

was then decanted into a mixture of pentane and water and the nickel rinsed twice with pentane. The rinses and the aqueous mixture were combined and the pentane phase washed with water and dried over calcium chloride. The pentane was then evaporated and the residue crystallized from ethanol to give 70 mg. of *trans*-4-*tert*-butyl-1-phenylcyclohexane (III), m.p. 42°.

A more convenient route to III was achieved by shaking 6.0 g. of 4-*tert*-butyl-1-phenylcyclohexene,²¹ 200 mg. of 10% palladium-on-carbon, and 25 ml. of acetic acid under 40 p.s.i. of hydrogen at room temperature until the reaction was complete. The resulting mixture of stereoisomeric 4-*tert*-butyl-1-phenylcyclohexanes consisted of 45% of III and 55% of IV (by g.l.c.). The hydrogenation mixture was transferred to a boiling flask and refluxed for 1.5 hr. The mixture was then filtered into 30 ml. of water and the solid collected by filtration. Recrystallization from ethanol gave 3.9 g. of III, m.p. 41–42°. Further recrystallization raised the melting point to 42°.

Anal. Calcd. for C₁₈H₂₄: C, 88.82; H, 11.18. Found: C, 88.70; H, 10.94.

The preparation of IV was effected¹⁰ by refluxing a mixture of 1.64 g. of II, 5.0 g. of Raney nickel,²⁰ 70 mg. of sodium methoxide, and 25 ml. of ethanol for 30 min. The mixture was filtered and the filtrate was cooled in methanol–Dry Ice. The material which crystallized was collected by filtration and recrystallized twice from methanol to give 0.75 g. of IV, m.p. 24.5°.

Anal. Calcd. for C₁₈H₂₄: C, 88.82; H, 11.18. Found: 89.03; H, 11.18.

General Equilibration Procedure (Table I).—Equilibrations of III and IV were carried out by sealing in Pyrex tubes under nitrogen mixtures of 100 mg. of a mixture of 45% of III and 55% of IV, 40–50 mg. of potassium *tert*-butoxide,²² and 1.0 g. dry dimethyl sulfoxide. The tubes were then placed in refluxing reagent grade acetone (for 56.5°), benzene (for 80°), acetic acid (for 118°), or bromobenzene (for 155.5°); or in a thermostated water bath at 39°. Tubes were withdrawn periodically and the contents poured into water. The hydrocarbon mixture was extracted with pentane and the pentane extract washed and dried over calcium chloride. The pentane was evaporated and the residue analyzed at 200° by g.l.c. using a 14-ft. column packed with QF-1 on firebrick. Equilibrations were continued until steady state compositions of III and IV were reached. The equilibrium data in Table I represent averages of a total of at least ten analyses (planimeter integration) of at least two mixtures at equilibrium at each temperature. At 155.5°, appreciable decomposition of dimethyl sulfoxide oc-

curred during the 15 min. required to reach equilibrium. Extending the equilibration time to 30 min. did not effect the equilibrium composition. The chromatographic column was calibrated with known mixtures of pure (>99.9%) III and IV.

***cis*- and *trans*-4-Methyl-1-phenylcyclohexanes (V and VI).**—*trans*- and *cis*-4-methyl-1-phenylcyclohexanols were prepared through the reaction between phenylmagnesium bromide and 4-methylcyclohexanone. The resulting mixture (10 g.) of stereoisomeric carbinols was separated by chromatography as described for I and II. The *trans*-carbinol, 4.70 g. melting at 63.5° after recrystallization from pentane, was eluted first.

Anal. Calcd. for C₁₃H₁₈O: C, 82.06; H, 9.53. Found: C, 81.87; H, 9.53.

The *cis*-carbinol, 4.22 g. melting at 68–69.5° after recrystallization from pentane, was eluted last.

Anal. Calcd. for C₁₃H₁₈O: C, 82.06; H, 9.53. Found: C, 82.15; H, 9.63.

A mixture of 1.05 g. of *cis*-4-methyl-1-phenylcyclohexanol, 6.0 g. of Raney nickel,²⁰ and 20 ml. of ethanol was stirred at room temperature¹⁰ for 20 min. The mixture was then worked up as described for the preparation of III using Ni (Raney), except the pentane extract was treated with 5 g. of silica gel to remove the unreacted carbinol. Distillation of the product gave 0.6 g. of V boiling at 104° (6 mm.), *n*_D²⁰ 1.5190.

Anal. Calcd. for C₁₃H₁₈: C, 89.59; H, 10.41. Found: C, 89.70; H, 10.60.

The preparation of VI was carried out in the same manner as for the *cis* stereoisomer V except that the reaction mixture was refluxed for 13 min. Distillation afforded 0.8 g. of VI boiling at 90° (3 mm.), *n*_D²⁰ 1.5123.

Anal. Calcd. for C₁₃H₁₈: C, 89.59; H, 10.41. Found: C, 89.26; H, 10.91.

Both the n.m.r. (Fig. 4 and 5) and the infrared spectra of V and VI (obtained by the above procedure) show that these products are probably greater than 90% configurationally homogeneous.

When the hydrogenolysis of *cis*-4-methyl-1-phenylcyclohexanol was carried out by refluxing for 15 min. a mixture of 300 mg. of the carbinol, 3.0 g. of Ni (Raney), and 10 ml. of ethanol, it was apparent from the infrared spectrum of the product that equilibration had progressed to a significant extent leading to a contamination of V by roughly 20–40% of VI.

Acknowledgment.—Support of this work from the Louis Block Fund of the University of Chicago and from the Petroleum Research Fund (Grant No. 1536) of the American Chemical Society is gratefully acknowledged.

(21) E. W. Garbisch, Jr., *J. Org. Chem.*, **26**, 4165 (1961).

(22) A sample of this material was provided by the MSA Research Corporation, Callery, Pa.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Thietane Dioxide Derivatives *via* the Interaction of Sulfonyl Chlorides with Ketene Diethylacetal¹

BY WILLIAM E. TRUCE AND JOHN R. NORELL

RECEIVED JUNE 3, 1963

The formation of nine new thietane 1,1-dioxide derivatives, from the interaction of sulfonyl chlorides (RCH₂SO₂Cl), containing a hydrogen atom α to the sulfonyl group, with ketene diethylacetal in the presence of triethylamine, is described. Cyclization products are obtained when R is an acidifying group such as phenyl but not if R is an alkyl group. The possible intermediacy of sulfenes (RCHSO₂) is discussed.

