

Thermolysis of thiete 1,1-dioxide and related species¹

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Thiete 1,1-dioxide (1) rearranges to 5H-1,2-oxathiole-2-oxide (3) on heating in solution or in the vapor Intere 1,1-dioxide (1) rearranges to 5H-1,2-oxathiole-2-oxide (3) on heating in solution or in the vapor phase. The presence of phenol in the solution leads to formation of phenyl 2-propene-1-sulfonate (CH₂=CHCH₂SO₂OPh) in 15% yield. The results are rationalized in terms of a mechanism involving vinylsulfene (2). Flash thermolysis of some thietane 1,1-dioxides (16) and 3-thietanone 1,1-dioxides (15) gave products derived from extrusion processes, but 3-thietanol 1,1-dioxide (17) yielded, among other products, acetaldehyde and formaldehyde. The latter is believed to arise by "desulfinylation" of sulfene (CH₂=SO₂) formed along with the enol form of acetaldehyde by cycloreversion from 17.

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The present paper represents the results of the researches of two groups working in the same area, but, initially at least, with somewhat different aims and approaches. One group was primarily interested in finding new reactions involving the intermediacy of sulfenes $(RR'C=SO_2)$ as part of a systematic investigation² of the chemistry of these species. The objectives of the second group were simply the generation of a sulfene and its possible isolation and trapping at low temperature, by a high temperature-short contact time technique (flash thermolysis³) in the context of a general study of reactions under such conditions. For reasons detailed in the discussion of the individual experiments, thiete 1,1-dioxide (1) and certain other four-membered ring sulfones appeared to be promising substrates for the formation of sulfenes by thermolysis, and from the evidence presented herein it would appear that this expectation has, in some measure, been fulfilled. Part of this work has been summarized in two preliminary communications (3, 4).



molysis Part 3; for the previous part in each series see ref. 1. ¹Organic sulfur mechanisms Part 7 and Flash ther-

²See refs. 1 and 2 and earlier papers cited. ³The term "thermolysis" (Shorter Oxford Dictionary (S.O.D.) "decomposition or dissociation by heat") was selected rather than the demotic "pyrolysis". The latter, unrecognized by the S.O.D., presumably derives its signification from pyro- "done with, caused or produced by fire" and therefore appeared inappropriate.

Results and Discussion

Liquid and Low Temperature Vapor Phase Thermolyses

At the time this work was begun it seemed to us that thiete 1,1-dioxide (1) might undergo either (or both) of the following thermally-induced reactions: (i) rearrangement to vinylsulfene (2) analogous to the formation of butadiene from cyclobutene, (ii) fragmentation (not necessarily concerted) with formation of acetylene and sulfene ($CH_2 = SO_2$) itself. Either of these processes would be a new way of forming sulfenes which might well have advantages for looking at some of the properties of sulfenes not readily investigated by previously known routes to these species. We accordingly set out to obtain a sufficient quantity of 1 to investigate its thermolysis.

The synthesis of thiete 1,1-dioxide (1) was first reported by Dittmer and Christy (5), but we found it convenient to prepare 1 from 3-thietanol 1,1dioxide (4a) which was readily available via the sulfene-ketene acetal cycloaddition described by Truce and Norell (6). Dehydration of 4a to 1 was effected in 80-90% overall yield by converting 4ato the phenylmethanesulfonate ester (4b) (via the sulfene (7)), and treating the latter with triethylamine.

Thermal rearrangement of 1 was carried out successfully in the vapor phase and in solution, both procedures giving a good yield of a material shown below to be the cyclic sulfinic ester $3.^4$ For the gas phase reactions we used a simple quartz

^{*}By analogy with the designation "sultone" for a cyclic sulfonic ester, the name "sultine" has been suggested (8-10) for a cyclic sulfinic ester. Brevity commends its use.



tube heated by an oven and leading into a U-tube cooled in a Dry Ice - acetone trap and connected to a vacuum pump. The pressure was measured between the trap and the pump; this is not regarded as indicating the pressure in the tube, but merely as a way of comparing one run with another. With an oven temperature above 390° and a pressure reading of 0.005 mm, thiete dioxide (1) was completely converted to the sultine (3). At 350° and 0.05 mm both 1 and 3 were present in the product; in another run at 350° but with a pressure of 0.3 mm, the product was estimated to contain more than 70% of 3 and less than 30% of 1. In runs at 390 and 450° we obtained 80-90% yields of product estimated to be > 90%sultine (3).

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Liquid phase thermolysis of degassed benzene solutions at 220° for 20 min was also found to give the sultine (3) in good yield. In cyclohexane solution at 220° the result was much the same as in benzene, but in xylene the product was a dark brown material containing a small amount of 3; under the same conditions 3 was also found to be similarly decomposed.

Rigorous proof of the cyclic sulfinate structure (3) was obtained as follows. Elemental analysis and mass spectrometric determination of the molecular weight showed the molecular formula to be $C_3H_4O_2S$. The i.r. spectrum showed only weak absorption between 1300 and 1400 cm⁻¹, clearly indicating the absence of a sulfonyl group whereas a very strong band at 1135 cm⁻¹ (together with a slightly weaker band at 985 cm⁻¹) strongly suggested a sulfinic ester (11); confirmation of this was obtained by peroxide oxidation of 3 to 5. Sultone 5 has been described somewhat sketchily (12, 13); these sources report melting points of 78 and 83–84°, respectively, in accept-

able agreement with our value, 83-84°. The i.r. spectrum of 5 shows very strong bands at 1360 and 1190 cm⁻¹, characteristic of a sulfonic ester (11), while the n.m.r., spectrum showed a multiplet around 7.0 p.p.m. and an apparent triplet of the same integrated intensity at 5.1 p.p.m. Though the formation of 5 makes the possibility that the thermolysis product might have the isomeric enol sulfinate structure (7) distinctly remote, the question was settled by treating it with one equivalent of dilute sodium hydroxide. The i.r. spectrum of the product (6) showed absorption due to sulfinate anion and hydroxyl functions but nothing ascribable to a carbonyl group, as would have been expected from 7. Acidification with hydrochloric acid converted the sulfinate salt back to 3, showing that the alkaline treatment had not led to any deep-seated changes in the material.

