[Contribution from the Department of Chemistry of the Virginia Polytechnic Institute]

# Unsaturated Cyclic Sulfones. VI. Benzylsulfonyldienes *via* Ring Cleavage

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Several 2,5-dihydrothiophene 1,1-dioxides have been found to undergo ring cleavage in the presence of Grignard reagents. Alkylation of the intermediate dienesulfonylmagnesium halide with benzyl chloride, represents a novel synthesis of benzylsulfonyldienes.

In 1937 van Zuydewijn[3] reported that an ether or benzene solution of butadiene sulfone reacts with two molecules of methylmagnesium iodide (or ethylmagnesium iodide) to give some methane (or ethane) and an insoluble addition product. This product to which van Zuydewijn said that one could probably attribute the formula $R(MgI)_2$ failed to yield an acid after carbonation.

Recently Field and co-workers[4] have studied many reactions of Grignard reagents of aryl alkyl sulfones and found that such reagents add to carbonyl compounds and undergo other useful reactions characteristic of the more familiar types of Grignard reagents.

Truce and Buser[5] studied the reaction of ethylmagnesium bromide with tetrahydrothiophene 1,1-dioxide to give an intermediate which, with benzaldehyde, gave 2 - (phenylhydroxymethyl)tetrahydrothiophene 1,1-dioxide in 4% yield.

There are examples of the use of *n*-butyllithium in the metalation of certain sulfones, followed by carbonation.[6]

In preliminary studies[2] of the reaction of methylmagnesium chloride and of ethylmagnesium bromide with 2,5-dihydrothiophene 1,1-dioxide (I) the evolution of gas clearly indicated that organometallic transfer occurred. However, the addition of electrophilic reagents, such as aldehydes and alkyl halides, to the reaction mixture in the usual fashion produced no identifiable substances. Further work in this laboratory with I, 2-methyl-2,5-dihydrothiophene 1,1-dioxide (II), and 3-methyl-2,5-dihydrothiophene 1,1-dioxide (III) revealed the unusual behavior of these compounds in the presence of Grignard reagents.

The addition of an ether solution of ethylmagnesium bromide to a solution of I in benzene (inverse addition) in a 1:1 mole ratio showed that the Grignard reagent was consumed (96%) in the formation of ethane, and upon hydrolysis of the reaction mixture none of the original sulfone was recovered. Thus, I possessed only one active hydrogen per molecule. In a similar manner the use of a 1:2 mole ratio of sulfone I to Grignard reagent resulted in the reaction of the Grignard reagent, one half of which was converted to gas. After hydrolysis of the reaction mixture only in tractable resins were isolated. The addition of a solution of I in benzene to the ethereal Grignard reagent (direct addition) in a 1:1 mole ratio gave one equivalent of hydrogen per mole of sulfone; however, upon hydrolysis of the reaction mixture I was recovered in 46% yield. Thus, the order of addition of reactants does influence the course of reaction. In like manner I was added to an excess (1:2 mole ratio) of ethylmagnesium bromide. In addition to the gas which was evolved, an oil was obtained (after hydrolysis) which distilled b.p. 40°/0.008 mm., accompanied by decomposition. Analytical data supported the molecular formula $C_{12}H_{22}S_2O_3$ for the distillate. Although the structure is not established, it is suggested that the oil may be the anhydride of an unsaturated sulfinic acid as discussed later. The gas data and this oil led to the hypothesis that the attack of the Grignard reagent on the sulfone resulted in the cleavage of the ring.

In an attempt to confirm the ring opening hypothesis a study of the three sulfones (I, II, III) was undertaken. The direction of ring opening had to be established with II and III. In order to minimize the formation of polymer, the reactions of the sulfone and the Grignard reagent were performed at −20°. Attempts to isolate the free pentadienylsulfinic acid *per se* from its halomagnesium salt (V) or to prepare simpler derivatives such as a Diels-Alder adduct or the 2,4-dinitrophenyl sulfone from acidified V were unsuccessful.

The salt of the dienylsulfinic acid which was found to be stable was the one actually prepared in the ring opening reaction (inverse addition in a 1:1 mole ratio of sulfone to Grignard reagent).

