An Evaluation of Hofmann and Cope Elimination Routes to (∓)-2-*n*-Propylthietane

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A synthetic route to (±)-2-*n*-propylthietane **1** that utilises a silver oxide-induced Hofmann elimination is described together with an evaluation of the potential of a Cope elimination as an alternative and more cost-effective route to **1**. Some chemistry of the isomeric intermediate thiete sulfones **5** and **12** from each of these respective eliminations is presented.

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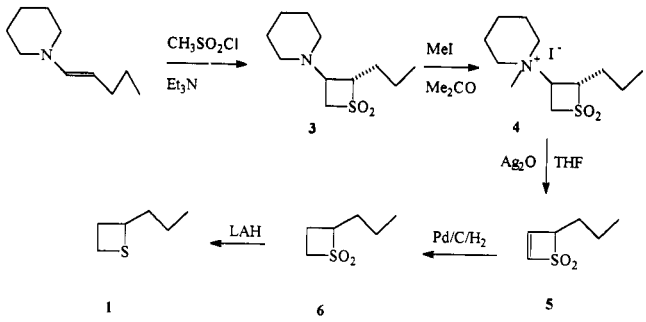
Introduction.

As a pivotal part of a number of programmes designed to evaluate the use of carnivore odours in mammal pest control we have been searching for a cost-effective large scale synthesis of (∓)-2-*n*-propylthietane **1**, a volatile malodorous compound found [1] as the *S*-epimer in the anal sac secretion of the stoat (*Mustela erminea*). This compound, either alone or in concert with 3-*n*-propyl-1,2-dithiolane **2**, has been shown to be effective at inducing fear responses in certain pest herbivores which lead to area avoidance and concomitant reduction in damage to vegetation [2-4].

1 2

The hitherto unpublished route (Scheme 1) presently employed in these laboratories for the large-scale preparation of **1** is based upon the known [5,6] $_{\pi}2+_{\pi}2$-cycloaddition of methylenesulphene to *trans*-*N*-pentenylpiperidine followed by a Hofmann elimination from the quaternary ammonium salt of the adduct **4** in anhydrous milieu and stepwise reductions of the endocyclic double bond in **5** and sulphone oxygen atoms in **6**. Here we detail the chemistry of this route and, in addition, report the results of attempts to optimise various steps in this sequence; in particular, the elimination leading to the propylthiete 1,1-dioxide **5**. Some interesting cycloaddition chemistry has also been revealed during the course of a Cope elimination from the *N*-oxide derivative of **3**.

Scheme 1



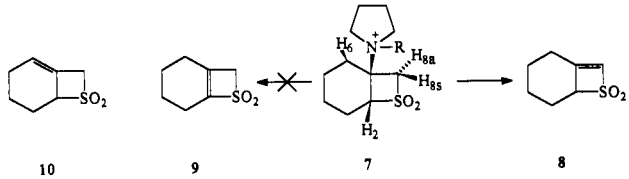
1 6 5

Results and Discussion.

In seeking alternatives to the use of methyl iodide and of silver oxide in particular for the large-scale production of **1** we have reinvestigated this sequence and focused principally upon the use of a potentially more cost-effective Cope elimination [7] from the *N*-oxide equivalent of the methiodide salt **4** to gain access to the thiete 1,1-dioxide **5**.

At the outset we showed that the use of methyl bromide as the quaternising agent gave much lower yields of the bromide salt and that the conversion of the thiete 1,1-dioxide **5** to thietane **1** could in fact be accomplished cleanly in a single step with lithium aluminium hydride. Contrary to the findings of an earlier report [8] no ring-opened products were obtained.

The Cope elimination from typically uncharacterised *N*-oxidised aminothietane 1,1-dioxides has been used with varying success as a route to thiete 1,1-dioxides. For example mild thermolysis (60°) of the *N*-oxide **7a**, prepared without isolation by treatment of the amine precursor with peracetic acid furnished only the bicyclic thiete 1,1-dioxide **8** [9].