The n.m.r. spectrum is in full agreement with structure 3 and possesses features of interest. The spectrum shows an ABXY pattern in which $\delta_A = 5.06, \delta_B = 5.41, \delta_X = 6.70, \delta_Y = 6.90 \text{ p.p.m},$ $J_{AB}^{n} = -15.9, J_{AX} = 2.55, J_{AY} = -1.84, J_{BX} = 2.70, J_{BY} = -1.57$, and $J_{XY} = 6.43$ Hz. Protons A and B are obviously those of the methylene group, the pronounced difference in chemical shift between them being in excellent agreement both with recent observations on the anisotropy of the sulfinyl group (succinctly summarized in ref. 14) and with the spectra of the following closely related compounds: (a) 8, $\delta_A = 5.42$, $\delta_B = 5.78$ p.p.m., $J_{AB} | 3.5 \text{ Hz} (15)$, (b) 9, $\delta_A = 5.31$, $\delta_B = 5.98 \text{ p.p.m.}$, $J_{AB} | 4 \text{ Hz} (8)$, and (c) 10 (obtained by flash thermolysis as described in the next section), $\delta_A = 5.32$, $\delta_B = 5.72$, $\delta_X = 6.81$ p.p.m., $J_{AB} - 16.0$, $J_{AX} 2.21$, $J_{BX} 1.95$ Hz. The previous work on the anisotropy of the sulfinyl group (cf. ref. 14) clearly indicates proton A in each of the above cases is the one cis to the sulfinyl oxygen.



Not long after we had encountered the formation of 3 from 1, Dittmer *et al.* made a preliminary announcement (16) of a similar rearrangement of a substituted naphthothiete CANADIAN JOURNAL OF CHEMISTRY, VOL. 48, 1970



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sulfone when heated in the presence of 9,10dihydroanthracene. There was no indication in their abstract (16) that these authors were particularly concerned about the possible intermediacy of a sulfene and we therefore carried on with our study. Much more recently these authors have published a full account of their work (8) in which they refer to 'an intermediate (dipolar or diradical in character)' which is represented by a sulfene structure and two other canonical forms. As we had surmised, the study of sulfenes was clearly not the primary purpose of their investigation and there is in fact relatively little overlap between their work and ours.

Having firmly established structure 3 for the thermolysis product, we turned our attention to the problem of gaining information about its mechanism of formation. Since it seemed likely to us that vinylsulfene (2) was a precursor of the sultine (3), and since trapping of an alleged intermediate is traditionally a good piece of circumstantial evidence for a mechanism, we tried a number of experiments with potential sulfene traps. Aniline, o-chloroaniline, or cyclohexanol led to only small amounts of brown intractable material, but phenol gave the hoped for ester 11 in roughly 15% yield. The ester (11) was identified by its spectra and an orthodox preparation from 2-propene-1-sulfonyl chloride (12), presumably via 1,2-addition to vinylsulfene (2) (17). When the sultine (3) was similarly heated with phenol only a brown tar was obtained, showing that the ester (11) did not arise from 3.

In the hope of finding a more efficient trapping

agent than phenol, we tried heating 1 with cyclohexylamine. The product, obtained in good yield, was, unexpectedly, *N*-cyclohexyl*methanesulfon*amide (13). The origin of 13 is not established but a plausible mechanism is suggested by the observation that cyclohexylamine and 1 react at room temperature to give the simple addition product 14. Thermal decomposition of 14 could lead to sulfene and *N*-vinyl-*N*-cyclohexylamine, followed by reaction of sulfene with cyclohexylamine to give 13. Such a fragmentation of 14 finds close parallel in the fission of 3-thietanol 1,1-dioxide to acetaldehyde and formaldehyde on flash thermolysis (see below).

Trapping experiments in the vapor phase gave only negative results. Neither 1–2 mm of ammonia (to trap sulfenes) nor 30 mm of oxygen (to trap possible free radical intermediates) gave any sign of products derived from reaction with the wouldbe trapping reagents.

As mentioned above, vinylsulfene (2) has been implicated (17) in the reaction of 2-propene-1sulfonyl chloride (12) with triethylamine and methanol-d. It therefore seemed conceivable that vinylsulfene so generated might yield the sultine 3 provided sulfene traps were absent, but experiments at 0 and -40° gave no sign of 3. This result was disappointing but not really surprising in view of the difference in reaction conditions, the requirement of a *cisoid* conformation of 2 to form 3, and the speed and variety of other reaction paths available to 2.

Another experiment was attempted which also gave negative results, though in this instance it is

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the result that would be expected from the vinylsulfene mechanism. It was argued that if the reaction were not an electrocyclic ring opening but merely a homolytic cleavage to the diradical (in which each of the odd electrons is orthogonal to the π -bond) which then closed to the sultine 3, a similar (though presumably slower) reaction might be observed on thermolysis of trimethylene sulfone, the saturated analogue of 1. Trimethylene sulfone was found to be stable to conditions which completely converted 1 to 4, but at 580° in the quartz tube it decomposed to give no recognizable products other than starting material nor any indication of a sultine. On flash thermolysis trimethylene sulfone also behaved differently from thiete 1,1-dioxide (1), as is described below.

Flash Thermolytic Experiments

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The original object of these experiments was the generation of sulfene. It was hoped that this could be achieved by inducing what would now be termed the reversal of a 2s + 2a addition in a cyclic sulfone. This assumed, probably unjustifiably, an analogy of sulfene with ketene. Generated in this way the sulfene might possibly be trapped at liquid nitrogen temperature where it would be available for reaction with subsequently added reagents and, eventually, for spectroscopic examination. The first of these objects has been achieved since the completion of the presently described experiments, and has been described elsewhere (1).

The apparatus used for the thermolytic experiments is described in the Experimental section. It consists of a flow system⁵ wherein the heated products are quenched rapidly by impinging on a liquid nitrogen-cooled cold-finger. The contact times were of the order of 1-5 ms. A similar apparatus has been described by Hedaya (19).

