Derivatives of Thiacyclobutene (Thiete). VI.[1] Synthesis and Properties of Some Thietes[2-4]

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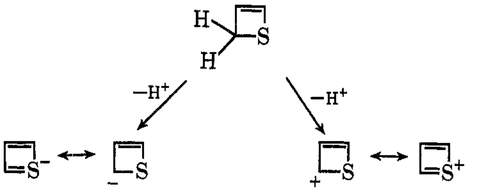
The synthesis and properties of five thiacyclobutenes (thietes) are described. Thietes are of theoretical interest because they have the potential of forming anions and cations isoelectronic with the anion and cation of cyclopentadiene. They are prepared by facile Hofmann eliminations from 3-aminothietane derivatives usually obtained *via* synthetic schemes which start with the addition of sulfene ($CH_2{=}SO_2$) to enamines. Thietes, while relatively stable at low temperatures, show a marked tendency to polymerize or to otherwise decompose over a period of time. Thietes (**4**, **5**), in which the sulfur-containing ring is fused to a six- or seven-membered carbocyclic ring, are less stable than thiete itself or thietes substituted with alkyl groups. Ring opening occurs when thietes are treated with acidified 2,4-dinitrophenylhydrazine to yield 2,4-dinitrophenylhydrazones. Several thietes can be oxidized to cyclic sulfones (thiete sulfones).

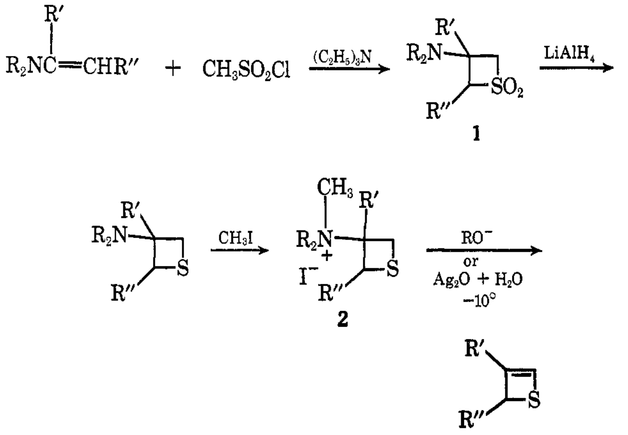
Thietes belong to a relatively new[3] class of compounds and represent, in a formal way, sulfur heterocyclic analogs of cyclopentadienes. Replacement of a formal double bond by a sulfur atom results in no change in the number of π electrons available for possible conjugation, and, since sulfur has approximately the same electronegativity as carbon,[5] this molecular modification may lead to a less drastic change in properties for these sulfur analogs of cyclopentadiene. Thietes are potential precursors of new 6-π-electron conjugated anions and of new 4-π-electron conjugated cations which may be considered as analogs of the anion and cation of cyclopentadiene, respectively.



The first thiete derivatives were sulfones,[6,7] although a relatively stable dithiete, 3,4-bis(trifluoromethyl)-1,2-dithiete, was reported in 1960.[8] The analogous diselenium compound has been reported recently.[9]

A thiete (2,2-dimethyl-3,8-diphenyl-2H-naphtho[2,3-*b*]thiete) in which the double bond was part of an aromatic system was prepared by reduction of the sulfone,[10] but thiete itself (**3**) could not be obtained by reduction of thiete sulfone.[6,11] Several oxetes have been reported.[12]

SCHEME I



3, $R' = R'' = H$
4, $R' = R'' = (CH_2)_4$
5, $R'' = R'' = (CH_2)_5$
6, $R' = C_2H_5$; $R'' = CH_3$
7, $R' = n\text{-}C_3H_7$; $R'' = C_2H_5$

Synthesis.—The general plan for the synthesis of thietes is given in Scheme I. The quaternary ammonium salt required for the Hofmann elimination in the preparation of **3** may be obtained also by treatment of 3-thietanol with *p*-toluenesulfonyl chloride and trimethylamine (eq 1). The amino sulfone required for the synthesis of **3** may be prepared alternatively by addition of the secondary amine to thiete sulfone (eq 2) or to 3-chlorothietane 1,1-dioxide.[6]

The preparation of the aminosulfones shown in Scheme I follows the procedure of Stork and Borowitz[7a,13] and Opitz and Adolph.[14] The reduction of the sulfone normally proceeds well, but the yield of product is reduced by concomitant elimination of R_2NH.[15] The Hofmann elimination is very facile,

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[1] Paper V: D. C. Dittmer, K. Ikura, J. M. Balquist, and N. Takashina, *J. Org. Chem.*, **37**, 225 (1972).

[2] The authors are grateful for support of this research by the National Science Foundation.

[3] Preliminary accounts of some of this research have been given: (a) D. C. Dittmer and F. A. Davis, *J. Amer. Chem. Soc.*, **87**, 2064 (1965); (b) D. C. Dittmer, K. Takahashi, and F. A. Davis, *Tetrahedron Lett.*, 4061 (1967).

[4] Taken in part from P. L.-F. Chang, Ph.D. Thesis, Syracuse University, 1970; F. A. Davis, Ph.D. Thesis, Syracuse University, 1966; and I. Stamos, Ph.D. Thesis, Syracuse University, 1969.

[5] D. W. Cruickshank and B. C. Webster, "Inorganic Sulfur Chemistry," G. Nickless, Ed., Elsevier, Amsterdam, 1968, p 10.

[6] D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961); D. C. Dittmer and M. E. Christy, *J. Amer. Chem. Soc.*, **84**, 399 (1962).

[7] (a) W. E. Truce, J. R. Norell, J. E. Richman, and J. P. Walsh, *Tetrahedron Lett.*, 1677 (1963); (b) W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc.*, **85**, 3236 (1963); (c) R. H. Hasek, P. G. Gott, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **28**, 2496 (1963); (d) G. Optiz and H. Schempp, *Z. Naturforsch.*, *B*, **19**, 78 (1964); (e) D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, **29**, 3131 (1964).