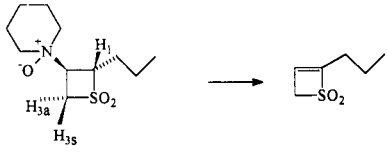
10 9 7 8

(a) R = —O⁻; (b) R = Me, I⁻

Mechanistically this is consistent with expectation in that the proton *syn* to the amine oxide function is eliminated. The corresponding quaternary ammonium salt **7b** under standard Hofmann elimination conditions that customarily involve a *trans* β-elimination also furnishes this sulphone **8**. It is interesting to note that despite the availability of other suitably *syn* disposed β-protons capable of forming planar five-membered transition states (required for Cope elimination) and an alternative suitably disposed *anti* β-proton (required for Hofmann elimination) only a single (and the same) product, **8**, was produced in each

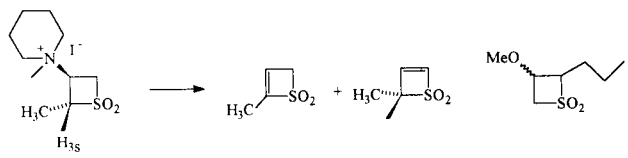
reaction. No evidence for the presence of isomers **9** and **10** was found. These observations clearly confirm the propensity for eliminations that involve the most acidic protons (H_{8s} and H_{8a}) in the molecule.

The amine oxide **11** was prepared in good yield by treatment of neat 3-piperidino-2-*n*-propylthietane 1,1-dioxide **3** with 30% hydrogen peroxide at ambient temperature and obtained as a colourless crystalline solid (monohydrate) that was stable when kept dry. Mild thermolysis at 80-90° effects the desired decomposition to give, after removal of the *N*-hydroxypiperidine with dilute acid, a highly crystalline solid (68%) possessing the stoichiometry of thiete 1,1-dioxide **5**. The ^{1}H- and ^{13}C-nmr and crystallographic data (Figure 1) however, clearly showed this to be the isomeric species **12**; no evidence for the presence of 4-*n*-propylthiete 1,1-dioxide **5** in the crude product was found. This could also be demonstrated simply by warming a d_6-DMSO solution of **11** immediately prior to recording nmr data. The apparent exclusivity with which this 2-*n*-propylthiete 1,1-dioxide isomer is obtained is unexpected and is to be contrasted with the findings of Dittmer and Davis [9] in that here apparently only the *syn* disposed thietane methine proton, H_1, participates in the elimination rather than the thietane methylene equivalent, H_{3s}. E_i elimination might have been expected to involve the *syn* methylene proton H_{3s} due to its relative incipient acidity when



11 12

compared to H_1 in a reaction that would have given the thiete dioxide **5** rather than the thermodynamically more stable isomer **12**. Under conditions that were used to effect this elimination (80-100° in the presence of *N*-hydroxypiperidine) 1,1-dioxide **5** was cleanly isomerised to **12**. It therefore appears that the Cope elimination proceeds as expected to give the 4-*n*-propylthiete 1,1-dioxide which then, under the influence of base, isomerises to the 2-*n*-propyl isomer **12**. This compound was also produced as the major product (70%) by the silver oxide-induced Hofmann elimination of methiodide salt **4** in aqueous solution, an observation that is consistent with the findings of Paquette and Freeman [10] who isolated dioxides **14** (67%) and **15** (33%) from an aqueous Hofmann elimination of methiodide salt **13**. Under anhydrous conditions only **15** was isolated.