The first substances examined were the ketosulfones 15a, b, and c because of their ready availability and because, in principle, ketene could be one of the products. However, the not surprising observation was made that all three substances lost sulfur dioxide and carbon monoxide virtually quantitatively to give ethylene, isobutylene, or styrene respectively. This presumably entails the extrusion of one of the small fragments followed by coupling to give the threemembered ring. A second extrusion then follows. There is analogy for all the separate steps of the sequence.



The thermolysis of thiete 1,1-dioxides was then investigated. The parent substance (1) itself gave, at 615° , the sultine 3 already obtained and characterized as described in the preceding section. Similarly 2-phenyl 1,1-thiete dioxide at 455° gave the sultine 10. Under these conditions fragmentation did not occur, and at higher temperature, as was later found, loss of the elements of sulfur monoxide⁶ took place (4). No sultine could be obtained from the thermolysis of 2,2-dimethyl thiete 1,1-dioxide.

The thermolysis of thietane 1,1-dioxide (16a) itself gave cyclopropane, propylene, and sulfur dioxide (Table 1). Similarly 2,2-dimethylthietane 1,1-dioxide (16b) gave 3-methyl-1-butene, 2methyl-2-butene, 2-methyl-1-butene, and sulfur dioxide. The initial process would appear to be homolysis of the carbon-sulfur bond followed normally by formation of the 1,3-diradical and closure (or hydrogen migration). The formation of cyclopropane and propene from such a 1,3radical has been proposed by Flowers and Frey from a study of the photolysis of cyclobutanone (23). The ratio of methylbutene formed in the thermolysis of 2,2-dimethylthietane 1,1-dioxide is close to that found by Flowers and Frey (24) in the

⁵The system derives from that of F. P. Lossing who over the years has pioneered this technique (see for instance ref. 18 and many subsequent papers from Dr. Lossing's laboratories). More recently, and roughly contemporarily with our own work E. Hedaya and his collaborators (19) have made several important and elegant contributions to the area.

⁶By analogy with the term "desulfonylation" (20) which refers to loss of sulfur dioxide, we designate the loss of sulfur monoxide as "desulfinylation". The process has been observed with episulfoxides (21) and sulfones at high temperature (22).

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TABLE	1
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Thermolysis of thietane and thietanone 1,1-dioxides

Compound	Temperature (°C)	Pressure (µ)			Products (%)				
		Pump	Furnace	(min)	SO ₂		Hydrocarbons		
15a	930 940	1 5	200 100	30 30	98.5 96.0		Ethylene 96.1 99.7		
15 b	940 945	1 1	100 100	30 30	97.3 95.3		Isobutylene 96.5 93.5		
15 c	930 950	1 1	100 50	30 15	97.2 92.5		Styrene 97.6 91.5		
16a*	960 950	7 5	90 110	15 15	69.1 50.6	Ethylene Trace	Propylene 43.5 46.2	Cyclopropane 51.2 52.5	
16 b	950 950	5 4	150 100	15 15	79.5 50.2	1-Methyl- 2-butene 21.2 20.8	3-Methyl-1 2-Methy 15.6 15.9	-butene plus d-1-butene	

*At 800° and 10–20 μ 16a gave in addition to the hydrocarbons a small amount of starting material (< 15%) and ~ 10% of the saturated sultine analogous to 3.

TABLE 2							
Products of thermolysis	s of 3-thietanol	1,1-dioxide (17) at 9	935°				

Pro	duct	МеСНО	MeCH(OMe) ₂	CH ₂ (OMe) ₂	EtCHO	MeCOMe	CH2=CHCHO	C_2H_6	C_2H_4	SO_2
Yield	Run 1 Run 2	2.8 4.5	24.0 23.3	6.4 6.9	23.1 21.1	26.8 23.2	2.3	$\begin{array}{c} 1.4 \\ 1.4 \end{array}$	10.0 6.9	*

*Not determined.

pyrolysis of dimethylcyclopropane. 3-Methyl-1butene and 2-methyl-2-butene plus 2-methyl-1butene were formed in the ratio of 1.0:0.96 as against 1.0:0.77 from the thietane 1,1-dioxide. At 800° and 10–20 μ , conditions sufficiently mild to give back a little unreacted starting material, **16***a* also gave a small amount (~10%) of the saturated sultine, 1,2-oxathiolane 2-oxide (25), presumably from the initially formed diradical.

Concurrent with the thermolysis of the thiete dioxides the flash thermolysis of 3-thietanol 1,1dioxide (17) was also investigated. Here it was hoped that occurrence of the desired fission could be detected by the observation of the formation of acetaldehyde. This (in its enolic form) would be, together with sulfene, the product of a reversed 2a + 2s addition. The product mixture obtained was complex (see Table 2). When thermolyzed with no trapping agent on the cold-finger, only a small percentage of chloroform-soluble material was obtained and a large amount of polymer was formed. When methanol (intended as a trap for any sulfene formed) was deposited on the coldfinger the products listed were obtained in the indicated yields.

The formation of some of the products could be readily explained. Extrusion of sulfur dioxide could give acetone and propionaldehyde by hydrogen migration or by closure to cyclopropanol and rearrangement. Some dehydration to thiete 1,1-dioxide could occur, and the high temperature rearrangement of this was known (4) to give acrolein.

The formation of acetaldehyde and its dimethyl acetal indicated that a third mechanism of decomposition was operative which could have been that originally desired. At the same time the formation of formaldehyde required explanation. Both observations can be rationalized if it be assumed that the initially formed sulfene rearranges to the cyclic isomer **18** which then undergoes desulfinylation (4). It would appear that the desulfinylation of sulfenes is a general process at temperatures above 700–800°. For instance, it has

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been further observed that methanesulfonyl chloride at 940° also gives formaldehyde, ethenesulfonyl chloride above 800° gives chloroacetaldehyde (presumably from chloromethyl sulfene), and 1,3-dithietane 1,1,3,3-tetroxide ("sulfene dimer") (26) at 900° yields formaldehyde as well as sulfur dioxide and ethylene.⁷ These results are readily and consistently accounted for by assuming thermal fragmentation or rearrangement to form a sulfene, followed by desulfinylation. It should be further pointed out that with those systems for which there is evidence for sulfene formation at the lower temperatures, *only* the desulfinylation product is found at the higher temperatures.