[8] C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, **82**, 1515 (1960); C. G. Krespan, *ibid.*, **83**, 3434 (1961).

[9] A. Davison and E. T. Shawl, *Inorg. Chem.*, **9**, 1820 (1970).

[10] L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965).

[11] C. L. Schelling, M.S. Thesis, Syracuse University, 1964; R. S. Henion, Ph.D. Thesis, Syracuse University, 1967.

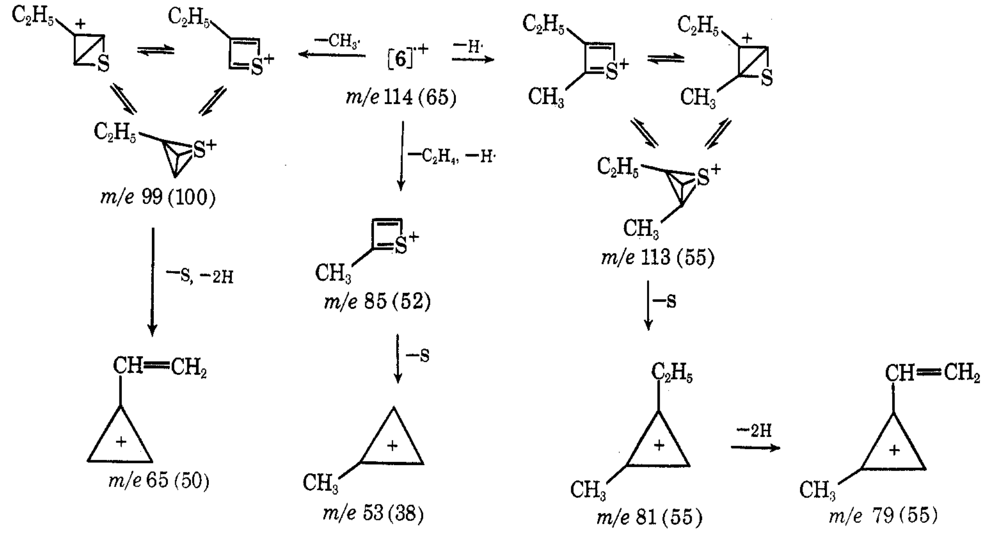
[12] L. E. Friedrich and G. B. Schuster, *J. Amer. Chem. Soc.*, **91**, 7204 (1969); W. J. Middleton, *J. Org. Chem.*, **30**, 1307 (1965); E. Müller, R. Mayer, B. Narr, A. Rieker, and K. Scheffler, *Justus Liebigs Ann. Chem.*, **645**, 25 (1961); J. Hollander and C. Woolf, Belgian Patent 671,439; *Chem. Abstr.*, **65**, 8875 (1966).

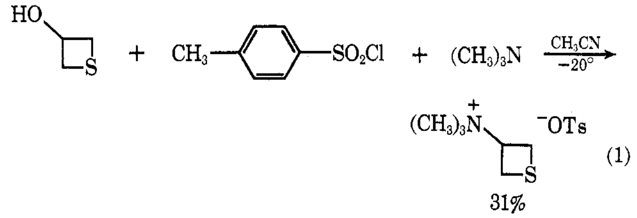
[13] G. Stork and I. J. Borowitz, *J. Amer. Chem. Soc.*, **84**, 313 (1962).

[14] G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962).

[15] Dr. John McCaskie in our laboratory has detected the amine during work-up of the reduction mixture.

SCHEME II





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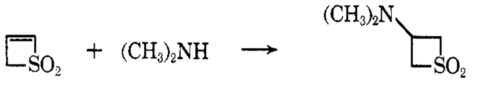
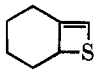


(2)

the only difficulty being the separation of the volatile components of the product mixture. In addition to thiete itself (**3**), thietes **4–7** were prepared as outlined in Scheme I. All of these thietes are liquids.



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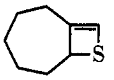

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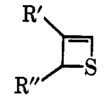

6, R′ = CH_3CH_2; R″ = CH_3
7, R′ = $CH_3CH_2CH_2$; R″ = CH_3CH_2

Thietes **4–7** can be oxidized to the corresponding sulfones, which aids in establishment of the cyclic structures and disposes of alternate tautomeric thioacrolein structures. The sulfones also may be prepared by elimination of amine from the aminosulfones **1**.

The thietes usually have three absorptions in the ultraviolet: 215–228 (ε 1100–2270), 236–248 (ε 2000–3050), and 285–294 (ε 50–567) mμ. The ^{1}H nmr spectrum of the thietes shows the following absorptions: δ 6.05–6.50 (α-olefinic proton), 5.60 (β-olefinic proton), 3.40–4.10 (protons on C-3).[16] Infrared absorption for the double bond is weak and difficult to assign; thietes **5**, **6**, and **7** have absorption at 1600–1625 cm^{-1}. Thietes **3**, **6**, and **7** show very intense ions in the mass spectrum corresponding to the thiete cation formed by loss of a hydrogen atom or an alkyl group.[17] The bicyclic compounds can yield the thiete cation by ring cleavage. As expected, thietes **4** and **5** have abundant parent ions.

Scheme II illustrates a typical mass spectral fragmentation pattern for a thiete (in this instance, **6**) with structures suggested for the various ions. The intensities of the mass spectral peaks relative to the peak of the most abundant ion at *m/e* 99 are given in per cent in parentheses. The observation of metastable ions in the spectrum of **6** at *m/e* 42.7, 77, and between 63 and 64 supports the proposed transformations *m/e* 99 → 65, 81 → 79, and 114 → 85. The structures of the thiete cations are as yet unknown, but a thiatetrahedrane configuration cannot be excluded.