13 14 15 16

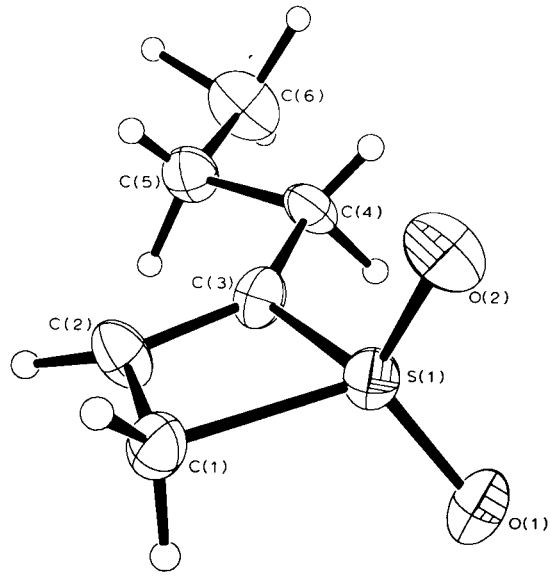
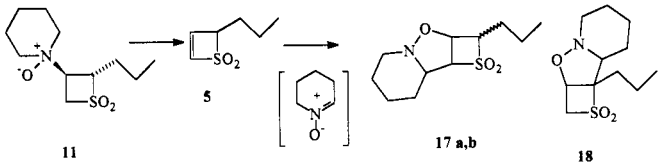


Figure 1. X-ray crystallographic structure of 2-*n*-propylthiete sulphone (**12**). Relevant data are reported elsewhere [28]. See Experimental.

An attempt to effect a *trans* β-elimination in **4** with stoichiometric sodium methoxide in methanol lead only to the formation of the Michael adduct **16**. The use of an equivalent of *n*-butyllithium in THF at -78° did however give the desired thiete 1,1-dioxide **5** in 50% yield. Here the methylide derived from the quaternary ammonium ion **4** is believed to be the intermediate species [11]. The use of peracetic acid to facilitate both amine oxidation and concomitant amine *N*-oxide elimination (by acetate ion) from 3-dimethylamino-2,4-diarylthietane 1,1-dioxides has been utilised successfully to prepare the corresponding *cis*- and *trans*-2,4-diarylthiete 1,1-dioxides [12,13]. A cursory investigation of the application of this reaction to the inactivated piperidinothietane 1,1-dioxide **3** with hydrogen peroxide in acetic acid lead to the rapid consumption of **3** but thereafter to complex product mixtures. With mCPBA, the elimination proceeded to give (after an alkaline workup) the 2-*n*-propylthiete 1,1-dioxide **12** as the only product. By analogy to the previous authors' findings this reaction is believed to produce the 4-*n*-propyl isomer **5** but to isomerise this during workup to the more stable compound **12**. Not surprisingly, the use of strong (7*M*) aqueous sodium hydroxide, which has recently been used to effect the Hofmann elimination in a suite of alkyl-substituted tetrahydropyridinium salts [14], gave only methyl *n*-butyl sulphone, albeit *via* the thiete 1,1-dioxide **5**.

In addition to the thiete 1,1-dioxide **12**, small amounts of additional products were isolated from the Cope elimination reaction of *N*-oxide **11**. Three species, each retaining the piperidinyl and propylthietane 1,1-dioxide moieties, were recovered by flash chromatography. Two were

clearly isomeric with a stoichiometry ($C_{11}H_{19}NO_3S$) corresponding only to the loss of two hydrogen atoms. The appearance in each of the ^{13}C-nmr spectra of four methine carbon atoms, in particular, suggested a dipolar cycloaddition of the nitrone derived from *N*-hydroxypiperidine (*i.e.* 3,4,5,6-tetrahydropyridine *N*-oxide) to the unsubstituted thiete 1,1-dioxide double bond in **5** rather than to that of the isomer **12**, which would have given rise to only two methine carbon atoms in addition to a single quaternary carbon atom in **18**.