In the 3-thietanol 1,1-dioxide experiment, if the foregoing be true, the yield of sulfur dioxide should equal that of the acetone and propionaldehyde combined; this is indeed approximately so. The remaining sulfur is extruded as SO and was observed as a red material on the Dewar surface which was transformed into a yellow insoluble polymer on being warmed to room temperature. This behavior is compatible with the disproportionation of sulfur monoxide to disulfur monoxide and conversion of the latter to poly(sulfur oxide) (27).

Discussion of the Mechanism of the Rearrangement of $1 \rightarrow 3$

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The evidence given above describing experiments on thiete 1,1-dioxide (1) and related compounds is not sufficient to prove the intermediacy of vinylsulfene (2) in the rearrangement of 1 to 3, but taken with other data does contribute to a persuasive circumstantial case for the sulfene mechanism. The argument may be summarized by the following points. (a) Thermal opening of four-membered rings containing an endocyclic double bond has in other instances been shown to be a cyclic, concerted process. (b) The product expected from trapping of a sulfene has been obtained in one case; the low yield in this reaction and the failure of other trapping experiments can be reasonably attributed to one or more of the following: (i) instability of the trapped product, (*ii*) fast unimolecular reaction of vinylsulfene (2), (iii) diversion of the course of the reaction by preliminary interception of the starting material by the would-be trapping reagent. (c) The thermolysis of trimethylene sulfone (16*a*), which cannot undergo analogous ring opening, gives different products, probably by a completely different route, from 1.⁸ (*d*) High temperature flash thermolysis of 1 gives the desulfinylation product, acrolein, and derivatives of 1 which have been similarly treated react analogously (3, 4). (*e*) Considerable evidence is now available concerning the "abnormal" route to and from sulfenes, and, in particular, there is independent evidence of formation of a substituted cyclic sulfinic ester from a vinylsulfene. Points (*a*)-(*d*) have already been discussed in recounting the experiments, but the final aspect of the argument, (*e*), requires amplification.

Point (e) concerns "abnormal" addition to sulfenes, which has been defined (3), as one leading to a sulfinyl derivative; this contrasts with "normal" addition which gives a sulfonyl derivative. By this definition formation of the sultine **3** from vinylsulfene (**2**) (and also of **18** from sulfene) would be an "abnormal" addition and a mention of the present status of such addition would seem relevant.

To complement our earlier approach to this question (28), we have recently obtained strong evidence (29) for the formation of methylsulfene from the α -chlorosulfinate anion. This reaction is the reverse of "abnormal" addition and shows that the free energy of the transition state for the "abnormal" route is not impossibly high. As the terminology implies, the "normal" addition ordinarily has the lower activation energy, but for reactions such as those discussed in this paper and earlier (28), in which the "normal" process merely gives back starting material, product formation via the "abnormal" route would seem eminently reasonable.

In addition to our general observations on the "abnormal" reaction, we have recently en-

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⁷D. L. Verdun and D. R. K. Harding, unpublished observations in these laboratories.

⁸The formation of a small amount of saturated sultine from 16a could be taken as indicating that 1 and 16a react by similar mechanisms, the cyclopropane and propylene merely arising from further reaction of the saturated sultine. Control experiments by D. R. K. Harding in these laboratories, however, show that the saturated sultine is *less* susceptible to thermal decomposition than 16a and only 25%, at the most, of the products from 16a could arise via the sultine. At the same time the complete absence of desulfonylation products for 1 over a temperature range from $615-950^{\circ}$ (4, 10) strongly suggests that the homolysis mechanism which easily accounts for the products from 16a cannot be important in the thermolysis of 1.



countered another reaction for which our preferred mechanism is a cyclization of a vinylsulfene to a sultine. The benzothiadiazine **19** on reaction with chlorine in an anhydrous medium gives **22** (30, and B. L. Huston and L. J. Danks, unpublished observations). An attractive rationalization of this observation is that **20**, the primary product of chlorination, undergoes a reverse Diels-Alder reaction with loss of nitrogen to give **21**, which then cyclizes in the same way as **2** to give **22**.

Experimental

Melting points were determined on a Kofler hot stage and are uncorrected. The i.r. spectra were obtained with a Beckman IR-10 spectrophotometer using sodium chloride cells. The n.m.r. spectra were determined either on a Varian A-60 or a Varian HA-100 instrument. The t.l.c. was carried out using Camag Kieselgel DF 5. Degassing of sealed tubes prior to thermolysis was carried out by freezing the mixture in liquid N₂, pumping with a vacuum pump for a few minutes, thawing, and then repeating the procedure twice more.

1,1-Dioxy-3-thietanyl Phenylmethanesulfonate (4b)

3-Thietanol 1,1-dioxide (17) (1 g, 8.2 mmoles), prepared by the method of Truce and Norell (6), and phenylmethanesulfonyl chloride (1.71 g, 9.0 mmoles) were dissolved in dry tetrahydrofuran (40 ml). Triethylamine (1.01 g, 10 mmoles) was added dropwise and with stirring to this solution and the mixture stirred for 1 h further. The solvent was then evaporated under reduced pressure; the residue was taken up in methylene chloride and this solution washed with water, dried, and the solvent evaporated leaving a colorless residue (2.2 g). Recrystallization from methylene chloride gave a product (2.01 g, 89%) melting at 189–190°.

Anal. Calcd. for $C_{10}H_{12}O_5S$: C, 43.49; H, 4.38; S, 23.20. Found: C, 43.62; H, 4.34; S, 23.01.