Thermal Stability.—The strain inherent in the unsaturated four-membered ring can be relieved by opening of the ring, which, in the case of thietes, would involve breaking a relatively weak carbon–sulfur bond.

The thietes described in this report are all somewhat thermally unstable. Thiete **4** is least stable; a neat sample has been observed to decompose explosively at room temperature. It is stable for at least 2 weeks at −10° but decomposes in about a week at 5°. A white solid (approximate empirical formula $C_7H_{10}S$) is obtained from the decomposition. Apparently, the material is some oligomer or polymer of the original compound. Attempts to purify the solid were not successful. Ultraviolet spectra of the material indicate the possible presence of an α,β-unsaturated sulfide functionality. Double bond absorption in the infrared appears at 1620 cm^{-1}. Oxidation with 30% hydrogen peroxide yields a sulfone as indicated by infrared absorption at 1320 and 1190 cm^{-1}. The double bond absorption of the sulfone "polymer" is at 1645 cm^{-1}, an increase of 25 cm^{-1} over that in the sulfide. A similar increase of 39 cm^{-1} was observed in the conversion of methyl vinyl sulfide to methyl vinyl sulfone.[18] A smaller increase (5 cm^{-1}) was observed in the oxidation of methyl allyl sulfide to methyl allyl sulfone.[18] Material obtained from the decomposition of neat **4** may be predominantly trimeric (mol wt 371; calcd for trimer, 378). The nmr spectrum of this supposedly trimeric material shows, in addition to absorption for the aliphatic protons of the cyclohexane ring, absorption at δ 3.2 (2 H), 4.5 (1 H), and 5.9–6.0 (3 H). The absorptions at δ 3.2 and 5.9–6.0 are similar to the absorptions of the protons on C-6

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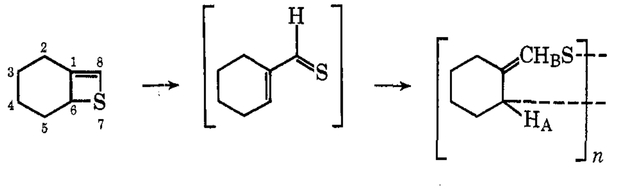
[16] Thiete sulfones show absorption for the olefinic protons in which the magnitude of the shielding is reversed, *i.e.*, the α proton is at higher field than the β proton.

[17] The chemistry of the thiete cation and, in particular, its complexes with transition metals are being investigated and will be described in a subsequent report.

[18] C. C. Price and R. G. Gillis, *J. Amer. Chem. Soc.*, **75**, 4750 (1953).

and C-8 of thiete **4** and may correspond to protons H_A and H_B.

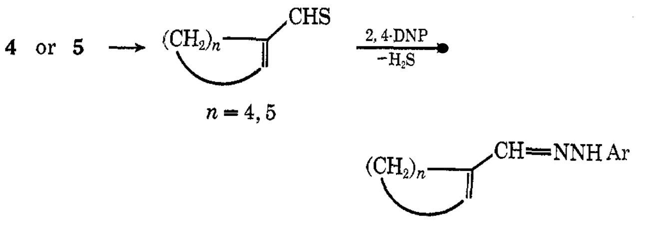
A material of high viscosity (inherent viscosity 0.75) was deposited from a pentane solution of **4** over a 24-hr period.[19] Although evidence is lacking concerning the involvement of 1,4 polymerization in acrolein,[20] the decomposition products of thiete **4**, on the basis of the above data, appear to be derived from a 1,4-addition reaction of a thioacrolein. A cyclic dimer and trimer are possible (although unlikely because of the large ring size) as well as linear oligomers and polymers.



Thiete **5** decomposes to a glassy solid at room temperature. In thietes **4** and **5** the exocyclic double bond creates enough strain so that rupture of the C–S bond occurs more readily than normal.

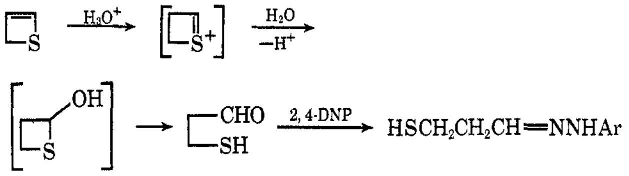
Thiete (**3**) itself is stable at room temperature for up to 1 hr and is much more stable in solution. When it is allowed to stand overnight, a clear, viscous oil if formed from which a white amorphous solid of empirical formula $(C_3H_4S)_n$ is obtained. Infrared absorption at 1600 and 930 cm^{-1} suggests the presence of an α,β-unsaturated sulfide group.

Reactions with 2,4-Dinitrophenylhydrazine.—Thiete **3** reacts quite differently from thietes **4** and **5** with acidic 2,4-dinitrophenylhydrazine (2,4-DNP). From **4** and **5** 2,4-dinitrophenylhydrazones of cyclohexene- and cycloheptenethioaldehyde are obtained, ring opening preceding hydrazone formation. These derivatives are identical with the 2,4-dinitrophenylhydrazones of 1-cyclohexene-1-aldehyde and 1-cycloheptene-1-aldehyde. Thiete **4** also forms the semicarbazone of 1-cyclohexene-1-aldehyde.



Thiete **3** apparently undergoes an acid-catalyzed hydration of the double bond followed by hydrolysis of the thiohemiacetal to β-mercaptopropionaldehyde which yields the 2,4-dinitrophenylhydrazone.[21] The derivative is acetylated with acetic anhydride in pyridine to give a compound identical with the 2,4-dinitrophenylhydrazone prepared from β-acetylthiopropionaldehyde obtained by addition of thiolacetic acid to acrolein. This reaction of **3** is analogous to the acid-catalyzed hydrolysis of alkyl propenyl sulfides to alkanethiols and propionaldehyde reported by Tarbell and Lovett.[22]

The differences in reactivity between **3** and **4** or **5** with acidic 2,4-dinitrophenylhydrazine probably reflect the differences in thermal stability of these thietes. In **4** or **5** the ring strain is such that ring opening to the α,β-unsaturated thioaldehyde occurs faster than the somewhat sterically hindered double bond is protonated. The greater thermal stability of **3** allows protonation of the double bond to be faster than ring opening to thioacrolein.