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[2] Taken in part from the Ph.D. dissertation of G. R. T., March 1957.

[3] E. deR. van Zuydewijn, *Rec. trav. chim.*, **56**, 1047 (1937).

[4] L. Field and J. M. McFarland, *J. Am. Chem. Soc.*, **75**, 5582 (1953); L. Field, *J. Am. Chem. Soc.*, **78**, 92 (1956); L. Field, J. R. Holsten, and R. D. Clark, *J. Am. Chem. Soc.*, **81**, 2572 (1959); L. Field and E. T. Boyd, *J. Org. Chem.*, **26**, 1787 (1961).

[5] W. E. Truce and K. R. Buser, *J. Am. Chem. Soc.*, **76**, 3577 (1954).

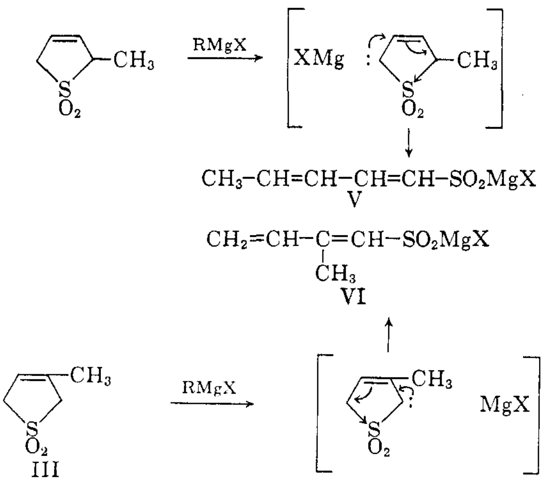
[6] W. E. Truce and M. F. Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951); H. Gilman and D. L. Esmey, *J. Am. Chem. Soc.*, **75**, 298 (1953).

The reaction of ethylmagnesium bromide with II at −20° produced a solid, insoluble in the reaction medium. When attempts to alkylate the solid *in situ* failed, the solid was separated by filtration and successfully alkylated in an ethanolic solution.

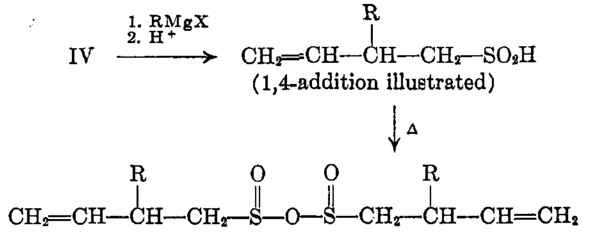
Salts of three dienylsulfinic acids were prepared using the ring opening reactions from I, II, and III. The salts from II and III are quite stable. They are white amorphous powders whose dust is quite irritating to nasal passages. After several months in light at 25° in a sealed vial there was no change in color or consistency. The corresponding salt from I was found to be less stable. Shelf-life of this salt was much shorter as illustrated by darkening in color and apparent polymerization. In fact, in order to alkylate this salt special precautions to exclude free-radical initiators had to be employed. No such precautions were necessary for the other two salts. Ultraviolet spectra of the three salts clearly revealed the diene moiety present in each. The spectra of the alkanesulfinic salts prepared during the proof of structure of the dienylsulfinic salts showed no conjugated diolefinic absorption.

For convenience the salts are referred to as halomagnesium salts, $RSO_2MgX$, although the true composition may well involve a mixture[7] or perhaps a specific complex as has been suggested for certain Grignard reagents.[8]

The ring opening reactions for II and III are shown in the following scheme.