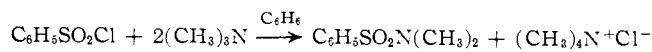
In aqueous media, as in the well-known Hinsberg test,² generally no reaction occurs between sulfonyl chlorides and tertiary amines. However, sulfonyl chlorides react with tertiary amines in nonprotic solvents to form unstable addition compounds,³ or by the over-all disproportionation reaction⁴

(1) Abstracted from the Ph.D. Thesis of John R. Norell, Purdue University, 1963.

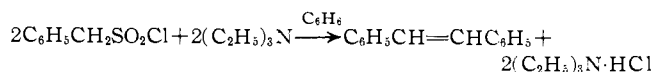
(2) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 103.

(3) (a) M. Kauffmann and D. Vorlander, *Ber.*, **43**, 2741 (1910); (b) G. L. Schwartz and W. M. Dehn, *J. Am. Chem. Soc.*, **39**, 2444 (1917); (c) L. Horner and H. Nickel, *Ann.*, **597**, 20 (1955); (d) H. Majda-Grabowska and K. Okon, *Roczniki Chem.*, **37**, 379 (1963), isolated pyridinium salts from benzenesulfonyl chlorides.

(4) L. W. Jones and H. F. Whalen, *J. Am. Chem. Soc.*, **47**, 1343 (1925).



If the sulfonyl chloride contains a hydrogen atom α to the sulfonyl group, then a different reaction occurs. With benzylsulfonyl chloride in the presence of triethylamine in benzene, Wedekind and Schenk⁵ found that *trans*-stilbene was formed in an unspecified yield.



As a reaction path these workers postulated initial abstraction of the proton by the base and loss of chlo-

(5) E. Wedekind and D. Schenk, *Ber.*, **44**, 198 (1911); recently J. F. King and T. Durst, *Tetrahedron Letters*, 585 (1963), obtained C₆H₅CClSO when the reaction was carried out in cyclohexane.

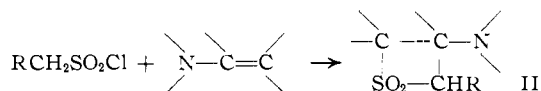
TABLE I
 3,3-DIETHOXYTHIETANE 1,1-DIOXIDES (III)

R	M.p., °C.	Yield, %	Calcd., %					Found, %				
			C	H	S	Other	Mol. wt.	C	H	S	Other	Mol. wt.
H ^a	49-50	65	43.30	7.22	16.49	...	194	43.59	7.10	16.74	...	202
C ₆ H ₅ ^b	89-90	70	57.75	6.72	11.86	57.96	6.70	11.90
<i>p</i> -NO ₂ C ₆ H ₄ ^c	113-114	54	49.51	5.44	10.17	N, 4.44	315	49.79	5.70	9.86	N, 4.18	328
<i>p</i> -CH ₃ C ₆ H ₄ ^b	72-73.5	55	59.12	7.10	11.28	...	284	59.34	7.13	11.39	...	286
<i>p</i> -ClC ₆ H ₄ ^b	82-83	Good	51.22	5.62	10.52	Cl, 11.63	305	51.18	5.76	10.25	Cl, 11.67	305
Cl ^b	72-74	31	36.76	5.73	14.02	Cl, 15.51	229	36.82	5.74	14.07	Cl, 15.31	232
CF ₃ ^c	103-105	61	36.64	5.00	12.23	F, 21.74	262	36.59	5.03	12.50	F, 22.00	269
CH ₂ =CH ^{a,f}	46-48	46	49.07	7.32	14.56	...	220	49.05	7.32	14.34	...	220
^{d,f}	118-120	6.5	49.07	7.32	14.56	...	220	49.36	7.40	14.27	...	220
CH ₂ =CH ^{a,g}	49-50	51										
^{d,g}	118-120	7.6										

^a Recrystallized from *n*-pentane. ^b Recrystallized from *n*-hexane. ^c Recrystallized from absolute ethanol. ^d Recrystallized from *n*-hexane and absolute ethanol. ^e From 2-propenesulfonyl chloride. ^f From 1-propenesulfonyl chloride.

ride ion to form an unstable intermediate, C₆H₅CH-SO₂ (I), for which they coined the term "sulfene," a sulfur analog to ketene. According to these authors, the "sulfene" lost sulfur dioxide to form a divalent species (C₆H₅CH), which dimerized to stilbene. Later evidence,^{6,7} however, cast some doubt on the intermediacy of carbene-like species in the formation of the substituted ethylenes. An alternate path suggested involved dimerization of the sulfene followed by loss of two molecules of sulfur dioxide to form the olefin. Sulfenes have also been postulated as intermediates resulting from the interaction of diazoalkanes with sulfur dioxide.⁸ The present status concerning the chemistry of "sulfene" intermediates has recently been surveyed.⁹

Few attempts have been made to trap sulfenes for useful synthetic purposes.^{8b,10} Almost simultaneously, two brief communications¹¹ appeared concerning the interaction of certain sulfonyl chlorides with enamines in the presence of triethylamine to form aminosulfones (II). The possibility of the intermediate formation of a sulfene followed by cycloaddition was presented.



These results prompted us to publish a preliminary report¹² briefly describing the interaction between ketene diethylacetal and methanesulfonyl chloride in the presence of triethylamine to yield 3,3-diethoxythietane 1,1-dioxide. It is the purpose of the present communication to expand on this reaction and in particular to report our observations where various sulfonyl chlorides and olefins were employed.

Results and Discussion

Description of the General Reaction.—When certain sulfonyl chlorides are dissolved in a nonprotic solvent

(6) H. Kloosterziel and H. J. Backer, *Rec. trav. chim.*, **71**, 1235 (1952).

(7) In an attempt to trap the carbene, derived from *p*-nitrobenzylsulfonyl chloride, with acenaphthylene fused to demonstrate carbene formation from sulfur ylides by H. Hruby and A. W. Johnson, *J. Am. Chem. Soc.*, **84**, 3586 (1962), only the stilbene derivative (44%) was obtained along with unreacted acenaphthylene (unpublished results from this Laboratory).