Experimental Section

Thiete (3).—3-(*N,N*-Dimethylamino)thietane[6] (6.1 g, 0.059 mol), prepared by reduction of 3-(*N,N*-dimethylamino)thietane 1,1-dioxide,[6,23] in methyl ethyl ketone (250 ml) was treated at 0° with methyl iodide (8.3 g, 0.059 mol). The product precipitated after 12 hr at 5°. Recrystallization from methyl alcohol gave white crystals: mp 209–210° dec (8.5 g, 56%); nmr (D_2O) δ 3.2 (N^+CH_3, 2 cis H), 3.8 (t, 2 trans H), 4.9 (t, $>CHN^+<$).

Anal. Calcd for $C_6H_{14}INS$: C, 27.80; H, 5.45; N, 5.39. Found: C, 27.50; H, 5.15; N, 5.10.

An alternate preparation of the quaternary salt involves treatment of 3-thietanol[6] (70 g, 0.78 mol) and trimethylamine (350 ml, 4.2 mol, dried over NaOH) in acetonitrile (500 ml) at −5 to −10° with *p*-toluenesulfonyl chloride (224 g, 1.18 mol) in acetonitrile (440 ml) added dropwise during 2 hr. The reaction mixture was allowed to stand in a freezer at −20° for 2 hr and excess amine was removed by an aspirator. The precipitate was collected by filtration and recrystallized twice from ethanol (350 ml) to give 3-thietanyltrimethylammonium tosylate (74 g, 0.44 mol, 31%): mp 240–242°; nmr (D_2O) δ 7.53 (m, 4, C_6H_4), 4.55 (m, 1, CHN^+), 3.69 (t, 2, CH_2S), 3.20 (d, 2, CH_2S), 2.95 (s, 9, NCH_3), 2.35 (s, 3, $C_6H_4CH_3$). The tosylate may be converted to the iodide by an ion exchange resin or by treatment with hydriodic acid.

Anal. Calcd for $C_{13}H_{21}NO_3S_2$: C, 51.48; H, 6.98; N, 4.62; S, 21.20. Found: C, 51.49; H, 7.11; N, 4.47; S, 21.40.

A solution of the methiodide of 3-(*N,N*-dimethylamino)thietane (40 g, 0.16 mol) in dimethylformamide (380 ml, −20°) was mixed with a solution of potassium 1-methylcyclohexoxide (46 g, 0.30 mol) in dimethylformamide (270 ml, −20°) and the mixture was stirred at −20° for 30 min. Glacial acetic acid (15 ml) was added, the mixture was warmed to 30°, and volatile materials were removed *in vacuo* (2 mm) and collected in two traps, one at −78° and one at liquid nitrogen temperature. Trimethylamine (9.4 g, 100%) was collected in the liquid nitrogen trap. The contents of the −78° trap were distilled as before, the volatile materials being collected in traps at −20 and −78°. In the −20° trap, about 100 ml of a dilute solution of thiete in dimethylformamide was collected, and in the −78° trap, a more concentrated solution (23 g) of thiete was obtained. Distillation of this concentrated solution at 20 mm and 30° gave thiete (9.1 g, 79%) which was collected in a trap at −78° and dried (Na_2SO_4): n^{25}D 1.5160; d^{25}_{25} 0.997; nmr ($CDCl_3$) δ 6.50 (d, 1, *J*, = 3 Hz, C=CHS), 5.60 (two triplets, 1, *J* = 3.2, 1 Hz), 3.80 (d, 2, *J* = 1 Hz). Other physical and spectral properties were reported previously.[3b]

When **3** was allowed to stand overnight or longer at room temperature, a white, amorphous solid and a colorless oil formed. Tlc of the oil indicated that it was a mixture of at least four components. The solid was insoluble in water, hydrochloric acid,

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[19] We are indebted to Professor L. Guy Donaruma of Clarkson College of Technology for the viscosity measurement.

[20] R. C. Schulz, *Angew. Chem., Int. Ed. Engl.*, **3**, 416 (1964).

[21] The hydrazine also may add directly to the sulfonium ion to ultimately yield the hydrazone. Conceivably, the mercaptoaldehyde also could be formed by addition of hydrogen sulfide (derived from hydrolysis of the thiocarbonyl group) to the double bond of the α,β-unsaturated aldehyde or thioaldehyde. However, the nearly quantitative yield of 2,4-dinitrophenylhydrazone would require a very efficient scavenging of the hydrogen sulfide. In fact, hydrogen sulfide is evolved and lost to the atmosphere, as indicated by odor and by lead acetate paper.

[22] D. S. Tarbell and W. E. Lovett, *J. Amer. Chem. Soc.*, **78**, 2259 (1956).

[23] P. L.-F. Chang and D. C. Dittmer, *J. Org. Chem.*, **34**, 2791 (1969).

sodium hydroxide, methanol, acetone, chloroform, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO); ir (KBr) 2980, 2870, 1600 (C=CS), 930 cm^{-1}.

Anal. Calcd for $(C_3H_4S)_n$: C, 49.95; H, 5.59; S, 44.46. Found: C, 48.23; H, 6.40; S, 42.57.