The possibility that the oil mentioned earlier, from I, may be an anhydride of a sulfinic acid could be explained as follows:



$$\mathrm{IV} \xrightarrow[2.\ H^+]{1.\ RMgX} CH_2{=}CH{-}\overset{R}{\overset{|}{C}}H{-}CH_2{-}SO_2H$$

(1,4-addition illustrated)

$$\downarrow \Delta$$

$$CH_2{=}CH{-}\overset{R}{\overset{|}{C}}H{-}CH_2{-}\overset{O}{\overset{\|}{S}}{-}O{-}\overset{O}{\overset{\|}{S}}{-}CH_2{-}\overset{R}{\overset{|}{C}}H{-}CH{=}CH_2$$

Ring opening in I to give the butadienylsulfinic salt (IV) may occur by rupture of either carbon-sulfur bond; however, the cleavage reactions in II and III are quite specific and occur as shown. The manner of ring opening in II is what would be expected with the Grignard reagent abstracting a proton from the less hindered and probably more reactive position 5. The bond between position 2 and the sulfur atom is therefore broken. In the case of III the formation of VI rather than its isomer is perhaps not so easily understood. It is interesting from steric considerations that the Grignard reagent preferentially attacked the more sterically hindered position in III, and it was surprising that the use of "bulkier" Grignard reagents such as phenylmagnesium bromide and 2,6-dimethylphenylmagnesium iodide attacked at position 2 exclusively with the formation of a salt corresponding to VI.

The successful alkylation of IV, V, and VI with benzyl chloride to give a series of benzylsulfonyl-1,3-butadienes represents a new and useful method of synthesis of these substituted, conjugated diolefins. The following sulfones were prepared: 1-benzylsulfonyl-1,3-butadiene, $CH_2{=}CH{-}CH{=}CH{-}SO_2{-}CH_2{-}C_6H_5$ (VII), 1-benzylsulfonyl-1,3-pentadiene $CH_3{-}CH{=}CH{-}CH{=}CH{-}SO_2{-}CH_2{-}C_6H_5$ (VIII), and 1-benzylsulfonyl-2-methyl-1,3-butadiene, $CH_2{=}CH{-}C(CH_3){=}CH{-}SO_2{-}CH_2C_6{-}H_5$ (IX). The structures of these compounds were established by physical data and by reduction to the corresponding benzyl alkyl sulfones. The hydrogenation of IX gave a sulfone which was previously unknown. The independent preparation of this compound is shown in the following scheme and is indicative of the method employed here for the preparation of sulfones from Grignard reagents *via* sulfur dioxide. The method appears to be a general one, and four benzyl alkyl sulfones were prepared.

The three benzylsulfonyldienes synthesized in the present investigation were not the first conjugated diolefins to be prepared which contained sulfonyl groups.[9]

The ultraviolet spectra of VII, VIII, and IX ($\lambda_{max}$ 236, 248, and 240 m$\mu$, respectively) are of interest because of the absence of the characteristic benzene ring absorption; however, the absorption maxima occur in the region of the spectrum charac-

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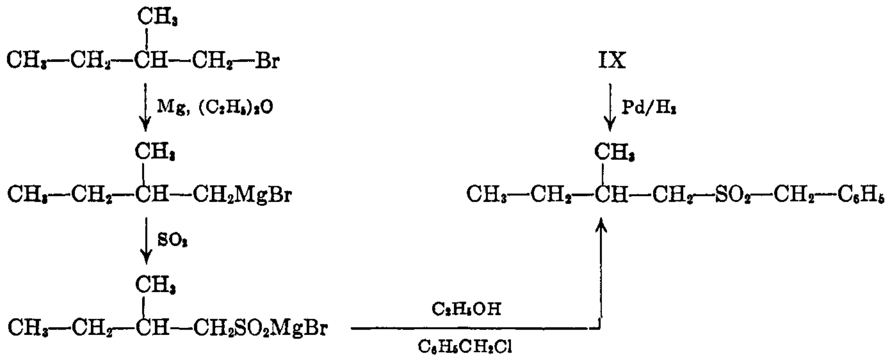
(7) V. Migrdichian, "Organic Synthesis," Reinhold Publishing Corp., New York, Vol. I, 1957, pp. 604, 717.

(8) R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **79**, 3476 (1957); R. E. Dessy, *J. Org. Chem.*, **25**, 2260 (1960).