(8) (a) H. Staudinger and F. Pfenniger, *Ber.*, **49**, 1941 (1916); (b) L. von Vargha and E. Kovacs, *ibid.*, **75**, 794 (1942); (c) H. Kloosterziel and H. J. Backer, *Rec. trav. chim.*, **71**, 1235 (1952); (d) G. Hesse, E. Reichold, and S. Majumdar, *Ber.*, **90**, 2106 (1957).

(9) (a) J. F. King, P. de Mayo, E. Morkved, A. B. M. A. Sattar, and A. Stoessl, *Can. J. Chem.*, **41**, 100 (1963); (b) J. R. Norell, Ph.D. Thesis, Purdue University, 1963.

(10) H. Kloosterziel, M. H. Deinema, and H. J. Backer, *Rec. trav. chim.*, **71**, 1228 (1952).

(11) (a) G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **84**, 313 (1962); (b) G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962).

(12) W. E. Truce, J. J. Breiter, D. J. Abraham, and J. R. Norell, *J. Am. Chem. Soc.*, **84**, 3030 (1962).

(13) S. M. McElvain, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 506.

such as benzene or ether and added to an equimolar mixture of ketene diethylacetal¹³ and triethylamine dissolved in the solvent, a white flocculent precipitate of triethylamine hydrochloride is formed immediately. After stirring, usually overnight, the salt is filtered and the solvent is removed *in vacuo*. A yellow oil or crystalline solid remains, which can be purified by recrystallization from *n*-pentane, *n*-hexane, ethanol, or mixtures of these solvents.

These white crystalline compounds have been identified as thietane derivatives (III) as shown in the equation

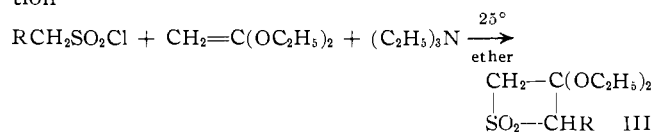


Table I lists the thietanes obtained, the yields of recrystallized material, melting points, and elemental analyses. The sulfonyl chlorides employed were either commercially available or synthesized according to known methods (see Experimental).

The structures assigned are supported by n.m.r. and infrared spectroscopy. Table II illustrates the n.m.r. data,¹⁴ which were obtained for the various

TABLE II

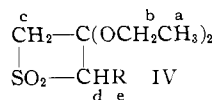
 N.M.R. VALUES (δ) FOR THE ADDUCTS OBTAINED^a

R						Relative areas a:b:c:d:e
	a	b	c	d	e	
H	1.25 3	3.48 4	4.19 1	3:2:2
C ₆ H ₅	1.10 3	3.45 4	4.12 1	5.37 1	7.34 c	6:4:2:1:5
<i>p</i> -NO ₂ C ₆ H ₄	1.18 3d	3.42 4	4.31 1	5.55 1	7.98 c	6:4:2:1:4
<i>p</i> -ClC ₆ H ₄	1.16 3	3.38 4	4.12 1	5.35 1	7.35 4	6:4:2:1:4
<i>p</i> -CH ₃ C ₆ H ₄ ^b	1.18 3	3.38 4	4.09 1	5.29 1	7.22 4	6:4:2:1:4:3
Cl	1.28 3	3.60 4	4.11 1	5.45 1	...	6:4:2:1
CH ₂ =CH	1.23 3	3.48 4	4.00 c	5.48 c	5.25 and 4.78 c	6:2:3:7:4 ^c
CF ₃	1.23 3	3.52 c	4.26 c	4.71 c	...	6:4:2:8

^a The multiplicity is expressed as: 1, singlet; 3, triplet; 3d, double triplet; 4, quartet; c, complex or multiplet. ^b For the *p*-CH₃ group the shift is 2.35 δ which appears as a singlet in a relative ratio of 3. ^c The c, d, and e hydrogens do not exhibit first-order splitting and appear as a complex; however, the total integrated relative area is 4.

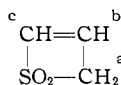
adducts. The chemical shifts, in δ -values, are tabulated according to the position of the protons on the thietane 1,1-dioxide molecule, IV, and are entered under the small letters. The italic numerals indicate the multiplicity of the signal observed. These data are readily generalized by noting that the methyl protons (a) of the ethoxyl group give signals at 1.1-1.3 δ and the corresponding methylene protons (b) occur at 3.4-3.6 δ .

(14) The n.m.r. spectra were obtained using a Varian A-60 spectrometer at a sweep width of 500 c.p.s. with TMS as an internal standard. The chemical shifts thus obtained are in δ -units (*i.e.*, 10 - τ).



The ring methylenes (c) all appear between 4.1–4.3 δ . If a substituent (R) is present there is a shift to lower fields and the ring hydrogen (d) then occurs about 5.3–5.5 δ . Interactions across the ring are also observed and are quite evident when R = Cl. The (d) hydrogen, in this case, can be resolved to a triplet with a very low coupling constant (J 0.5 c.p.s.) and the (c) hydrogen as a doublet (J 0.5 c.p.s.). Also when R is not hydrogen the two ethoxyl groups of the ketal moiety become unequivalent owing to *cis-trans* relationships with the R substituent. Thus multiplets or double triplets are observed in some cases.

These data help disprove the presence of such linkages as vinylic hydrogens or such linear structures as $\text{RCH}_2\text{SO}_2\text{CH}=\text{C}(\text{OC}_2\text{H}_5)_2$. For example, the signals for olefinic hydrogens in $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{CH}=\text{CHC}_6\text{H}_5$ occur at 6.3–6.6 δ and the benzylic protons give rise to a signal at 4.2 δ .¹⁵ The presence of the cyclobutane ring is also supported by the report of Dittmer and Christy¹⁶ concerning the reactions and properties of thiete sulfone. The methylene hydrogens give a doublet at 4.58 δ and the olefinic hydrogens occur at

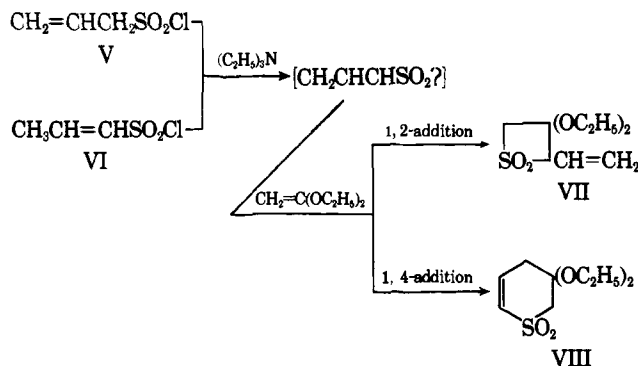


7.22 (b) and 6.80 δ (c).¹⁷ Our values for the methylene hydrogens are shifted to slightly higher fields owing to the absence of the olefinic linkage.