Aminosulfone Derivatives 1.—The aminosulfones were prepared by addition of sulfene obtained from methanesulfonyl chloride and triethylamine to the pyrrolidine enamines of cyclohexanone, cycloheptanone, diethyl ketone, and di-*n*-propyl ketone.[13,14,24] They were recrystallized from ethanol or ethanol–petroleum ether (bp 30–60°). The synthesis of 1-(1-pyrrolidinyl)-7-thiabicyclo[4.2.0]octane 7,7-dioxide was previously reported.[7e]

1-(1-Pyrrolidinyl)-8-thiabicyclo[5.2.0]nonane 8,8-dioxide [**1**, R′ = R″ = $-(CH_2)_5-$] had mp 80–81°; ir 1310, 1120 cm^{-1}; nmr ($CDCl_3$) δ 4.53 (t, 1, $-CHSO_2-$), 3.42, 4.20 (AB quartet, 2, CH_2SO_2-), 2.5–3.05 (m, 4, CH_2N-), 1.5–2.3 (m, 14).

Anal. Calcd for $C_{12}H_{21}NO_2S$: C, 59.30; H, 8.64; N, 5.77; S, 13.15. Found: C, 58.96; H, 8.92; N, 5.84; S, 13.27.

cis-2-Methyl-3-ethyl-3-(1-pyrrolidinyl)thietane 1,1-dioxide (**1**, R′ = CH_3CH_2, R″ = CH_3) was an oil: ir 1300, 1120 cm^{-1}; nmr ($CDCl_3$) δ 4.48 (quartet, 1, $CHCH_3$), 3.62, 4.13 (AB quartet, 2, CH_2SO_2), 2.70 (m, 4, CH_2N-), 1.75 (m, 6, CH_2CH_2N, CH_3CH_2-), 1.35 (d, 3, CH_3), 0.90 (t, 3, CH_3CH_2-).

cis-2-Ethyl-3-*n*-propyl-3-(1-pyrrolidinyl)thietane 1,1-dioxide (**1**, R′ = $CH_3CH_2CH_2$, R″ = CH_3CH_2) had mp 60–61°; ir 1300, 1120 cm^{-1}; nmr ($CDCl_3$) δ 4.32 (quartet, 1, $C\mathbf{H}CH_2CH_3$), 3.70, 4.20 (AB quartet, 2, CH_2SO_2), 2.72 (m, 4, CH_2N-), 1.30–2.30 (m, 10, $C\mathbf{H}_2CH_2N$, $CH_3C\mathbf{H}_2C\mathbf{H}_2$, $CH_3C\mathbf{H}_2-$), 1.10 (t, 6, $C\mathbf{H}_3CH_2CH_2$, $C\mathbf{H}_3CH_2$).

Anal. Calcd for $C_{12}H_{23}NO_2S$: C, 58.80; H, 9.38; N, 5.72; S, 13.05. Found: C, 59.07; H, 9.36; N, 5.67; S, 12.92.

Aminothietane Methiodides 2.—The corresponding sulfone (0.1 mol) in dry ether (200 ml) was added dropwise to a solution of lithium aluminum hydride (11.4 g, 0.300 mol) in dry ether (200 ml) cooled in an ice bath. When the addition of the sulfone was completed, the reaction mixture was stirred for 6 hr at the temperature of the ice bath. Excess hydride was destroyed by dropwise addition of ethyl acetate (50 ml), a 20% solution of ammonium chloride (60 ml), and finally a 1:1 mixture of concentrated ammonium hydroxide and ammonium chloride solutions (*ca.* 70 ml, the addition was stopped when a granular precipitate formed). The ether solution was removed from the precipitate and dried ($MgSO_4$). Removal of the ether by means of a water aspirator left the amino sulfide as an oil. Yields varied from 63 to 85%.

Methyl iodide (equimolar with sulfide) was added to a solution of the sulfide in methyl ethyl ketone (1.5–2.0 l. per mol of sulfide) at 5°, and the solution was allowed to stand overnight at room temperature. The precipitated salt was removed by filtration, and more methyl iodide (0.25–0.5 equiv) was added to the filtrate from which additional salt precipitated overnight.[25] The salts were recrystallized from methanol–ether.

1-(1-Methylpyrrolidinium)-7-thiabicyclo[4.2.0]octane iodide [**2**, R′ = R″ = $-(CH_2)_5-$] (37% yield) had mp 133–135°; nmr (D_2O) δ 4.5 (1, CHS–), 3.8 (m, CH_2N^+, $-\mathbf{CH}_{cis}H_{trans}S-$), 3.2 (s, 4, CH_3N^+, $CH_{cis}\mathbf{H}_{trans}S-$), 2.2 [m, 12, $C\mathbf{H}_2CH_2N^+$, $-(CH_2)_4-$].

Anal. Calcd for $C_{12}H_{22}INS$: C, 42.47; H, 6.53; N, 4.13; S, 9.45. Found: C, 42.61; H, 6.49; N, 3.93; S, 9.47.

1-(1-Methylpyrrolidinium)-8-thiabicyclo[5.2.0]nonane iodide [**2**, R′ = R″ = $(CH_2)_5-$] (54% yield) had mp 139–140°; nmr (DMSO-d_6) δ 4.6 (s, 1, CHS–), 3.0–4.0 (m, 6, $-CH_2S-$, $-CH_2N^+$), 2.98 (s, 3, N^+CH_3), 1.5–2.3 [m, 14, $C\mathbf{H}_2CH_2N^+$, $-(CH_2)_5-$].

Anal. Calcd for $C_{13}H_{24}INS$: C, 44.30; H, 6.81. Found: C, 44.27; H, 6.98.

cis-2-Methyl-3-ethyl-3-(1-methylpyrrolidinium)thietane iodide [**2**, R′ = C_2H_5-, R″ = CH_3] (45% yield) had mp 117–118°; nmr (DMSO-d_6) δ 4.52 (quartet, 1, $CH_3C\mathbf{H}$), 3.0–4.0 (m, 6, $-CH_2S-$, CH_2N^+), 2.92 (s, 3, CH_3N^+), 2.15 (m, 6, $C\mathbf{H}_2CH_2N$, $CH_3C\mathbf{H}_2-$), 1.40 (d, 3, $C\mathbf{H}_3CH$), 1.35 (t, 3, $C\mathbf{H}_3CH_2$).