(9) E. Rothstein, *J. Chem. Soc.*, 309 (1937); V. Baliah and Sp. Shanmuganathan, *J. Indian Chem. Soc.*, **35**, 31 (1958); *J. Org. Chem.* **23**, 1233 (1958); A. P. Terent'ev and A. V. Dombrovskii, *Zhur. Obshchei Khim.*, **21**, 704 (1951).



teristic of 1,3-dienes. The spectra were obtained in ethanol and in cyclohexane, and only a very slight solvent influence was observed. The reduction of IX gave benzyl 2-methylbutyl sulfone whose spectrum showed $\lambda_{max}$ 253, 259, 265, and 269 mμ. As expected in this case the characteristic diene absorption is of course absent, and the benzene absorption is clearly recognized.

## EXPERIMENTAL[10]

*2,5-Dihydrothiophene 1,1-dioxide* (I). Crude I, prepared during the course of earlier work,[11] was purified and dried prior to use.

*2-Methyl-2,5-dihydrothiophene 1,1-dioxide* (II). The procedure used here was a modification of the previously reported method.[12] Reaction time was reduced to 2 hr., and the temperature employed was 80–85°. Treatment of the crude reaction product with water, followed by extraction with chloroform, drying with magnesium sulfate, and the removal of solvent gave an almost colorless oil. Repetition of this procedure gave a colorless oil, $n^{20}_{D}$D 1.4942, $d^{20}_{4}$ 1.2433 in 84% yield based on an 85% *trans* content of the diene.[13]

*3-Methyl-2,5-dihydrothiophene 1,1-dioxide* (III). The procedure used was essentially that reported by Krug and Yen[14] and the purified III was obtained in 84% yield.

*Preparation of Grignard reagents.* Solutions of methylmagnesium chloride and of ethylmagnesium bromide in ethyl ether were prepared according to the customary procedure. The concentration of the Grignard reagent in the solutions was generally 0.1 mole per 100 ml. of ether. In one preparation of ethylmagnesium bromide from 21.8 g. (0.20 mole) of ethyl bromide and 4.9 g. (0.20 mole) of magnesium in 150 ml. of ether, titration of an aliquot of the Grignard reagent by the Gilman method[15] showed 0.18 mole of reagent to be present in solution. All preparations were performed under a nitrogen atmosphere. After the Grignard reagent was prepared the sulfone was either added to the Grignard reagent (direct addition) or the Grignard reagent was added to the sulfone (inverse addition). Gas evolved during reaction and hydrolysis was measured with a wet-test meter. The gas evolved from the reaction flask was passed through a Dry Ice–methanol cooled trap (−60°) before volume measurements were made, and all volumes were corrected to standard pressure and temperature.

*1:1 Mole ratio of Grignard reagent and* I. The Grignard reagent was slowly added (inverse addition) to a solution of I in dry benzene, and the gas which was evolved represented 96% of the Grignard reagent employed.

*2:1 Mole ratio of Grignard reagent and* I. In a similar manner methylmagnesium chloride solution was slowly added (inverse addition) to a solution of I in dry ether, and the gas obtained represented 44% of the Grignard reagent employed. Upon hydrolysis of the reaction mixture there was obtained an additional 10% of gas.

*1:1 Mole ratio of Grignard reagent and* I. A solution containing 0.18 mole[16] of ethylmagnesium bromide was prepared. To this solution 21.2 g. (0.18 mole) of I dissolved in 156 ml. of dry benzene was added (direct addition), and the gas obtained represented 35% of the Grignard reagent employed. Hydroquinone was added to the chilled reaction mixture which was then hydrolyzed with cold dilute sulfuric acid. An additional 8% of gas was obtained. The organic layer was separated, and the solvent was removed at reduced pressure to give some crude solid. The water solution was extracted with six 30-ml. portions of chloroform, and the removal of the chloroform gave more crude solid. The two solid fractions were combined and recrystallized from ethanol to give 9.8 g. (46%) recovery of I.