The infrared spectra of the thietanes show no absorbances in the carbonyl or olefin regions, which preclude the structures $\text{RCH}_2\text{SO}_2\text{CH}=\text{C}(\text{OC}_2\text{H}_5)_2$ or $\text{RCH}_2\text{SO}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$. In general, the infrared absorbances of the products exhibit a strong band in the 7.4–7.5 μ region indicative of the asymmetric stretching modes in a sulfone.¹⁸ The symmetric stretching mode of a sulfone usually appears as a strong band at about 8.7 μ . All of our products exhibit a weak and ill-defined absorbance at 8.4–8.6 μ and a strong absorbance at 9.0–9.2 μ (ether linkage³). Similarly, trimethylene sulfone¹⁹ shows, in addition to a strong "asymmetric" absorption at 7.5 μ , a weak band at 8.60 and a more intense one at 8.90 μ .

None of the products decolorizes a potassium permanganate solution except those derived from the olefinic sulfonyl chlorides, thus indicating no unsaturation. Further chemical studies are the subject of a forthcoming communication.

Allylsulfonyl chloride²⁰ (V) and 1-propenesulfonyl chloride (VI)²¹ possess the interesting possibility of forming the same intermediate, and hence identical products with ketene diethylacetal and triethylamine. Indeed, when the reaction was carried out, two products were isolated from each of these sulfonyl chlorides, with combined yields of 50–60%. The ratio of products in both cases was about 7:1, with the lower-melting isomer (m.p. 46–48°) predominating over the other (m.p. 118–120°), and both possessing identical elemental analyses. Each compound gave a positive Baeyer



test for unsaturation; however, neither isomer decolorized bromine in carbon tetrachloride. The isomer containing the terminal vinyl group would *a priori* be expected to decolorize this reagent rapidly; however, allylsulfonyl chloride does not give a positive bromine test. This result cast some doubt on the structures of the sulfonyl chlorides. Although previously reported in the literature,²⁰ the position of the double bond in allylsulfonyl chloride was confirmed by n.m.r. The proton spectrum of this material showed a doublet at 4.35 δ indicative of the hydrogens α to the sulfonyl group and a cluster of peaks at 5.6–6.0 δ resulting from the olefinic hydrogens. The ratio was exactly 2:3, respectively. The infrared spectrum contains a weak band at 6.1 μ and very strong bands at 7.30 and 8.58 μ . The location of the double bond in 1-propenesulfonyl chloride is also confirmed by its n.m.r. spectrum, which gives a doublet at 2.08 δ corresponding to the methyl group and a complex at 6.7–7.1 δ indicative of the olefinic protons. The relative areas are 3:2.

The n.m.r. spectrum for the low melting isomer supports structure VII. For the ethoxyl group there exists a pair of triplets at 1.23 δ ($\text{O}-\text{CH}_2-\text{CH}_3$) and a quartet at 3.48 δ ($-\text{O}-\text{CH}_2-\text{CH}_3$) in the ratio of 6.2:3.7. A singlet at 4.00 δ accounts for the ring methylene with a relative area of two. The remainder of the spectrum is complex owing to the olefinic linkage. Since the coupling constants are in close proximity, it does not exhibit first-order splitting; however, the summation of the relative areas of these peaks is four.

The infrared spectrum of VII shows a very weak absorbance at 6.10 μ . According to Bellamy²² the absorbance in this region by a terminal methylene group is of a medium or variable intensity. Strong C-H out-of-plane deformation bands are present at 10.68 and 10.10 μ , the latter also being indicative of a terminal methylene.²² The sulfone bands resemble the previously-studied thietane dioxides with the 7.5 μ band appearing quite strong, whereas the band at 8.55 μ is less intense.

The high melting isomer, which is assigned structure VIII, is substantiated by the n.m.r. spectrum. A triplet at 1.19 δ (OCH_2CH_3) and a quartet at 3.50 δ (OCH_2CH_3) make up the ketal linkage. A doublet at 2.62 δ accounts for the allylic methylene and possesses a J -value of 3 c.p.s. A peak superimposed on the signal for the methylene of the ethoxyl group occurs at 3.50 δ and is attributed to the methylene α to the sulfone group. The remaining protons show a signal at 6.39 δ which appears to be a poorly resolved doublet and corresponds to the ethylenic hydrogens. The relative ratios of the peaks are in excellent agreement with the assigned structure. The infrared spectrum shows an olefin band at 6.09 μ and sulfone absorbances at 7.63 and 8.75 μ . The absence of a band at 10.2 μ tends

(22) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1956, p. 50.

(15) Unpublished results from this Laboratory.

(16) D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1325 (1961).

(17) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, 1962, Spectrum No. 22.

(18) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 863 (1957).

(19) "The Sadtler Standard Spectra," Midget Edition, The Sadtler Research Laboratories, Philadelphia 2, Pa., 1962, Spectrum No. 5407.

(20) N. S. Johary and L. N. Owen, *J. Chem. Soc.*, 1309 (1955).

(21) C. Rondstvedt and P. K. Chang, *J. Am. Chem. Soc.*, **77**, 6537 (1955).

to eliminate the possibility of a terminal methylene group.