Thiete 1,1-Dioxide (1)

1,1-Dioxy-3-thietanyl phenylmethanesulfonate (1.0 g, prepared as above) was suspended in benzene (50 ml) at 50°. A solution of triethylamine (3.6 ml) in benzene (10 ml) was added and the mixture stirred for 1 h further. The solvent was evaporated and the residue extracted with ether (three portions of 60 ml). The solvent of the combined extracts was evaporated and the residue recrystallized from benzene – petroleum ether giving a product (360 mg, 96%) melting at 47–49° and showing i.r. and n.m.r. spectra agreeing well with those already reported (5, 31).



The gas phase thermolyses were carried out in a quartz test tube (30 cm long and 1 cm outside diameter) fitted with a B10 male ground glass joint. The latter was connected to a Pyrex U-tube which could be cooled by immersing the lower part in a Dewar flask containing a Dry Ice-acetone mixture. Thiete 1,1-dioxide (100 mg; 0.96 mmole) was placed at the closed end of the quartz tube, which was then fitted with the U-tube and evacuated to 0.02 mm Hg (measured between the cold trap and the pump). In the meantime the quartz tube was heated to 450° by means of a furnace so arranged that the closed end containing the organic material protruded about 3 cm out of the furnace. After about 45 min all of the thiete 1,1-dioxide had passed through the tube and a yellow liquid with a sharp irritating odor had collected in the U-tube (88 mg, 85%). This liquid was distilled twice in a small cold-finger distillation apparatus; b.p. 90°/15 mm. The i.r. spectrum (CCl₄) showed absorption at 3090(w), 2920(w), 2860(w), 1600(w), 1445(w), 1335(w), 1280(m), 1195(w), 1135(s), 1085(m), 1005(m), 985(s), 920(m), 705(s), 645(m), 615(m). The n.m.r. values given in the Results and Discussion were obtained from a spectrum determined on the HA-100 instrument using the LAOCOON III computer program. The signs of the coupling constants could not be rigorously assigned; those giving best agreement between observed and computed spectra are given.

Anal. Calcd. for C₃H₄O₂S: C, 34.60; H, 3.87; S, 30.79. Found: C, 34.45; H, 3.85; S, 30.68.

Thermolyses carried out at 450° and 0.005 mm and at 390° and 0.005 mm in the same apparatus gave similar results.

The above quartz thermolysis tube was fitted with a tubulation at the closed end to allow gases to be added during the reaction. In one experiment ammonia was passed through the tube during the thermolysis of a sample of thiete 1,1-dioxide (60 mg). A second trap cooled in liquid nitrogen was added to retain the ammonia. The pressure measured between the liquid nitrogen trap and the pump varied between 1 and 2 mm. The product contained in the front trap (50 mg) was shown by i.r. and t.l.c. to be an approximately 1:1 mixture of thiete 1,1dioxide (1) and the cyclic sulfinic ester (3); there was no indication of any product derived from reaction with ammonia. When a sample of thiete 1,1-dioxide was passed through the tube at 450° in the presence of a rapid stream of oxygen (pressure between the traps and pump > 30mm), the product (43 mg) was also found by i.r. and t.l.c. to be 1:1 mixture of thiete 1,1-dioxide and the sultine (3) with no sign of material derived from any reaction with oxygen.

(b) In Solution

Thiete 1,1-dioxide (1) (15 mg) was dissolved in benzene

(1 ml) contained in a thick-walled Pyrex tube (outer diameter 1 cm). The sample was degassed and sealed under reduced pressure and the tube heated in a Carius oven at 280° for 10 min. The tube was cooled and the benzene evaporated leaving an oil (11 mg) identical in i.r. spectrum and t.l.c. behavior with the sultime (3) obtained from the gas phase thermolyses.

Similar thermolyses at 220° for 30 min and 230° for 10 min gave products containing both unreacted thiete I,1-dioxide and the sultime (3). Use of xylene as the solvent in an experiment carried out at 270° for 45 min led to a dark brown product which was shown by t.l.c. to have, amongst others, one component with the same R_f value as the sultime (3). Similar treatment of sultine 3 also gave an extensively decomposed material.

Reaction of Sultine 3 with Sodium Hydroxide

The sultine (3) (45 mg, 0.43 mmole) was dissolved in 0.1 N sodium hydroxide (4.3 ml) and the solution stirred at room temperature for 2 h. The water was evaporated under reduced pressure leaving a gummy residue, insoluble in ether, methylene chloride, or chloroform, which was taken up in methanol (2 ml). A small portion of this was deposited on a sodium chloride plate and the solvent evaporated leaving a film; the i.r. spectrum of this film showed bands at 1020 and 960 characteristic of sulfinate anions (11), a very strong hydroxyl band at 3300, absorption presumably due to water around 1650 and no sign of any peaks between 1700 and 200 cm⁻¹.

The methanol was evaporated from the major portion remaining above and the residue dissolved in 5 N HCl (3 ml). The solution was saturated with sodium chloride and continuously extracted with methylene chloride for 26 h. The organic extract was dried with magnesium sulfate and the solvent evaporated leaving an oil (28 mg) which was identified as sultine 3 by i.r., t.l.c., and v.p.c.

Oxidation of Sultine 3 with Hydrogen Peroxide

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The sultine (3) (49 mg) was dissolved in a solution (1 ml) obtained by mixing glacial acetic acid (3 ml) with 30% hydrogen peroxide solution (0.8 ml), and the resulting solution refluxed for 2 h. The reaction mixture was cooled, poured into water, and extracted with methylene chloride. The methylene chloride extracts were washed with saturated sodium carbonate solution, dried over magnesium sulfate, and the solvent evaporated, leaving a nearly colorless solid (40 mg) which on recrystallization from ether melted at 83-84°. Preparation of the unsaturated sultone (5) has been reported (without experimental details) previously; reported m.p. 78° (12) and 83-84° (13). The i.r. spectrum displayed strong bands at 1360 and 1190 cm⁻¹, the n.m.r. spectrum showed only a complex multiplet around 7.0 and an apparent triplet at 5.1 p.p.m. with the same integrated intensity as the other band.