*2:1 Mole ratio of Grignard reagent and* I. The Grignard reagent was prepared by adding a solution of 98.1 g. (0.90 mole) of ethyl bromide in 800 ml. of dry ether to 21.9 g. (0.90 g.-atom) of magnesium. To this solution was added (direct addition) 47.2 g. (0.40 mole) of I in 300 ml. of solution. A solution of 113.5 g. (0.90 mole) of distilled methyl sulfate in 125 ml. of ether was then added over a 30-min. period. The mixture was heated to 40–45° for 12 hr. and then cooled and hydrolyzed in the usual manner; very little polymer had formed. The organic phase was separated, and removal of the ether and benzene at reduced pressure gave 31 g. of dark, viscous oil. The water phase was extracted with six 50-ml. portions of chloroform, and the removal of the chloroform gave 15.7 g. of dark, red oil.

The 15.7 g. of red oil was subjected to a vacuum distillation and 5.3 g. of a light yellow oil, b.p. 40°/0.008 mm., $n^{27}_{D}$D 1.5298, was obtained. The remainder charred in the distillation flask. Qualitative analysis of the distilled oil showed sulfur present and halogens absent.

*Anal.* Calcd. for $C_{12}H_{22}S_2O_3$: C, 51.76; H, 7.96; S, 23.03. Found: C, 52.10; H, 7.85; S, 23.26.

The infrared spectrum of the oil (film between salts) showed the following principal frequencies: 3472, 2959, 2817,

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[10] All melting points and boiling points are in °C. and uncorrected. The analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained using a Beckman IR-5 spectrophotometer, and ultraviolet spectra were obtained using a Perkin-Elmer Spectracord. Anhydrous sulfur dioxide was supplied through the courtesy of the Virginia Smelting Co., West Norfolk, Va., and Enjay Chemical Co., Elizabeth, N. J., donated the 1,3-pentadiene used in the preparation of II.

[11] R. C. Krug, G. R. Tichelaar, and F. E. Didot, *J. Org. Chem.*, **23**, 212 (1958).

[12] R. C. Krug and J. A. Rigney, *J. Org. Chem.*, **23**, 1697 (1958).

[13] E. J. Frank, *J. Am. Chem. Soc.*, **69**, 2313 (1947).

[14] R. C. Krug and T. F. Yen, *J. Org. Chem.*, **21**, 1082 (1956).

[15] H. Gilman, P. D. Wilkinson, W. P. Fishel, and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923).

1818, 1626, 1587, 1453, 1412, 1370, 1307, 1250, 1136, 1044, 1020, 962, 918, 802, 778 cm.$^{-1}$.

The molecular weight of the above sample was determined using the Rast method: calcd. 278; found, 262, 221, 230. The material readily decolorized a solution of bromine in chloroform to give an oil which could not be purified. A sample of the distilled oil decomposed on standing in the open at room temperature.

*Preparation of the bromomagnesium salts* IV, V, *and* VI. One mole of ethylmagnesium bromide in 1 l. of ether was added dropwise to 132.2 g. (1.000 mole) of 2-methyl-2,5-dihydrothiophene 1,1-dioxide in 1 l. of toluene. The addition was carried out at $-20° \pm 3°$. After the addition, the white slurry was allowed to warm to 10°. Then 1.1 g. (0.01 mole) of hydroquinone was added and the slurry was filtered, washed thoroughly with ether, and dried in vacuum. The dried powder (V) weighed 231.6 g. and was found to be quite stable to light at room temperature, $\lambda_{max}$ 235 m$\mu$ in ethanol (0.01 g./l.).

In a similar manner VI was prepared from 3-methyl-2,5-dihydrothiophene 1,1-dioxide in ether to afford the white salt. This sulfinic salt is apparently also stable to light at room temperature, $\lambda_{max}$ 233 m$\mu$ in ethanol (0.01 g./l.).

Now IV was prepared in a similar manner from 2,5-dihydrothiophene 1,1-dioxide with the exception that owing to the apparent instability of the salt, peroxides, and free-radical initiators had to be carefully excluded. A detailed preparation is given later.