The various *p*-substituted-benzylsulfonyl chlorides were prepared and treated with ketene diethylacetal and triethylamine as shown in Table I. With *p*-nitrobenzylsulfonyl chloride, in addition to a good yield of the thietane, there was also obtained a small amount of the stilbene derivative. It was noticed that during the reaction a fleeting red color (intermediate?) appeared as the sulfonyl chloride was added to the reactants. No stilbene derivatives were isolated with any of the other sulfonyl chlorides. The thietanes prepared from *p*-methyl and *p*-chlorobenzylsulfonyl chlorides were difficult to purify from the reaction mixture. It was desirable to have a *p*-substituent, which would be electron donating, such as the methoxyl group. However, this compound has escaped preparation. Ziegler and Sprague²³ reported that they were unable to synthesize it by chlorination of the isothiuronium or Bunte salts. We attempted to use a method which required no free chlorine, such as the action of thionyl chloride in DMF²⁴ on the sodium sulfonate, but obtained only *p*-methoxybenzyl chloride and ring chlorination products.

When the cyclization is carried out with 2,2,2-trifluoroethanesulfonyl chloride a heavy white precipitate of triethylamine hydrochloride is obtained, but evaporation of the solvent leaves a solid which is difficult to purify. After seven recrystallizations from *n*-hexane the product is obtained as homogeneous white crystals, but melts over a fairly wide range (98–103°), and does not give a satisfactory elemental analysis. Employing an "inverse addition" the product was obtained and on recrystallization from ethanol and *n*-hexane it melted at 103–105°.

The other sulfonyl chlorides tabulated gave no difficulties in preparation of the thietanes.

Sulfonyl Chlorides which Yielded No Thietane.—Conspicuously absent in Table I are alkanesulfonyl chlorides such as ethane-,²⁵ *n*-butane-,²⁶ cyclopentane-,²⁶ isopropyl-,²⁷ or β -phenylethylsulfonyl²⁷ chloride, which, under the conditions described, yielded no thietanes. Instead only high boiling intractable oils were obtained, none of which possessed properties similar to the expected thietane sulfones. These oils distilled over a very wide range and could not be fractionated efficiently. Ethyl ethanesulfonate was found by preparative v.p.c. to be the major product of the reaction with ethanesulfonyl chloride. This probably arises from the decomposition of ketene diethylacetal caused by the sulfonyl chloride. For example, benzenesulfonyl chloride yields ethyl benzenesulfonate when mixed with an ethereal solution of ketene diethylacetal.²⁸ In all cases where no adduct was formed, instead of a flocculent white precipitate of triethylamine hydrochloride, there was obtained a brown gummy resin, which possessed a strong odor of the sulfonyl chloride. From this resin, after leaching with acetone, there was invariably obtained triethylamine hydrochloride in 40–50% yields.

In hopes of preparing an analog of sulfene, CH₂=SO, methanesulfonyl chloride²⁹ was treated with ketene diethylacetal. However, instead of a crystalline thietane

there were obtained only yellow oils boiling over a very wide range, which showed several peaks on the v.p.c.

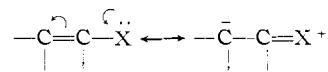
Variations in the Olefin.—Employing the conditions described, we have been able to form thietanes only with ketene diethylacetal and the sulfonyl chlorides listed in Table I.³⁰ Many other olefinic compounds have been tried without success. In addition to those reported in our initial communication,¹² we have been unsuccessful in forming thietanes from methanesulfonyl chloride and: 1-ethoxy-1-ethylmercaptoethene,³¹ 1,1-bis-(4,4'-dimethoxyphenyl)-ethene,³² 1,1-bis-(4,4'-dimethylaminophenyl)-ethene,³³ diethylimino carbonate,³⁴ acrolein, benzalaniline, methyl acrylate, trifluorochloroethylene, and hexachlorobutadiene. In each case the olefin was recovered unchanged, if it did not polymerize or decompose under the reaction conditions and there was not observed the white flocculent precipitate of triethylamine hydrochloride, but rather a brown gummy resin with a strong odor of the sulfonyl chloride.

Variations in the Base and Solvent.—Although few bases were studied, it became immediately apparent that a strong organic base was needed, in particular, triethylamine. Pyridine (p*K*_a 5.23),³⁵ which is a weaker base than triethylamine (p*K*_a 10.87)³⁵ will not give a thietane with benzylsulfonyl chloride and ketene diethylacetal under the reaction conditions. Stronger bases such as the alkoxides will form esters with the sulfonyl chlorides and also will react with the thietane, hence precluding their use.

Of the several nonprotic solvents used, best yields were obtained with diethyl ether or benzene. In controlled 0.05 molar runs the following solvents were employed giving the indicated yields of recrystallized 3,3-diethoxythietane 1,1-dioxide: diethyl ether, 56.1%; benzene, 68.5%; *n*-pentane, 25.7%; acetonitrile, 23.6%; benzene (without nitrogen), 48.2%; chloroform, 45%; dimethylformamide, 35%. The varying yields may be a consequence of the different work-up procedures necessitated by the various solvents.

Conclusions

For four-ring formation to occur, it appears that a highly-polarizable double bond is required, the polarization being induced by strongly electron-donating substituents. In other words, the double bonds, which



form a cyclic product, are those which are very readily attacked by electrophilic moieties or show appreciable nucleophilicity such as ketene acetals³⁶ or enamines.³⁷

For a particularly facile cyclization process, the hydrogen(s) α to the sulfonyl group needs to be labilized by an electron-attracting substituent. If the base cannot abstract the proton at a fast enough rate, an addition compound of the amine with the sulfonyl chloride may form^{3,4} and result in the resins observed in certain examples. The formation of these complexes seems to be a very fast reaction and occurs rapidly even at Dry Ice temperature with benzenesulfonyl chloride and triethylamine.⁴

(30) For variations in some ketene acetals see D. J. Abraham, Ph.D. Thesis, Purdue University, 1963.

(31) H. J. Alkema and J. F. Arens, *Rec. trav. chim.*, **79**, 1257 (1960).

(32) P. Pfeiffer and R. Wizinger, *Ann.*, **461**, 145 (1928).

(33) G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954).

(34) H. Tieckelmann and H. W. Post, *J. Org. Chem.*, **13**, 268 (1948).

(35) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co., Ltd., London, 1962, p. 140. These p*K*_a values are for aqueous solutions.

(36) S. M. McElvain, *Chem. Rev.*, **45**, 453 (1949).

(37) G. Stork, A. Brizzolara, H. Landesman, J. Szmuskovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(23) C. Ziegler and J. M. Sprague, *J. Org. Chem.*, **16**, 621 (1951).