Anal. Calcd for $C_{11}H_{22}INS$: C, 40.04; H, 6.90. Found: C, 40.13; H, 6.85.

cis-2-Ethyl-3-*n*-propyl-3-(1-methylpyrrolidinium)thietane iodide (**2**, R′ = C_3H_7, R″ = C_2H_5) (23% yield) had mp 120–121°; nmr (DMSO-d_6) δ 4.3 (complex d, 1, $CH_3CH_2C\mathbf{H}$), 3.1–4.0 (m, 6, CH_2S-, CH_2N^+), 3.0 (s, 3, CH_3N^+), 1.60–2.40 (broad s, 10, $CH_3C\mathbf{H}_2C\mathbf{H}_2-$, $C\mathbf{H}_2CH_2N^+$, $CH_3C\mathbf{H}_2$), 0.9 (m, 6, $C\mathbf{H}_3CH_2-$, $C\mathbf{H}_3CH_2CH_2-$).

Anal. Calcd for $C_{13}H_{26}INS$: C, 44.00; H, 7.32. Found: C, 44.02; H, 7.48.

Thietes 4–7.—Potassium *tert*-butoxide (0.00087 mol/ml) in dry (CaH_2) dimethylformamide (*ca.* 20 ml) was added 1 ml at a time through a syringe cap to a stirred solution of quaternary salt (**2**) (0.009 mol) in dry dimethylformamide (50 ml)–pentane (50 ml) cooled to −10° in a 300-ml, three-necked round-bottomed flask fitted with a mechanical stirrer, syringe cap, and nitrogen inlet. A few minutes elapsed between additions of base. After 9.5 ml of base had been added, the stirring was continued for 10 min. Then the pentane and dimethylformamide layers were allowed to separate. The pentane layer was removed by a syringe and placed in a flask at −20° (Dry Ice–isopropyl alcohol). Additional pentane (30 ml) was added to the dimethylformamide in the original reaction flask, the mixture was stirred for about 15 min, and the pentane was removed as before and combined with the original pentane layer. This process was continued until about 300 ml of pentane was consumed. The combined pentane solutions at −10° were washed with cold 10% hydrochloric acid and twice with cold water. The pentane solution was dried ($MgSO_4$) at −10° and the pentane was removed at 0° on a rotary evaporator to leave the thiete as a colorless oil.

7-Thiabicyclo[4.2.0]-1(8)-octene (**4**)[8a] (50–55% yields) had ir[26] (−50°, between KBr plates) 2900 (s), 2850 (s), 1430 (s), 1310 (w), 1120 (m), 950 (w), 780 (s), 740 cm^{-1} (s); uv max ($CHCl_3$, −10°) 247, 260 mμ (sh); nmr ($CDCl_3$, −30°) δ 6.1 (s, 1, C=CH), 3.7 (m, 1, –CHS–), 1.8 [m, 8, $-(CH_2)_4-$]; mass spectrum (70 eV) *m/e* (rel intensity) 128 (5.2), 127 (9.2), 126 (100, parent), 125 (9), 93 (96), 91 (67), 77 (68).

Anal. Calcd for $C_7H_{10}S$: mol wt, 126. Found: mol wt, 127.[27]

If thiete **4** is warmed to room temperature, decomposition occurs with the evolution of heat. The glassy solid obtained was insoluble in ethanol, methanol, ether, ethyl acetate, and pentane but was soluble in chloroform: ir (KBr) 2950, 2940, 1620 (C=CS), 1445, 975, 915, 800 cm^{-1}; nmr ($CDCl_3$) δ 6 (2), 5.9 (1), 4.5 (1), 3.2 (2), 1.2–2.4 (24); mass spectrum (70 eV) *m/e* (rel intensity) 252 (2), 126 (85), 93 (100), 91 (69), 77 (62), 45 (42).

Anal. Calcd for $(C_7H_{10}S)_3$: C, 66.62; H, 7.99; S, 25.41; mol wt, 378. Found: C, 65.01; H, 7.35; S, 27.54; mol wt, 371.

Oxidation of this apparently trimeric material with excess 30% hydrogen peroxide in acetic acid for 12 hr at room temperature and for 1 hr at 70° gave a gummy solid, mp 110–125°, after removal of solvent (water aspirator) and recrystallization (ether): ir (KBr) 2950, 1725, 1645 (C=C), 1320 (SO_2), 1190 (SO_2), 945, 930, 890, 845, 790, 755 cm^{-1}.

Anal. Calcd for $(C_7H_{10}O_2S)_n$: C, 53.15; H, 6.33. Found: C, 51.20; H, 6.80.

8-Thiabicyclo[5.2.0]-1(9)-nonene (**5**) (76% yield) had ir (film) 3050 (w), 1600 (w), 775 cm^{-1} (s); uv max (pentane) 228 mμ (sh, ε 1100), 248 (2000), 252 (2000), 256 (1715), 294 (567); nmr ($CDCl_3$) δ 6.05 (s, 1, CC=H), 3.40 (doublet of doublets, 1, CHS–), 1.4–2.5 [m, 10, $-(CH_2)_5-$]; mass spectrum (20 eV) *m/e* (rel intensity) 142 (3), 141 (5), 140 (29, parent), 112 (10), 111 (17), 107 (11), 106 (18), 97 (16), 91 (30), 84 (13), 71 (34), 58 (50), 57 (52), 43 (100).

Anal. Calcd for $C_8H_{12}S$: C, 68.60; H, 8.57. Found: C, 68.55; H, 8.85.