Thermolysis of Thiete 1,1-Dioxide in Benzene-Phenol

Thiete 1,1-dioxide (90 mg) was dissolved in benzene (1 ml) contained in a thick-walled Pyrex tube as described above and phenol (0.3 g) added. The tube was degassed and sealed under vacuum and heated in a Carius oven at 220° for 30 min. The dark brown reaction mixture was taken up in ether and washed with portions of 10% aqueous sodium hydroxide and water. The ether solution was dried over magnesium sulfate and the solvent

evaporated leaving a dark brown oil (25 mg) which showed bands at 1370 and 1140 cm⁻¹ characteristic of a sulfonic ester. A number of similarly executed runs gave the following results: (*i*) 15 mg heated at 270–280° for 10 min gave 7 mg of crude product, (*ii*) 12 mg heated at 270–280° for 15 min gave 8 mg of crude product, (*iii*) 40 mg heated at 185° for 2 h gave 4 mg of crude product, (*iv*) 400 mg heated at 250° for 15 min gave 80 mg of crude product.

The crude product (~ 150 mg) from a number of such runs was subjected to preparative t.l.c. using benzene as the developing solvent. The purified sulfonate (~ 70 mg) obtained from the chromatography was distilled in a glass tube (b.p. 85°/0.005 mm) and the distillate subjected to preparative v.p.c., (GE-SE 30 on Chrom W at 140°). The sample of phenyl 2-propene-1-sulfonate so obtained had $n_D^{25} = 1.5216$, strong i.r. bands at 1390, 1370, 1170, 1150, and 870 cm⁻¹, and the following n.m.r. signals: 7.5 (5H, s), a multiplet between 5.4 and 6.4 (3H), and a doublet at 4.1 p.p.m. (2H).

Preparation of Phenyl 2-Propene-1-sulfonate (11) from 2-Propene-1-sulfonyl Chloride (12)

Triethylamine (2 ml) in methylene chloride (5 ml) was added dropwise to a stirred solution of 2-propene-1sulfonyl chloride (12) (500 mg) and phenol (1 g) in methylene chloride (50 ml) at room temperature. The stirring was continued for 1 h after the addition. The reaction mixture was then washed with 2 N HCl, 10% aqueous NaOH, and water, respectively. The methylene chloride extract was dried and the solvent evaporated yielding a colorless oil (500 mg). A specimen for analysis, determination of physical properties, and comparison with the material from the thermolytic experiments was obtained by v.p.c. as described above; the i.r. and n.m.r. spectra were identical to those of the specimen of (11) obtained from thiete 1,1-dioxide (1); $n_D^{25} = 1.5211$.

Anal. Calcd. for $C_9H_{10}O_3S$: C, 54,53; H, 5.08; S, 16.18. Found: C, 54.59; H, 4.85; S, 16.28.

Reaction of Sultine 3 with Phenol

The sultine (3) (80 mg) was dissolved in benzene (1 ml) in a thick-walled Pyrex tube and phenol (0.5 g) added. The tube was degassed, sealed under vacuum, and heated at 245° for 15 min. The dark brown reaction mixture was taken up in ether (10 ml) and washed with dilute NaOH and water. The organic phase was dried and the solvent evaporated leaving a brown tar (5 mg) which showed no distinctive features either on t.l.c. or in its i.r. spectrum.

Attempted Trapping of the Sulfene with Amines and

Cyclohexanol

These experiments were carried out in degassed solutions in dry benzene in sealed tubes as described above.

Aniline (0.5 ml) was added to a solution of thiete 1,1-dioxide (1) (45 mg) in benzene (0.5 ml) and the mixture heated at 240° for 30 min to give an almost black product which was diluted with methylene chloride and washed with 2 N HCl and water. Evaporation of the solvent gave a small amount (5 mg) of a dark brown residue showing no distinct features on t.l.c. o-Chloroaniline (0.5 ml) in benzene (0.5 ml) containing the thiete dioxide (30 mg) was heated for 20 min at 220°. Similar work-up gave only a few milligrams of brown product showing only a brown streak on t.l.c. Cyclohexanol (0.5 ml) was added to a solution of the thiete dioxide (30 mg) in benzene (0.5 ml) which was then heated at 230° for 15 min. The residue (3 mg) obtained after work-up was a dark brown tar showing no distinct spots on t.l.c.

Cyclohexylamine (0.6 ml) was added to a solution of thiete 1,1-dioxide (40 mg) in benzene (0.3 ml) and the mixture heated at 220° for 30 min. The reaction product was poured into methylene chloride (15 ml) and washed with dilute HCl. Evaporation of the solvent gave a residue (45 mg), which after sublimation melted at $102-104^{\circ}$; this was identified as *N*-cyclohexyl methanesulfonamide (13) by comparison of m.p., mixed m.p., i.r., and n.m.r. spectra with an authentic specimen (m.p. $104-105^{\circ}$, after recrystallization from methanol) prepared from methanesulfonyl chloride; reported melting points are 105-106.5 (32) and 106° (33).

Reaction of Thiete 1,1-Dioxide with Cyclohexylamine at Room Temperature

Cyclohexylamine (38 mg) was added to thiete 1,1dioxide (40 mg) and the mixture shaken at room temperature for 1 to 2 min, after which time the mixture had crystallized. Recrystallization from ether gave crystals 3-(N-cyclohexylamino)-thietane 1,1-dioxide (14), melting at 93-94°.

Anal. Calcd. for C₉H₁₇NO₂S: C, 53.19; H. 8.43; N, 6.89. Found: C, 53.37; H, 8.53; N, 6.79.

Reaction of 2-Propene-1-sulfonyl Chloride with Triethylamine

A solution of the propenesulfonyl chloride (15 mg) in dry ether was slowly treated at 0° with a solution (1 ml) prepared by mixing triethylamine (0.2 ml) with ether (10 ml). A precipitate formed; the solution was stirred at 0° for 30 min. It was then washed with diluted HCl. The t.l.c. showed no sign of the cyclic sulfinate ester. Similar experiments carried out at room temperature and -40° showed no significant indication of the presence of the cyclic sulfinic ester.