(24) R. S. Kittila, "A Review of Catalytic and Synthetic Applications for "DMF and DMAC," Industrial and Biochemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington 98, Del., 1959, p. 10.

(25) Commercially available from Eastman Chemicals.

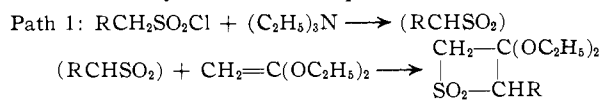
(26) J. Milionis, Ph.D. Thesis, Purdue University, 1951, p. 49.

(27) T. B. Johnson and J. M. Sprague, *J. Am. Chem. Soc.*, **58**, 1348 (1936).

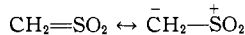
(28) S. M. McElvain and D. Kundiger, *ibid.*, **64**, 254 (1942).

(29) I. B. Douglass, *Org. Syn.*, **40**, 62 (1960).

Possible Reaction Paths.—One feasible route by which these four-ring compounds may arise is a β -elimination-cycloaddition sequence^{5,9,11}

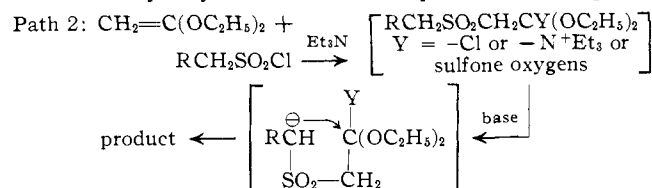


The high polarity required of the olefins would seem to support a polarized (ylide type) structure for the "sulfene." This ylide structure for sulfenes was proposed

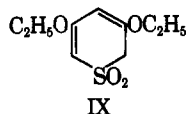


by Hesse and co-workers^{8d} in connection with their preparation of ethylenesulfone from the interaction of diazomethane with sulfur dioxide. The high yield of product is also consistent with this path.

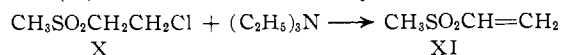
An alternative reaction path involves an electrophilic attack by the sulfonyl chloride on the olefin followed by cyclization. This postulate is given



some support by the fact that benzenesulfonyl chloride causes polymerization (*via* carbonium ion?) of ketene diethylacetal.²⁸ Also it has been found in this Laboratory³⁸ that methanesulfonyl chloride reacts with ketene diethylacetal in the absence of triethylamine to produce IX in low yield. However, if this second mechanism

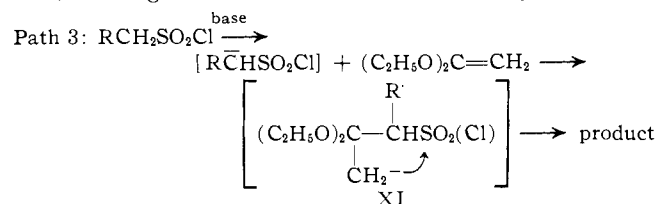


is involved, substantial amounts of olefinic substitution products, $\text{RCH}_2\text{SO}_2\text{CH}=\text{C}(\text{OC}_2\text{H}_5)_2$, should be obtained. In this regard, when β -chloroethyl methyl sulfone (X) is treated with triethylamine a high yield

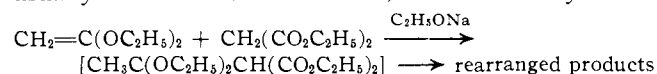


of methyl vinyl sulfone (XI) is obtained³⁹ and none of the thietane 1,1-dioxide is found.

A third mechanistic possibility is abstraction of the α -proton followed by nucleophilic attack of the resulting carbanion on the ketene acetal. A displacement by the resulting nucleophilic carbon atom on the sulfonyl chloride would then give the desired product. But, although such attacks on ketene diethylacetal are



known, they are not common and require forcing conditions. Malonic ester will react with ketene diethylacetal and attack at the positive center of the olefin.³⁶ Amines will also add in this manner at temperatures usually above 100°. In brief, ketene diethylacetal



(38) W. E. Truce, D. J. Abraham, and P. S. Radhakrishnamurti, *Tetrahedron Letters*, 1051 (1963).

(39) G. D. Buckley, J. L. Charlsh, and J. D. Rose, *J. Chem. Soc.*, 1515 (1947).

generally exhibits nucleophilic character and is attacked by electrophilic agents on the terminal methylene group.³⁶

Although path I seems to be the favored reaction path, more definitive experiments are needed before the possibility of a "sulfene" intermediate in these cyclizations can be stated with certainty.

Experimental⁴⁰

Materials.—Ketene diethylacetal was prepared from bromoacetaldehyde diethylacetal⁴¹ according to the method of McElvain and Kundiger.¹³ Triethylamine (Matheson, Coleman, and Bell, b.p. 88–90°) and Mallinckrodt anhydrous diethyl ether were used as obtained. The sulfonyl chlorides were prepared according to the references cited below and the physical constants agreed closely with those recorded in the literature. These included: methanesulfonyl chloride,⁴² b.p. 49–50° (9 mm.); benzenesulfonyl chloride,⁴¹ m.p. 87–91°; *p*-nitrobenzenesulfonyl chloride,⁴³ m.p. 91–93°; *p*-chlorobenzenesulfonyl chloride,⁴⁴ m.p. 89–93°; *p*-methylbenzenesulfonyl chloride,⁴³ m.p. 78.5–79.5°; chloromethanesulfonyl chloride,⁴⁵ b.p. 85° (30 mm.); 2,2,2-trifluoroethanesulfonyl chloride,⁴⁶ b.p. 62.5° (60 mm.), n_D^{20} 1.3908; 2-propenesulfonyl chloride,⁴⁷ b.p. 74–75° (15 mm.) n_D^{20} 1.4750; 1-propenesulfonyl chloride,⁴⁸ b.p. 44–47° (0.7 mm.), n_D^{20} 1.4796. Owing to modifications in the references cited above, detailed syntheses are given only for 2-propene- and 2,2,2-trifluoroethanesulfonyl chloride.