3-Ethyl-4-methyl-2-thiacyclobutene (**6**) (67% yield) had ir (film) 3100 (w), 1625 (w), 810 (s), 755 cm^{-1} (m); uv max (pentane) 225 mμ (ε 1710), 247 (2250), 289 (420); nmr ($CDCl_3$) δ 6.16 (s, 1, C=CH), 4.10 (quartet, 1, $CH_3C\mathbf{H}S-$), 1.97 (quartet, 2, $CH_3C\mathbf{H}_2-$), 1.55 (d, 3, CH_3-), 1.00 (t, 3, $C\mathbf{H}_3CH_2-$); mass spectrum (20 eV) *m/e* (rel intensity) 114 (65, parent), 113 (55), 99 (100), 85 (52), 81 (55), 79 (55), 67 (13), 65 (50), 53 (38), 41 (54).

Anal. Calcd for $C_6H_{10}S$: C, 63.08; H, 8.83; S, 28.09. Found: C, 63.19; H, 8.92; S, 28.14.

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(24) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963); I. J. Borowitz, *ibid.*, **86**, 1146 (1964).

(25) The salt of *cis*-2-ethyl-3-*n*-propyl-3-(1-pyrrolidinyl)thietane was precipitated by addition of petroleum ether (bp 30–60°) or ethyl ether.

(26) The infrared spectrum was obtained by means of a special cell: E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296 (1950); A. B. Palmer, Ph.D. Thesis, Syracuse University, 1963.

(27) Obtained at −10° by nmr by means of a standard (benzil): S. Barcza, *J. Org. Chem.*, **28**, 1914 (1963). A value of 126 was obtained from the mass spectrum as noted. This thiete was too unstable for elemental analysis.

3-*n*-Propyl-4-ethyl-2-thiacyclobutene (**7**) (85% yield) had ir (film) 3100 (w), 1625 (w), 760 (s); uv max (pentane) 225 mμ (ϵ 2270), 247 (3050), 291 (345); nmr ($CDCl_3$) δ 6.18 (s, 1, C=CH), 4.0 (quartet, 1, CHS–), 1.20–2.25 (m, 6, $CH_3CH_2CH_2$–, CH_3CH_2–), 1.0 (t, 6, $CH_3CH_2CH_2$–, CH_3CH_2–); mass spectrum (20 eV) *m/e* (rel intensity) 142 (100, parent), 141 (16), 140 (38), 127 (28), 113 (74), 112 (29), 111 (50), 99 (35), 85 (32), 79 (45), 67 (49), 43 (36).

Anal. Calcd for $C_8H_{14}S$: C, 67.60; H, 8.57. Found: C, 67.55; H, 8.85.

Thiete Sulfones.—Peracetic acid (20 ml, 40%) was added dropwise during 30 min to the pyrrolidinyl sulfone [**1**, R_2 = $(CH_2)_4$] (0.044 mol) in a 125-ml erlenmeyer flask cooled in an ice–salt bath. After the addition was completed, the mixture was allowed to remain in the bath for 30 min longer. The reaction mixture was allowed to stand (1) at room temperature for 12 hr and then at 30–32° for 12 hr for the sulfone derived from cycloheptanone, (2) at room temperature for 48 hr for the sulfone derived from methyl ethyl ketone or (3) at room temperature for 12 hr and then at 30–32° for 5 hr for the sulfone derived from di-*n*-propyl ketone. The reaction mixture was cooled, cold water (*ca.* 100 ml) was added, and the mixture was saturated with sodium chloride and extracted with chloroform. The chloroform extracts were washed with 10% hydrochloric acid and dried (Na_2CO_3). Removal of the chloroform left an oil which was chromatographed on Florisil and eluted with ether–petroleum ether.

The product from the pyrrolidinyl sulfone derived from cycloheptanone consisted of an exo and an endo isomer. The mixture was treated with potassium hydroxide in dry methanol, cooled with ice, and neutralized with a cold 10% solution of hydrochloric acid. The solution was diluted with water and saturated with sodium chloride and the organic layer was extracted with chloroform, which was dried ($MgSO_4$) and evaporated to leave the endo sulfone, which was purified by column chromatography on Florisil (ether eluent) and recrystallized from ether. The sulfone of **4** was reported previously.[7e]

8-Thiabicyclo[5.2.0]-1(7)-nonene 8,8-dioxide (66% yield) had mp 65–66°; ir (KBr) 1660 (w), 1290 (s), 1170 (s), 1120 (s), 805 cm^{-1} (s); nmr ($CDCl_3$) δ 4.32 (s, 2, CH_2SO_2–), 2.43 (s, 4, CH_2-C=CCH_2), 1.75 [m, 6, –$(CH_2)_3$–].

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.80; H, 6.99. Found: C, 55.61; H, 7.16.

2-Methyl-3-ethyl-2-thiacyclobutene 1,1-dioxide (67% yield) had mp 46–47°; ir (film) 1650 (w), 1290 (s), 1180 (s), 1120 cm^{-1} (s); nmr ($CDCl_3$) δ 4.31 (s, 2, CH_2SO_2–), 2.42 (quartet, 2, CH_3CH_2–), 1.90 (s, 3, CH_3–), 1.15 (t, 3, CH_3CH_2).

Anal. Calcd for $C_6H_{10}O_2S$: C, 49.25; H, 6.82. Found: C, 49.15; H, 6.73.

2-Ethyl-3-*n*-propyl-2-thiacyclobutene 1,1-dioxide (74% yield) had $n^{25}D$ 1.4775; ir (film) 1650 (w), 1300 (s), 1230 (s), 1180 (s), 1130 (s), 1090 cm^{-1} (s); nmr ($CDCl_3$) δ 4.30 (s, 2, CH_2SO_2–), 2.1–2.6 (m, 4, CH_3CH_2–, $CH_3CH_2CH_2$–), 0.8–1.9 (m, 8, CH_3CH_2–, $CH_3CH_2CH_2$–).

Anal. Calcd for $C_8H_{14}O_2S$: C, 55.20; H, 8.45. Found: C, 55.30; H, 8.29.