The ^1H-nmr data were inadequate to permit stereochemical assignments at the centres associated with ring fusion in each of the isomeric adducts but ^{13}C-^1H and ^1H-^1H COSY spectral correlations revealed the relevant methine connectivities. A single crystal X-ray structure determination carried out on one adduct **17a** (mp 120°) (Figure 2) indeed confirmed the structure as one formally resulting from 1,3-dipolar cycloaddition of the cyclic nitrone to the endocyclic double bond of **5**. It possesses an almost planar thietane ring with the three substituents *cis* to one another. Moreover, the regiochemical integrity of the addition is consistent with expectation from a qualitative consideration of FMO theory [15] which reveals that cycloaddition of simple nitrones to strongly electron-deficient dipolarophiles is HOMO (dipole)-LUMO (dipolarophile) controlled. The isomeric adduct **17b** (mp 65°) is tentatively assumed to be that resulting from an underside approach to **5**; although a unit cell was established for the crystals by a film study, insufficient diffraction data could be collected.

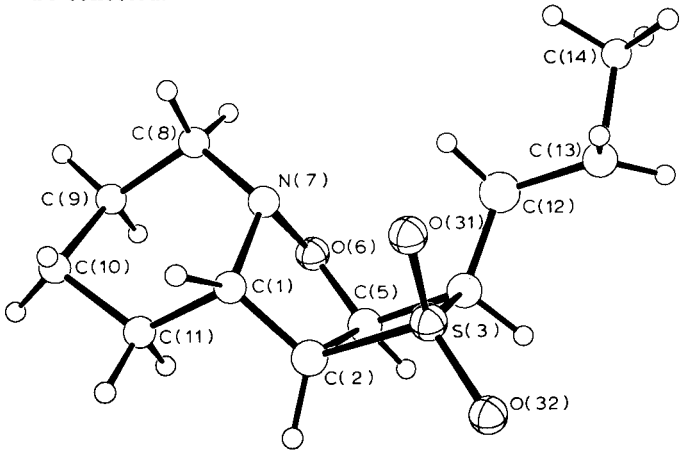
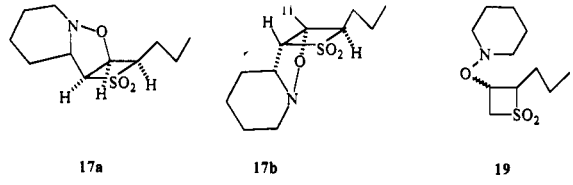
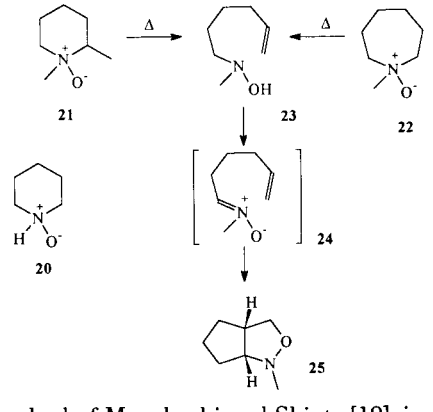


Figure 2. X-ray crystallographic structure of *exo*-7-aza-6-oxa-4-*n*-propyl-3-thiatricyclo[5.4.1.^{1,7}1^{2,5}]undecane 3,3-dioxide (**17a**).

