carboxylic function.[1-4] The products are isolated ordinarily as the corresponding salts after neutralization of the acidic sulfonation mixture. Consequently, the nature of possible intermediates has not been established and the presence of some by-products may have been overlooked. Moreover, the purity of the isolated products is questionable in many cases, since disulfonates may accompany the desired monosulfonates, and the separation between the two might prove to be very difficult.

It has been established[1,3] that carbonyl compounds which contain no α-hydrogen atoms are inert toward sulfur trioxide. It has also been shown that sulfonation of γ-branched olefins[5] is accompanied by the migration of either methyl or hydrogen to the incipient adjacent positive center.

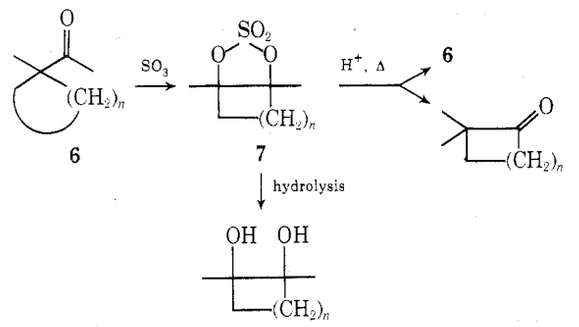
This note presents results of a study of sulfur trioxide sulfonation of pinacolone as a model compound (Scheme I).

Scheme I

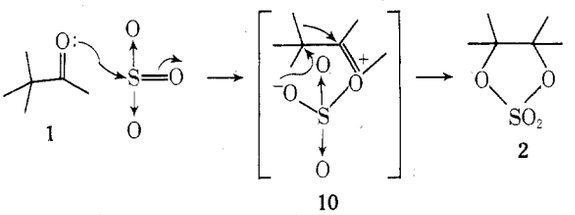


Direct sulfonation of pinacolone with liquid sulfur trioxide afforded a 36% yield of the cyclic tetramethylene sulfate **2**. The isolation of **2** is interesting both synthetically and mechanistically. First, **2** is required for the preparation of highly C-methylated compounds.[6] Alternative methods of preparation are laborious and result in overall low yields.[6] Secondly, other cyclic sulfates may be prepared using the same method. An extension of our findings would be the development of useful methods for initial ring expansion followed by formation of either ketones or glycols according to Scheme II.

Scheme II



In accord with the suggested mechanisms for the sulfonations of ketones,[1] and for the anhydrous acid-catalyzed epoxide–ketone[7] rearrangement the following mechanism for the formation of **2** is proposed.



The yield of sulfate **2** shows that migration of a methyl group from the adjacent quarternary carbon, to form a stable tertiary carbonium ion, successfully competes with the abstraction of available hydrogen from the α position. Rearranged products obtained in the sulfonation of γ-branched olefins[5] presumably arise from an analogous zwitterionic species.

We have found that heating of **2** under aqueous acidic conditions resulted in a rapid pinacol-type rearrangement to give back the starting pinacolone in good yield. This appears to be the first example of a direct transformation from a cyclic sulfate to a ketone.

The monoketosulfonate[8] **3** was not the only sulfonate obtained by direct sulfonation of pinacolone. The nmr spectrum of the initial product (after extractions and crystallizations) always revealed two types of *t*-butyl groups[9] and both methylene and methine protons. This and the finally separated disulfonate **4** after numerous crystallizations clearly showed the main product **3** to contain an appreciable amount of the disulfonate **4**. Disulfonate **4** was formed regardless of whether sulfur trioxide itself or the dioxane complex[4] was used. The alternative route *via* bromination followed by the Strecker reaction[10] proved to be the way of choice for obtaining pure **3** (Scheme I). Selective reduction of **3** with sodium borohydride afforded **5** in high yield. This suggests a convenient method of obtaining hydroxysulfonic acids from ketosulfonates.

Experimental Section

Tetramethylethylene sulfate (2). Sulfur trioxide (20.5 g, 0.256 mol) was distilled out of Sulfan (stabilized liquid sulfur trioxide, Allied Chemicals) into a cooled (0–5°) stirred solution of 1,2-dichloroethane (100 ml). Pinacolone **1** (25.65 g, 0.256 mol) in 45 ml of 1,2-dichloroethane was added over a period of 25 min. The exothermic reaction caused the temperature of the reaction mixture to reach 11°. Stirring was continued for 20 min, allowing the temper-