*1-Benzylsulfonyl-1,3-pentadiene* (VIII). Into 80 ml. of commercial absolute ethanol was dissolved 21.5 g. (0.091 mole) of the bromomagnesium salt of 1,3-pentadiene-1-sulfinic acid (V). To this solution was added 11.4 g. (0.091 mole) of benzyl chloride, and the reaction mixture was heated to reflux for 12 hr. After being cooled, the solution was diluted with 200 ml. of water and extracted with five portions of ether. The ether solution was dried over magnesium sulfate and was concentrated to give an oil. The oil was refrigerated in an equal volume of ethanol and after a day, 2.1 g. of solid was collected from the flask. After another two weeks at $-15°$, a second crop of crystals, weighing 3.1 g. were collected. The total crude product weighed 5.2 g. (26%). Four recrystallizations from ethanol gave pure VIII, m.p. 94.5–95.0°.

*Anal.* Calcd. for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35; S, 14.43. Found: C, 65.20; H, 6.51; S, 14.30.

The infrared spectrum of VIII (0.38% in KBr wafer) showed the following principal frequencies: 3472, 3021, 1644, 1589, 1499, 1451, 1404, 1367, 1312, 1261, 1222, 1206, 1162, 1154, 1121, 995, 954, 936, 921, 884, 794 and 701 cm.$^{-1}$.

In one preparation, the only product isolated appeared to be a polymorph of VIII which melted 99.0–99.5°.

*1-Benzylsulfonyl-2-methyl-1,3-butadiene* (IX). The procedure for the preparation of VIII was employed for the preparation of IX using the salt of the sulfinic acid prepared from ethylmagnesium bromide and III. The crude product was isolated in 21% yield and was recrystallized from methanol, m.p. 84.5–85.0°.

*Anal.* Calcd. for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35; S, 14.43. Found: C, 65.19; H, 6.56; S, 14.34.

The infrared spectrum of IX (0.46% in KBr wafer) showed the following principal frequencies: 3472, 3021, 1633, 1574, 1499, 1459, 1418, 1322, 1290, 1262, 1207, 1164, 1152, 1118, 1074, 990, 929, 895, 852, 798, 781, and 697 cm.$^{-1}$.

The above procedure was repeated using the Grignard reagent from bromobenzene to synthesize VI. The crude IX (21% yield) after recrystallization melted 84.5–85.0°. A mixed melting point with IX showed no depression.

The procedure used to prepare IX was repeated using the Grignard reagent from 1-iodo-2,6-dimethylbenzene to synthesize VI. The crude IX (14% yield) after recrystallization melted 84.5–85.0°. A mixed melting point with IX showed no depression.

*1-Benzylsulfonyl-1,3-butadiene* (VII). The apparatus consisted of a 3-l., three neck, round bottom flask equipped with ball-joint stirrer, a dropping funnel having a pressure equalizing tube, and a distillation head. The distillation head was equipped with a receiving flask which could be used to remove solvents under vacuum. The system was heated with a flame and as it cooled, nitrogen was passed through the apparatus. The ether used in the preparation of the Grignard reagent and as the solvent for I, was taken from a freshly opened container and had been allowed to be in contact with anhydrous ferrous sulfate for 40 hr. to render it peroxide-free. The apparatus was exposed to the minimum amount of light.

One mole of ethylmagnesium bromide in 1 l. of ether was added slowly to 118.2 g. (1.000 mole) of 2,5-dihydrothiophene 1,1-dioxide in 1 l. of ether which was cooled to $-20° \pm 1°$. The slurry was then stirred for 2 hr. while the temperature increased to 5°. To the slurry was added 1.1 g. (0.010 mole) of hydroquinone, and approximately 1.5 l. of ether was removed *in vacuo*. To the resulting solid (IV) was added 1.5 l. of commercial absolute ethanol and 101.3 g. (0.8000 mole) of benzyl chloride. The solution was heated to reflux and ether was removed so that the temperature of the solution was maintained at 75°. The total heating time was 7 hr. The reaction mixture was cooled to 39°, and approximately 1 l. of ethanol was removed *in vacuo*. The residual solution was cooled to 0°. A solid formed after 8 hr. and was divided into two portions. The ultraviolet spectrum of the solid shows $\lambda_{max}$ 228 m$\mu$ in ethanol (0.01 g./l.).