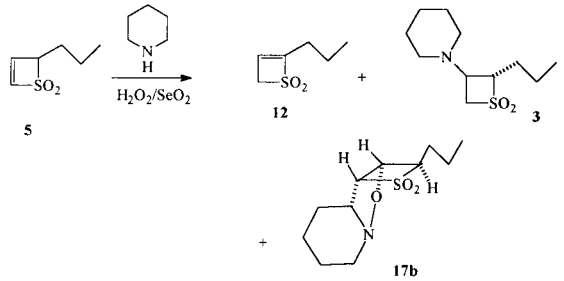


The only other product isolated from this reaction was shown to be isomeric with the *N*-oxide precursor **11** and tentatively assigned from nmr data as the piperidinyloxy Michael adduct **19**. The ^1H- and ^{13}C-resonances for the thietane 1,1-dioxide moiety were concurrent with those observed for compounds **16** and **27** resulting from alcohol addition to **5**. An attempt was made to formally authenticate the identities of **17a** and **17b** as products of 1,3-dipolar cycloaddition of the tetrahydropyridine *N*-oxide to the thiete 1,1-dioxide **5**. The precise origin of the dipole however is unclear as the Cope elimination product, in general, is known [7,16] to be an *N*-hydroxylamine. In the case of *N*-hydroxypiperidine it is also known [17] that the tautomeric *N*-oxide **20** contributes to the chemistry of this compound (*e.g.* during benzylation). In the present case this species might well represent an "oxidisable" intermediate *en route* to the 1,3-dipole itself. An earlier report [18] describes a similar phonemenon during pyrolysis of both *N*-methyl α-pipecoline *N*-oxide **21** and *N*-methylhexamethyleneimine *N*-oxide **22**. The isolation of the *cis*-fused isoxazolidine **25**, albeit as a minor component, is apparently produced as a result of an initial (auto)oxidation of the major terminally-unsaturated hydroxylamine **23** to give the nitrone **24** which then undergoes an intramolecular 1,3-dipolar cycloaddition to give **25**.

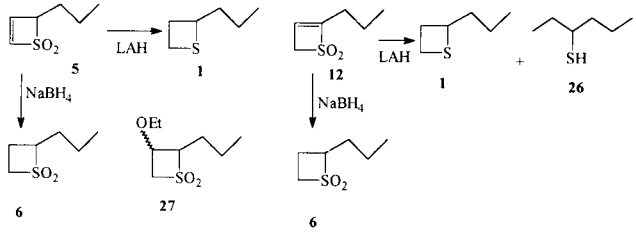


The method of Murahashi and Shiota [19], in which secondary amines are converted by oxidation with perselenous acid to the corresponding nitrones, was applied to the *in situ* generation of 3,4,5,6-tetrahydropyridine *N*-oxide and subsequent trapping with **5**. In addition to the isomeric sulphone **12** and the 3-piperidinylthietane 1,1-dioxide **3**, the latter resulting from Michael adduction by piperidine, only a single cycloadduct was isolated (23%). This was shown to be identical to the adduct whose struc-

ture was assigned as **17b**. When repeated under identical conditions with thiete 1,1-dioxide **12**, no cycloadducts were isolated and **12** was recovered unchanged. Furthermore, no Michael addition of piperidine, to give **3**, was observed.



The finding that 2-*n*-propylthiete 1,1-dioxide **12** was readily accessible in good yield (68%) from a reaction - the Cope elimination - that negated the use of silver oxide suggested that this variation might present as a better alternative to that shown in Scheme 1, most particularly if the 1,1-dioxide **12** could be as efficiently reduced to the thietane **1**. To this end the fate of each of the thiete 1,1-dioxides **5** and **12** towards reduction with lithium aluminium hydride or sodium borohydride was investigated. Contrary to expectation the reaction of **5** with LAH proceeded without ring opening and the thietane **1** was isolated in quantitative yield. Under identical conditions isomer **12** furnished a mixture (*ca* 1:3) of **1** and 3-mercaptohexane **26**, with the latter always predominating (gc-ms). Retention of the thietane ring in these reductions is apparently unusual as previous studies [8,20] with the parent thiete dioxide have shown that *n*-propylmercaptan is the only isolable product.