Hydrogenation of Thiete 1,1-Dioxide

Thiete 1,1-dioxide (120 mg) was added to a suspension of prehydrogenated 5% Pd on barium carbonate catalyst (200 mg) in ethyl acetate (10 ml), and the mixture shaken with hydrogen. Hydrogen uptake was complete in 20 min. Filtration and evaporation of the solvent gave the product (118 mg) which on crystallization from ethyl acetate – pentane gave trimethylene sulfone 16*a* (112 mg) m.p. 73–75°; reported m.p. 74–75° (*cf.* ref. 5). Use of 5% Pd on charcoal catalyst also gave trimethylene sulfone but only in about 30% yield.

2-Phenyl-3-thietanone 1,1-Dioxide

3,3-Diethoxy-2-phenylthietane 1,1-dioxide (6) (10 g) was dissolved in concentrated hydrochloric acid (100 ml) and stirred for 18 h. The crystalline precipitate (8.2 g) was triturated with chloroform and the residue crystallized from benzene-dioxane to give 5.6 g (71%) of the thietanone (evidently the enol form), m.p. 172–174°; $v_{max}(Nujol)$, 3100 (broad), 1680, 1265, 1105 cm⁻¹; $\delta(CD_3COCD_3)$: 7.92 (5H, m) 4.55 (2H, s); $\lambda_{max}(EtOH)$, 265 nm (ε 13 200).

Anal. Calcd. for $C_9H_8O_3S$: C, 55.10; H, 4.11; S, 16.31. Found: C, 55.11; H, 4.13; S, 16.23.

The chloroform soluble portion gave, after chromatog-

raphy, 3-ethoxy-2-phenyl 2-thiete 1,1-dioxide, m.p. 132–132.5° [lit. (6) 132–134°]; δ (CDCl₃): 1.4 (3H, t, J = 7 Hz), 4.15 (4H, q, J = 7 Hz), 4.57 (2H, s), 7.40 (5H, m). The thietanone gave with diazomethane 3-methoxy-2-phenyl 2-thiete 1,1-dioxide, m.p. 132–132.5; v_{max} (CHCl₃) 1662, 1307, 117 cm⁻¹; δ (CDCl₃): 3.90 (3H, s), 4.59 (2H, s), 7.39 (5H, m); λ_{max} (EtOH) 264 nm (ϵ 14 500).

2-Phenyl-2-thiete 1,1-Dioxide

3 - N, N-dimethylamino-2-phenylthietane 1,1-dioxide (34) (1 g) was dissolved in 50 ml of a methanol-chloroform mixture and 0.85 ml methyl iodide added. After 24 h the crystals (1.05 g) of quaternary salt were isolated by filtration, m.p. 212°. The salt (3 g) was dissolved in water (120 ml) and 3 g silver oxide added. The triethylamine was removed, with warming under reduced pressure, and the product isolated with methylene chloride to give, after crystallization from methylene chloride – light petroleum (60-80°), the thiete 1,1-dioxide (1.1 g; 74%), m.p. 94.5-95°, identical in all respects with the material prepared by Wells and Abbott (34) by a different route.

2,2-Dimethyl-thietane 1,1-Dioxide (16b)

2,2-Dimethylthiete 1,1-dioxide (640 mg) (35) in ethanol was hydrogenated over palladized charcoal (100 mg, 5%) until one molecular equivalent of hydrogen was absorbed. The crude product, m.p. $61-62^{\circ}$ was sublimed to give 580 mg of the thietane 1,1-dioxide, m.p. $70-71^{\circ}$; $v_{max}(CCl_4)$ 1323, 1128 cm⁻¹; $\delta(CCl_4)$ 1.57 (6H, s), A_2X_2 at $\delta_A = 4.14$, $\delta_X = 6.57 J_{AA'}$ 18.59 Hz, $J_{XX'}$ 17.70 Hz, J_{AX} 6.48 Hz, $J_{AX'}$ 10.43 and $J_{A'X'}$ 6.48 Hz.⁹ Anal. Calcd. for C₅H₁₀O₂S: C, 44.77; H, 7.52; S, 23.85. Found: C, 44 81; H, 7.36; S, 23.76.

High Temperature Reactions

The apparatus used for most of these experiments is shown schematically in Fig. 1*a*. In a later modification, the Dewar system has been greatly enlarged and is followed by a second Dewar as shown in Fig. 1*b*. A description of the oven of the first type follows.

The furnace unit was a brass cylinder 11×2.5 (diam.) $\times \frac{1}{8}$ in. and was wrapped with 9 coils of $\frac{1}{4}$ in. copper tubing (water cooling). The ends of the cylinder were two 🛔 in. brass flanges 5 in. in diameter. An end plate, with a $\frac{1}{2}$ in. O-ring connector, a Hastings gauge, and two pairs of metal-to-porcelain through connectors, was bolted to one end of the cylinder. A second plate with a 1 in. O-ring butt connector was bolted to the other end. Vacuum seal was maintained with $\frac{1}{8}$ in. Viton O-rings. The reactor tube was inserted through the $\frac{1}{2}$ in. O-ring connector into the cylinder. This tube consisted of an inner 1/8 in. i.d. ceramic thermocouple well and an outer $\frac{1}{2}$ in. o.d. ceramic tube. The two tubes were fused to Pyrex glass of the same diameter and were joined together at the inlet end outside the end plate. A 1/8 in. stainless steel shielded MgO insulated chromel-alumel thermocouple was used and was attached to a Barber-Coleman Model 471 temperature controller. The first 4 in. of the outer tube were wound with 6 ft of 22 gauge Nichrome spaced between turns of $\frac{1}{8}$ in. asbestos rope, and covered

⁹Calculated spectrum using a LAOCOON III computer program with iteration.