The first portion was separated and effort was spent attempting to purify the solid. These attempts failed because of the instability of the solid and its solubility in water and alcohol.

The second portion was dissolved in 950 ml. of water and extracted with five portions of ether which was then dried over magnesium sulfate and concentrated to give an orange oil. The oil was digested in six portions of 200 ml. of hot petroleum ether (b.p. 30–60°) and the petroleum ether solution was chilled to $-15°$. A crystalline solid weighing 6.3 g. precipitated and was filtered. The filtrate was concentrated to 400 ml. and chilled to give an additional 0.2 g. of solid. Total crude product weighed 6.5 g. (13% based on total reaction mixture). The crude product was recrystallized twice from petroleum ether and twice from methanol to give pure VII, m.p. 61.0–61.5°. If the product was not pure, it tended to discolor and apparently polymerize at room temperature.

*Anal.* Calcd. for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81; S, 15.40. Found: C, 63.34; H, 5.69; S, 15.64.

The infrared spectrum of VII (0.54% in KBr wafer) showed the following principal frequencies: 3412, 3030, 2906, 1620, 1569, 1490, 1449, 1400, 1303, 1282, 1253, 1200, 1131, 1113, 1070, 975, 925, 886, 794, and 696 cm.$^{-1}$.

*Benzyl pentyl sulfone from* VIII. In a Parr hydrogenation apparatus, 0.9 g. (0.004 mole) of VIII in 100 ml. of commercial absolute ethanol was reduced with hydrogen (40 p.s.i.) in the presence of 0.4 g. of 10% palladium-on-charcoal. After the suspension was filtered, the ethanol was evaporated leaving a white solid. The product was recrystallized twice from ethanol to give pure benzyl pentyl sulfone, m.p. 102–102.5° (lit.,[16] 100.5°). A mixed melting point with an authentic sample showed no depression.

The infrared spectrum of the sulfone (0.3% in KBr wafer) showed the following principal frequencies: 3508, 3003, 1477, 1459, 1410, 1322, 1298, 1262, 1207, 1170, 1158, 1123, 1075, 1034, 973, 930, 886, 790, 742, and 702 cm.$^{-1}$.

*Benzyl butyl sulfone from* VII. The hydrogenation procedure was repeated using VII, and the product after recrystallization from ethanol melted 96.5–97.0° (lit.,[17] 96°). A mixed melting point with an authentic sample showed no depression.

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(16) I. J. Buchi *et. al.*, *Helv. Chim. Acta*, **35**, 1527 (1952).

(17) H. J. Backer and G. J. De Jong, *Rec. trav. chim.*, **70**, 377 (1951).

The infrared spectrum of the sulfone (0.54% in KBr wafer) showed the following principal frequencies: 3424, 2958, 2932, 2857, 1492, 1464, 1449, 1400, 1314, 1293, 1258, 1204, 1166, 1153, 1117, 1095, 1074, 1031, 1002, 928, 901, 887, 787, 741, 728, and 700 cm.$^{-1}$.

*Benzyl 2-methylbutyl sulfone from* IX. The hydrogenation procedure was repated using IX, and the product after recrystallization from ethanol melted 82.5–83.0°. A mixed melting point with an authentic sample of benzyl 2-methylbutyl sulfone showed no depression.

*Benzyl pentyl sulfone.* A Grignard reagent was prepared from 30.2 g. (0.200 mole) of 1-bromopentane and 4.9 g. (0.20 g.-atom) of magnesium in 200 ml. of ether. The solution was maintained at $-15 \pm 5°$ while anhydrous sulfur dioxide was introduced slowly for approximately 1 hr. The resulting slurry was allowed to warm to room temperature and was separated by filtration. The solid material was washed with ether and dried in *vacuo.* There was a quantitative yield of the sulfinic salt which was dissolved in 200 ml. of commercial absolute ethanol. To this solution was added 25.3 g. (0.200 mole) of benzyl chloride and the reaction mixture was heated to reflux for 10 hr. The hot solution was diluted with 500 ml. of water and 31.2 g. (69%) of white solid precipitated. The product was recrystallized twice from methanol and melted 101.0–101.5°.