Preparation of 2,2,2-Trifluoromethanesulfonyl Chloride.⁴⁶—To a solution of 2,2,2-trifluoroethyl-1-*p*-toluenesulfonate⁴⁹ (145.3 g., 0.57 mole) in 200 ml. of dimethyl sulfoxide (DMSO) at 80° was added dropwise a freshly prepared solution of sodium disulfide (Na_2S_2), which was made by dissolving 76.3 g. (0.32 mole) of sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) in 111 ml. of DMSO and 32 ml. of water and adding 12.1 g. (0.38 mole) of sulfur until dissolution was complete. When all the Na_2S_2 solution had been added (1 hr.) the mixture was allowed to stir at 85–90° for 1 hr. and at 25° for 45 min. The dark mixture was diluted with 350 ml. of water and steam distilled until about 2 l. of distillate had been collected. The lower yellow layer of the distillate was separated (44.9 g.) and the aqueous portion extracted once with 50 ml. of ether and the combined extracts dried over MgSO_4 . After removal of the ether, the yellow-orange residue was fractionated giving 30.2 g. (12%) of bis-(2,2,2-trifluoroethyl) disulfide; b.p. 60–64° (60 mm.), n_D^{20} 1.3908 (lit.⁴⁶ b.p. 57° (47 mm.), n_D^{20} 1.385).

The above disulfide (30.0 g., 0.13 mole) was suspended in 75 ml. of water at 60°. A rapid stream of chlorine was passed into the stirred solution with the temperature being kept at 60–70° by use of an ice bath. When excess chlorine had been added (*ca.* 1 hr.), as evidenced by the yellow-green color of the solution, the layers were separated and the lower organic layer (30.5 g.) was dried over MgSO_4 . Distillation gave 26.3 g. (56%) of the sulfonyl chloride, b.p. 65.5–66° (50 mm.), n_D^{20} 1.3881 (lit.⁴⁶ b.p. 65° (45 mm.), n_D^{20} 1.3873).

Preparation of 2-Propenesulfonyl Chloride.—Sodium 2-propenesulfonate was prepared by addition of 100 g. (0.82 mole) of freshly distilled 3-bromopropene to a vigorously stirred solution of 100 g. (0.79 mole) of sodium sulfite in 400 ml. of water at 50–60° contained in a creased flask. An almost homogeneous solution was obtained after 2 hr. The water was removed on a Rinco rotatory evaporator to a white solid which could be recrystallized from 80% ethanol.

Recrystallized sodium 2-propenesulfonate (31.9 g., 0.22 mole) and phosphorus oxychloride (64.4 g., 0.42 mole) were placed in a

(40) All melting points are uncorrected. The infrared spectra were run on a Perkin-Elmer Infracord or Perkin-Elmer Model 21 spectrometer. The molecular weights were determined by a Mechrolab vapor pressure osmometer.

(41) Obtained from Aldrich Chemical Co., Milwaukee, Wis.

(42) Obtained from Distillation Products Industries, Eastman Organic Chemicals Department, Rochester 3, N. Y.

(43) J. M. Sprague and T. B. Johnson, *J. Am. Chem. Soc.*, **59**, 1838 (1937).

(44) G. Dougherty and R. H. Barth, U. S. Patent 2,293,971, Aug. 25, 1942 [*Chem. Abstr.*, **37**, 889 (1943)].

(45) T. B. Johnson and I. B. Douglass, *J. Am. Chem. Soc.*, **63**, 1571, (1941).

(46) R. E. Oesterling, U. S. Patent 3,006,964, Oct. 31, 1961. Note: *Chemical Abstracts* reference [*Chem. Abstr.*, **56**, 9967c, (1962)] is in error as to the preparation of this compound; the original patent should be consulted.

(47) (a) N. S. Johary and L. N. Owen, *J. Chem. Soc.*, 1309 (1955); (b) M. A. Belous and I. Y. Postovskii, *Zh. Obshch. Khim.*, **20**, 1701 (1950) [*Chem. Abstr.*, **45**, 2391 (1951)].

(48) C. R. Rondstedt and P. K. Chang, *J. Am. Chem. Soc.*, **77**, 6537 (1955).

(49) W. F. Edgell and L. Parts, *ibid.*, **77**, 4899 (1955).

500-ml., 3-necked flask and heated at 120° for 4 hr. with vigorous stirring. The gray mass was then poured into 300 ml. of ice water and allowed to stand for 1 hr. so as to hydrolyze the unreacted phosphorus oxychloride. The two layers were separated and the aqueous layer was extracted with chloroform (2 × 50 ml.). After drying over Na₂SO₄, removal of chloroform left a brown oil which was distilled at 74–75° (15 mm.), *n*_D²⁰ 1.4750, to give 17.1 g. (55%) of the colorless 2-propenesulfonyl chloride.

General Procedure for Preparation of the Thietane 1,1-Dioxides.—In order to avoid repetition, the method for obtaining the title compounds is generalized. Detailed procedures, however, are given for the reactions of 1-propene and 2-propenesulfonyl chlorides with ketene diethylacetal as the separation of isomers necessitated different methods of work-up. The experiments in which no adduct was obtained are similar to that described for the reaction between ethanesulfonyl chloride and ketene diethylacetal.

The sulfonyl chloride (0.03–0.05 mole) was dissolved in anhydrous diethyl ether (50–75 ml.) or an equivalent amount of tetrahydrofuran. This solution was added dropwise (1–2 hr.), under a nitrogen atmosphere, to a stirred equimolar solution of triethylamine (0.03–0.05 mole) and ketene diethylacetal (0.03–0.05 mole) in diethyl ether (150 ml.) at room temperature (25°) contained in a 300-ml. 3-necked flask. A white precipitate formed immediately, and the solution was allowed to stir 2–12 hr. after the addition was complete. The precipitated triethylamine hydrochloride was filtered and washed with small portions of anhydrous ether to give the dried salt in 80–100% yields, m.p. 253–256° dec. The filtrate was evaporated to a yellow oil or solid on a Rinco rotatory evaporator, and the residue recrystallized from *n*-pentane, *n*-hexane, or ethanol (see Table I). An analytical sample usually required two additional recrystallizations and was dried *in vacuo* over phosphorus pentoxide.