FIG. 1. (a, b) A, quarter-swing butterfly valves; B, trapping agent inlet; C, vacuum gauge*; D, vacuum seal coupling; E, thermocouple well; F, main oven; G, sublimation oven; H, water-cooling coil; I, ball bearing race; J, liquid nitrogen cold-finger; K, connection leading to the sample-handling manifold: L, connection to main pump. *The apparatus in Fig. 1a also has a Hastings gauge located adjacent to the vacuum seal coupling D and is not shown on the drawing.

with a layer of asbestos paper. The last 4 in, were loosely bound with an additional 4 ft of the same wire. The ends of both wirings were attached to the through-connectors.¹⁰ Liquids after distillation from the Dewars or U-tube collectors were transferred in the usual way

¹⁰More recently platinum-iridium wire has been used to permit the attainment of temperatures up to 1300°.

through a vacuum line. Gases were collected in a 75 ml stainless steel bomb filled with $\frac{3}{16}$ stainless steel balls, the whole being cooled in liquid nitrogen. The apparatus was evacuated using a Welch Model 1403 pump and a Consolidated Vacuum Corporation VMF-20 oil diffusion pump. The pressure was monitored at several stations using Hastings gauges. In more recent modifications we have used a Speedivac ED-500 pump. In the presently

described experiments pressures of the order of 100 µ were used. More recently pressures between 1-40 µ have been routine.

For analytical purposes, calibrating compounds in known amounts were added to the products. These are specified in the text. Sulfur dioxide was also estimated iodometrically.

Contact times were calculated from the formula

$$T = 0.16 \, \frac{V_{\rm r} \cdot p \cdot t}{T_{\rm r} \cdot m}$$

where P is the pressure, V_r the volume of the hot zone of reactor, T_r the reaction temperature (°K), t the time of reaction (s), m the moles of material passed. The contact times used were of the order of ms, but in view of the dubious significance of the term so derived the values should only be given a relative sense.

The thermolyses for these relatively non-volatile substances were carried out by placing a known weight of material in the first section of the furnace. The material was slowly sublimed through the hot zone with a small stream of nitrogen to minimize back sublimation. Any starting material which did sublime backwards was washed out and weighed. Traps were cooled in liquid nitrogen. All materials were shown to be sublimed unchanged.

Thermolyses

(a) Thietane 1,1-Dioxide (16a)

(i) Approximately 80 mg of the substance was thermolyzed at 465, 595, and 765° (100 μ). The only non-gaseous material observed was starting material in 92.5, 78.6, and 36.5% yield, respectively.

(ii) Approximately 90 mg of the substance was thermolyzed at 950° at 100 µ. After completion of the reaction and cooling, 5.0 ml of propane gas was added. The mixture was analyzed on a 5 ft $\times \frac{3}{16}$ in. 10% Ethofat on chromosorb P column at 100°. The products were identified by i.r. and retention time as ethylene, propylene, and SO₂ (see Table 1).

(b) 2,2-Dimethyl-thietane 1,1-Dioxide (16b)

(i) At 465 and 610° (180 µ) 71 and 40% recoveries were obtained.

(ii) Thermolysis at 950° (120 μ) using methyl formate as calibrating compound gave, using a 5 ft $\times \frac{3}{16}$ in. Porapak S at 150° column, the results in Table 1. The products were identified by i.r. spectra and v.p.c. retention time, and the hydrocarbons also by n.m.r.

(c) 3-Thietanone, 2,2-Dimethyl- and 2-Phenyl-3-

thietanone 1,1-Dioxides (15a, b, and c, respectively) About 200 mg of the ketone was thermolyzed at near 930° ($\sim 200 \mu$). Propane, *n*-pentanol, and *n*-propanol were used as the calibrating compounds, respectively. The columns used were 5 ft $\times \frac{1}{14}$ in. Porapak S at 80° for the first analysis, 20 $\times \frac{1}{4}$ in. 10% FFAP on chromosorb P at 110° for the second and third. In the first and third cases the SO₂ analysis was confirmed iodometrically. The results are contained in Table 1.

(d) 3-Thietanol 1,1-Dioxide (17)

(i) Methanol (0.5 ml) was placed in the trap (a U-tube) and 200 mg of the alcohol thermolyzed at 935° (110 μ). Methyl formate (calibrating compound) was added, the products washed with 0.5 ml methanol, and the mixture analyzed (20 $\times \frac{1}{4}$ in. 10% FFAP on chromosorb P at 50°). The following substances were isolated and the means of identification are indicated parenthetically: acetaldehyde (n.m.r., v.p.c.), dimethoxymethane (i.r., n.m.r., v.p.c.), propionaldehyde (v.p.c., 2,4-dinitrophenylhydrazone), acetone (i.r., n.m.r., v.p.c., 2,4-dinitrophenylhydrazone), acetaldehyde dimethyl acetal (i.r. n.m.r., v.p.c.), acrolein (v.p.c., 2,4-dinitrophenylhydrazone).

(ii) A cold-finger trap was used omitting methanol. A thermolysis at 940° (100 μ) with propane as calibrating compound gave ethane, ethylene, and sulfur dioxide identified by v.p.c. retention time and i.r. spectrum. The results are given in Table 2.

(e) Thiete 1,1-Dioxide (1)

146 mg of the dioxide were thermolyzed at 615° (10 μ). Undecomposed material (55 mg) was recovered and 64 mg (70%, based on unrecovered starting material) of the sultine (3) was obtained.

(f) 2-Phenylthiete 1,1-Dioxide

200 mg of the dioxide were thermolyzed at 455° (50 μ). A mixture of phenyl vinyl ketone (10) and the sultine (10) was obtained. This was separated by thin-layer chromatography (eluent: CHCl₃) to give the pure sultine (55 mg, 27%), m.p. 74.5-75.5°, v_{max}(CCl₄) 1135, 1028 cm⁻¹, and an ABX pattern at $\delta_A = 5.32$, $\delta_B = 5.72$, $\delta_{\rm X} = 6.81, J_{\rm AB} = 15, J_{\rm AX} = 2.21, \text{ and } J_{\rm BX} = 1.95 \text{ Hz},$ and a five proton singlet at 7.47.

Anal. Calcd. for C₉H₈O₂S: C, 60.00; H, 4.48; S, 17.77. Found: C, 60.18; H, 4.57; S, 17.87.

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