Reduction of thiete 1,1-dioxide **5** with sodium borohydride in aqueous ethanol gave a mixture of compounds retaining the dioxide residue, namely thietane 1,1-dioxide **6** and the 3-ethoxythietane derivative **27**. The structure of the latter compound, which derives from a precedented Michael addition [20] of ethanol to the 1,1-dioxide **5** was assigned on the basis of ^{1}H- and ^{13}C-nmr data and a comparison of such with respect to the 3-methoxy adduct **16**, although the stereochemistry (*i.e. cis* or *trans*) remains unresolved. In view of the fact that the piperidine Michael adduct, obtained as a by-product in the nitrone cycloaddition to thiete 1,1-dioxide **5**, was identical in all respects to the known *trans*-3-piperidino-2-*n*-propylthietane 1,1-dioxide **3** (see previous Discussion), it is not unreasonable to infer a *trans* disposition between the substituents at C2 and C3.

Table 1: Positional and Thermal Parameters[a]

Atom	x	y	z	Biso
C12	0.0313(23)	0.135(7)	0.7578(16)	0.6(7)
C13	0.1328(28)	0.026(9)	0.7892(17)	2.2(9)
C14	0.1298(24)	-0.158(8)	0.8530(15)	0.7(7)
H121	0.008	-0.259	0.800	1.3(18)
H122	-0.021	-0.023	0.746	1.3(18)
H131	0.186	0.187	0.810	3.0(18)
H132	0.165	-0.068	0.745	3.0(18)
H141	0.105	-0.148	0.903	1.5(18)
H142	0.205	-0.232	0.865	1.5(18)
H143	0.080	-0.310	0.822	1.5(18)
H1	-0.151	-0.049	0.532	2.2(23)
H2	-0.087	0.438	0.525	2.2(23)
H4	0.075	0.459	0.698	2.2(23)
H5	-0.086	0.630	0.652	2.2(23)
S3	0.0400(10)	0.1575(24)	0.603(6)	1.04(17)
031	0.0389(22)	-0.122(5)	0.5997(13)	1.04(17)
032	0.1199(15)	0.234(5)	0.5716(10)	1.04(17)
C1	-0.1701(27)	0.126(8)	0.5617(18)	1.3(3)
C2	-0.0840(25)	0.303(8)	0.5720(17)	1.3(3)
C4	0.0227(26)	0.301(8)	0.6896(17)	1.3(3)
C5	-0.0777(25)	0.419(7)	0.6535(17)	1.3(3)
06	-0.1633(16)	0.304(5)	0.6778(11)	1.3(3)
N7	-0.1750(19)	0.041(7)	0.6372(14)	1.3(3)
C8	-0.2695(24)	-0.053(7)	0.6527(16)	1.4(4)
C9	-0.3653(24)	0.107(7)	0.6096(16)	1.4(4)
C10	-0.3612(24)	0.110(7)	0.5256(19)	1.4(4)
C11	-0.2659(25)	0.246(7)	0.5176(17)	1.4(4)
H81	-0.281	-0.255	0.637	3.6(33)
H82	-0.273	-0.033	0.711	3.6(33)
H91	-0.364	0.301	0.632	3.6(33)
H92	-0.432	0.002	0.617	3.6(33)
H101	-0.422	0.232	0.498	3.6(33)
H102	-0.371	-0.075	0.498	3.6(33)
H111	-0.266	0.431	0.546	3.6(33)
H112	-0.255	0.259	0.461	3.6(33)

[a] Estimated standard deviations are given in parenthesis following the digit to which they refer.

Torsion Angles for non-hydrogen atoms[a]