Reaction of 2-Propenesulfonyl Chloride with Ketene Diethylacetal.—To a stirred solution of 3.22 g. (0.028 mole) of ketene diethylacetal and 2.80 g. (0.028 mole) of triethylamine in 100 ml. of anhydrous ether was added a solution of 3.89 g. (0.028 mole) of 2-propenesulfonyl chloride in 50 ml. of anhydrous ether. The solution turned cloudy with the first drop and a heavy white precipitate formed. After stirring overnight the triethylamine hydrochloride (3.55 g., 100%, m.p. 242–252°) was filtered from the solution. Removal of the ether on a Rinco rotatory evaporator left a yellow semicrystalline solid. This solid was dissolved in 300 ml. of hot *n*-hexane, and on cooling 0.40 g. (6.5%) of light yellow crystals precipitated. These could be purified by suspending them in 30 ml. of hot *n*-hexane and adding ethanol dropwise until dissolution was complete. After three recrystallizations, white platelets, identified as compound VIII (see Table I), were obtained, m.p. 118–120°.

The initial 300 ml. of *n*-hexane was evaporated to dryness giving 2.79 g. (46%) of light yellow crystals (m.p. 46–49°). After three recrystallizations from *n*-pentane, the soft white crystals melted at 46–48°, and were identified as compound VII (see Table I).

Reaction of 1-Propenesulfonyl Chloride with Ketene Diethylacetal.—In a manner similar to the preceding experiment, 7.03 g. (0.05 mole) of 1-propenesulfonyl chloride in ether was allowed to react with a solution of 5.80 g. (0.05 mole) of ketene diethylacetal and 5.05 g. (0.05 mole) of triethylamine to give triethylamine hydrochloride in 81% yield. Evaporation of the ether left a yellow oil which was boiled in 400 ml. of *n*-hexane, and, when cooled, there was obtained a yellow solid. Recrystallization from ethanol and water gave 0.76 g. (7.6%) of light yellow crystals, m.p. 114–118°. Two additional recrystallizations gave white platelets, m.p. 118–120°. A mixture melting point with the high melting isomer from 2-propenesulfonyl chloride gave no depression (m.p. 118–120°) and their infrared spectra were superimposable.

The initial 400 ml. of *n*-hexane was evaporated to a yellow oil, which, when recrystallized from *n*-pentane (tendency to oil), gave 5.14 g. (51%) of crystals which melted at 42–46°. A second recrystallization from *n*-pentane raised the melting point to 49–50°. A mixture melting point with the low-melting isomer from 2-propenesulfonyl chloride showed no depression (48–50°) and the infrared spectra were identical.

Reaction of Ethanesulfonyl Chloride with Ketene Diethylacetal.—Ethanesulfonyl chloride (7.72 g., 0.06 mole) was dissolved in 60 ml. of anhydrous ether and added dropwise to a solution of ketene diethylacetal (6.96 g., 0.06 mole) and triethylamine (6.06 g., 0.06 mole), dissolved in 150 ml. of anhydrous ether. After about 5 ml. of the sulfonyl chloride solution had been added, a white finely-divided precipitate formed which turned yellow and finally coagulated to a brown gummy resin. After stirring overnight the resin was filtered from the solution and suspended in acetone. The acetone dissolved the resin leaving 5.40 g. (65%) of triethylamine hydrochloride, m.p. 256–257° dec. Removal of the initial ether solution gave a dark oil which possessed the strong odor of ethanesulfonyl chloride. Attempts to recrystallize this oil from common organic solvents failed. It was then distilled, but could not be efficiently fractionated, and gave 4.63 g. of distillate boiling over a wide range; b.p. 45–102° (1.0 mm.). On a preparative vapor phase chromatograph⁵⁰ twelve peaks were observed. The major peak (ca. 55–70%) was collected with a retention time of 7 min. on the column described and was identified as ethyl ethanesulfonate by comparing its retention time and physical properties with an authentically prepared sample.⁵¹ The sulfonate was obtained in approximately 35% yield based on ethanesulfonyl chloride.

Acknowledgments.—The authors are very grateful to the Phillips Petroleum Company, Gulf Research and Development Corporation, and the National Institutes of Health under Grant CY-4536 for support of this work.

(50) An Aerograph Autoprep Model A-700, by Wilkens Instrument and Research, Inc., Walnut Creek, Calif., with a 20 ft. × 3/8 in. aluminum column packed with 20% GE-SF-96 on 60/80 firebrick at 200° and a helium flow rate of 200 ml./min. was used.

(51) L. Carius, *J. prakt. Chem.*, [2] **2**, 267 (1870).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

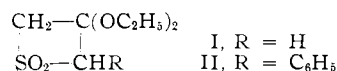
Reactions of 3,3-Diethoxythietane 1,1-Dioxide and 2-Phenyl-3,3-diethoxythietane 1,1-Dioxide¹

BY WILLIAM E. TRUCE AND JOHN R. NORELL

RECEIVED JUNE 3, 1963

The compounds referred to in the title were studied with regard to their acidic and basic hydrolyses, pyrolyses, and reactions with reducing agents.

In a previous paper² the synthesis and physical properties of nine new substituted thietane sulfones³ were discussed. The present communication is concerned with some of the chemistry of these compounds, in particular when R is hydrogen (I) or phenyl (II).



(1) Abstracted from the Ph.D. Thesis of John R. Norell, Purdue University, 1963.

(2) W. E. Truce and J. R. Norell, *J. Am. Chem. Soc.*, **85**, 3231 (1963).

(3) D. C. Dittmer and M. E. Christy, *ibid.*, **84**, 399 (1962), have discussed their findings on the reactions of thiete sulfone, but other than this recent article, there appear to be no reports concerning the reactions of these compounds.

Acid Hydrolysis.—Two independent methods^{4,5} have recently been used for the preparation of 3-thietanone; however, the corresponding sulfone, 3-thietanone 1,1-dioxide (III), has remained unknown.⁶ When I is dissolved in concentrated hydrochloric acid at 25°, a white solid precipitates after about 15 min., which can be recrystallized from dioxane or sublimed at 100° (1.0 mm.) to give the ketosulfone III. The structural assignment is supported by elemental analysis, molecular weight determination, n.m.r., and infrared spectroscopy. In the n.m.r. spectrum there exists a

(4) R. Mayer and K. F. Funk, *Angew. Chem.*, **73**, 578 (1961).

(5) H. Prinzbach and G. Veh, *Z. Naturforsch.*, **16b**, 763 (1961).

(6) See W. E. Truce and J. R. Norell, *Tetrahedron Letters*, in press, for a brief communication concerning this compound.