Oxidation of Thiacyclobutenes.—An ether solution of monoperphthalic acid (0.017 mol) was added to a solution of the thiete (**4–7**) in pentane (50 ml) at −20° in a three-necked flask equipped with a stirrer and nitrogen inlet. After the reaction mixture was stirred for 4 days at −15 to −20°, it was allowed to warm to 0° and was stirred for 1 day more. The precipitated phthalic acid was removed and washed with chloroform or ether and the washings were combined with the mother liquor. The solution was washed with sodium carbonate solution and the solvent was removed by evaporation. The oil which remained was treated with cold potassium hydroxide in absolute methanol. The mixture was cooled in an ice bath, neutralized with cold 10% hydrochloric acid, diluted with water, and saturated with sodium chloride. The organic layer was extracted with chloroform, which was dried ($MgSO_4$) and removed by evaporation to leave the sulfone, which was chromatographed on Florisil and eluted with ether–petroleum ether.

From **4** was obtained 7-thiabicyclo[4.2.0]-1(8)-octene 7,7-dioxide, mp 88–89° (lit.[7e] mp 88–89°), whose ir and nmr spectra were identical with those of an authentic sample.

Thiete **5** yielded 8-thiabicyclo[5.2.0]-1(9)-nonene 8,8-dioxide as an oil [nmr ($CDCl_3$) δ 6.5 (C=CH)]. The oil was treated with potassium hydroxide, which isomerized it to 8-thiabicyclo-[5.2.0]-1(7)-nonene 8,8-dioxide (9% yield), mp 65–66°, whose ir and nmr spectra were identical with those of a sample prepared by the amine oxide elimination described in the preceding section.

Thiete **6** yielded an oily mixture which contained 3-ethyl-4-methyl-2-thiacyclobutene 1,1-dioxide [nmr ($CDCl_3$) δ 6.47]. Isomerization with potassium *tert*-butoxide in *tert*-butyl alcohol gave 2-methyl-3-ethyl-2-thiacyclobutene 1,1-dioxide (7% yield), mp 46–47°, whose ir and nmr spectra were identical with those of an authentic sample prepared by the amine oxide elimination.

Thiete **7** also gave an oily mixture containing 3-*n*-propyl-4-ethyl-2-thiacyclobutene 1,1-dioxide [nmr ($CDCl_3$) δ 6.5]. Isomerization with potassium hydroxide in methanol gave 2-ethyl-3-*n*-propyl-2-thiacyclobutene 1,1-dioxide (12% yield) whose refractive index, ir, and nmr spectra were identical with those of an authentic sample.

Reaction of Thietes with 2,4-Dinitrophenylhydrazine. A. Thiete (3).—Thiete (**3**, 0.072 g, 0.001 mol) was treated with 2,4-dinitrophenylhydrazine (in phosphoric acid–ethanol) to give yellow crystals of the 2,4-dinitrophenylhydrazone of β-mercaptopropionaldehyde (0.250 g, 0.00092 mol, 92%), mp 140–142°. The sample was purified by recrystallization from ethanol.

Anal. Calcd for $C_9H_{10}N_4O_4S$: C, 40.00; H, 3.73; N, 20.74. Found: C, 39.90; H, 3.75; N, 20.60.

The 2,4-dinitrophenylhydrazone (0.250 g, 0.0009 mol) in pyridine (20 ml) was treated with excess acetic anhydride (5 ml) at room temperature. After 15 min, water (50 ml) was added to the reaction mixture. The precipitate was recrystallized from ethanol, mp 127–128° (lit.[28] mp 127.5°), and its infrared spectrum was identical with that of the 2,4-dinitrophenylhydrazone of β-acetylthiopropionaldehyde.

B. Thietes 4 and 5.—Thietes **4** and **5** were treated with 2,4-dinitrophenylhydrazine reagent[29] in a manner similar to the treatment of **3**. The derivatives may require purification by chromatography on neutral alumina and recrystallization. Thiete **4** yielded the 2,4-dinitrophenylhydrazone of 1-cyclohexene aldehyde, mp 218–220° (lit.[30] mp 219–220°). The ir and uv spectra were identical with those of an authentic sample of the derivative. Hydrogen sulfide was detected by lead acetate paper. Treatment of **4** with semicarbazide[29] resulted in evolution of hydrogen sulfide and the formation of the semicarbazone of 1-cyclohexene aldehyde, mp 210–213 (lit.[30] mp 213–214°). The ir and uv spectra were identical with those of an authentic sample.

Likewise **5** yielded the 2,4-dinitrophenylhydrazone of 1-cycloheptene aldehyde, mp 214–215° (lit.[31] mp 210–212°).

Registry No.—**1** [R',R'' = –$(CH_2)_5$–], 33527-81-0; **1** [R' = CH_3CH_2; R'' = CH_3], 33527-82-1; **1** [R' = $CH_3CH_2CH_2$; R'' = CH_3CH_2], 33527-83-2; **2** [R' = R'' = –$(CH_2)_4$–], 33527-84-3; **2** [R' = R'' = –$(CH_2)_5$–], 33527-85-4; **2** [R' = C_2H_5; R'' = CH_3], 33527-86-5; **2** [R' = C_3H_7; R'' = C_2H_5], 33527-87-6; **2** [R = CH_3; R' = R'' = H], 33527-47-8; **3**, 503-31-1; **4**, 33527-89-8; **4** (trimer), 33520-74-0; **4** (sulfone polymer), 33520-75-1; **5**, 33608-40-1; **6**, 33527-90-1; **7**, 33527-42-3; 3-thietanyltrimethylammonium tosylate, 33527-43-4; 8-thiabicyclo[5.2.0]-1(7)-nonene 8,8-dioxide, 33527-41-2; 2-methyl-3-ethyl-2-thiacyclobutene 1,1-dioxide, 33527-44-5; 2-ethyl-3-*n*-propyl-2-thiacyclobutene 1,1-dioxide, 33527-45-6; β-mercaptopropionaldehyde (2,4-DNPH derivative), 17515-61-6.

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