*Benzyl isopentyl sulfone.* The procedure for the preparation of benzyl pentyl sulfone was employed using 1-bromo-3-methylbutane. The reflux time was shortened to only 3 hr. Yield of product: 13%, m.p. 103.5–104.0° (lit.,[18] 103–104°).

The infrared spectrum of the sulfone (0.38% in KBr wafer) showed the following principal frequencies: 3496, 3030, 2923, 1503, 1477, 1459, 1414, 1319, 1282, 1265, 1209, 1170, 1160, 1123, 1035, 930, 892, 832, 790, 743, and 701 cm.$^{-1}$.

*Benzyl butyl sulfone.* The procedure for the preparation of benzyl pentyl sulfone was employed, using 1-bromobutane. The yield of product was 53%, m.p. 96.0–96.5°.

*Benzyl 2-methylbutyl sulfone.* The procedure for the preparation of benzyl pentyl sulfone was employed using 1-bromo-2-methylbutane. The sulfone was isolated in 66% yield, m.p. 83.5–84.0°.

*Anal.* Calcd. for $C_{12}H_{18}O_2S$: C, 63.68; H, 8.02; S, 14.17. Found: C, 63.90; H, 8.16; S, 14.32.

The infrared spectrum of the sulfone (0.31% in KBr wafer) showed the following principal frequencies: 3508, 3039, 2985, 2941, 1506, 1464, 1412, 1315, 1267, 1210, 1173, 1160, 1123, 1076, 1038, 931, 894, 788, and 701 cm.$^{-1}$.

BLACKSBURG, VA.

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[CONTRIBUTION FROM ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

# The Structure and Reactions of Pernitrosomesityl Oxide[1]

JEREMIAH P. FREEMAN

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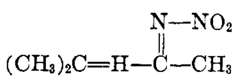
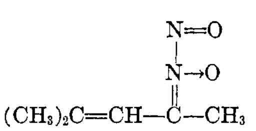
Evidence is presented to establish that the structure of pernitrosomesityl oxide is that of 3,5,5-trimethylisopyrazole 1,2-dioxide. Its reduction products were also examined and structures assigned, and correlations with acid-catalyzed addition products were made. The first pair of isomeric α,β-unsaturated aliphatic azoxy compounds was synthesized.

When mesityl oxide oxime is treated with a nitrite ester in acetic acid, a white solid, $C_6H_{10}N_2O_2$, called pernitrosomesityl oxide (I) is produced in good yield.[2] The nitrimine structure Ia was suggested[2] for this material based upon the investigations of Scholl[3] on pernitroso compounds of the terpene series. This formulation was rejected by Fusco[4] in favor of structure Ib which contains the unique *N*-nitrosonitrone function. Later investigators could not confirm or deny either structure but believed that pernitrosomesityl oxide had a different structure than did pernitrosocamphor.[5] Since the arguments[4] for structure Ib were based on the unsupported assignment of structures to products obtained by acid treatment of pernitrosomesityl oxide, an investigation of these products as well as of the pernitroso compound was indicated.



$$(CH_3)_2C{=}H{-}\overset{\overset{\displaystyle N{-}NO_2}{\|}}{C}{-}CH_3$$

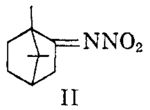
Ia



$$(CH_3)_2C{=}CH{-}\overset{\overset{\overset{\displaystyle N{=}O}{|}}{\overset{N\rightarrow O}{\|}}}{C}{-}CH_3$$

Ib

Since pernitrosocamphor possesses the nitrimine structure II,[6] it was originally supposed that pernitrosomesityl oxide possessed a similar structure. However, comparison of some physical and chemical properties of the two compounds suggested that they contained different arrangements of the pernitroso function. The first striking difference between pernitrosomesityl oxide and other aliphatic pernitroso compounds is its comparatively



II

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[1] This research was carried out under Army Ordnance Contract DA-01-021-ORD-11878.

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[5] J. W. Suggitt, G. S. Myers, and G. F. Wright, *J. Org. Chem.*, **12**, 373 (1947).

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