C4	C12	C13	C14	-174(4)	C13	C12	C4	S3	67(2)
C13	C12	C4	C5	180(4)	031	S3	C2	C1	11(2)
031	S3	C2	C5	118(3)	032	S3	C2	C1	145(3)
032	S3	C2	C5	-108(3)	C4	S3	C2	C1	-104(3)
C4	S3	C2	C5	2(2)	031	S3	C4	C12	14(2)
031	S3	C4	C5	-114(3)	032	S3	C4	C12	-123(3)
032	S3	C4	C5	109(3)	C2	S3	C4	C12	125(3)
02	S3	C4	C5	-3(2)	N7	C1	C2	S3	68(2)
N7	C1	C2	C5	-28(2)	C11	C1	C2	S3	-165(4)
C11	C1	C2	C5	93(3)	C2	C1	N7	O6	46(2)
C2	C1	N7	C8	157(4)	C11	C1	N7	O6	-79(3)
C11	C1	N7	C8	32(2)	C2	C1	C11	C10	-162(4)
N7	C1	C11	C10	-42(2)	C3	C2	C5	C4	-3(1)
S3	C2	C5	O6	-120(3)	C1	C2	C5	C4	114(4)
C1	C2	C5	O6	-3(2)	C12	C4	C5	C2	-124(4)
C12	C4	C5	O6	-15(2)	S3	C4	C5	C2	3(1)
S3	C4	C5	O6	111(3)	C2	C5	O6	N7	31(2)
C4	C5	O6	N7	-75(2)	C5	O6	N7	C1	-49(2)
C5	O6	N7	C8	-171(3)	C1	N7	C8	C9	-39(2)
O6	N7	C8	C9	70(2)	N7	C8	C9	C10	54(2)
C8	C9	C10	C11	-62(2)	C9	C10	C11	C1	57(2)

[a] E.s.d's given in parentheses refer to last printed digits.

In aprotic solvent (glyme) only the double bond in **12** was reduced to give the thietane 1,1-dioxide **6** in quantitative yield. This observation immediately presents a realistic opportunity for the development of a potentially more cost-effective route to the target thietane **1**, especially since 2-*n*-propylthiete 1,1-dioxide **12** is accessible in good yield from the easily prepared *N*-oxide precursor **11**. Studies are continuing.

Table 2: Bond distances

Atoms	Distance (Å)
C(12)-C(13)	1.50(5)
C(12)-C(4)	1.50(5)
C(13)-C(14)	1.51(5)
S(3)-O(31)	1.44(3)
S(3)-O(32)	1.46(2)
S(3)-C(2)	1.83(4)
S(3)-C(4)	1.80(4)
C(1)-C(2)	1.46(5)
C(1)-N(7)	1.46(4)
C(1)-C(11)	1.52(5)
C(2)-C(5)	1.59(5)
C(4)-C(5)	1.52(5)
C(5)-O(6)	1.44(4)
O(6)-N(7)	1.54(4)
N(7)-C(8)	1.44(4)
C(8)-C(9)	1.61(4)
C(9)-C(10)	1.54(5)
C(10)-C(11)	1.49(5)

Table 3: Bond Angles

Atoms	Angle (°)
C(13)-C(12)-C(4)	117(3)
C(12)-C(13)-C(14)	112(3)
O(31)-S(3)-O(32)	116(2)
O(31)-S(3)-C(2)	113(2)
O(31)-S(3)-C(4)	117(2)
O(32)-S(3)-C(2)	113(2)
O(32)-S(3)-C(4)	113(2)
C(2)-S(3)-C(4)	81(2)
C(2)-C(1)-N(7)	108(3)
C(2)-C(1)-C(11)	113(3)
N(7)-C(1)-C(11)	116(3)
S(3)-C(2)-C(1)	116(3)
S(3)-C(2)-C(5)	89(2)
C(1)-C(2)-C(5)	105(3)
C(12)-C(4)-H(4)	112(2)
C(12)-C(4)-S(3)	119(3)
C(12)-C(4)-C(5)	121(3)
S(3)-C(4)-C(5)	92(2)
C(2)-C(5)-C(4)	98(3)
C(2)-C(5)-O(6)	102(3)
C(4)-C(5)-O(6)	113(3)
C(5)-O(6)-N(7)	104(2)
C(1)-N(7)-O(6)	99(3)
C(1)-N(7)-C(8)	119(2)
O(6)-N(7)-C(8)	103(2)
N(7)-C(8)-C(9)	113(3)
C(8)-C(9)-C(10)	108(3)
C(9)-C(10)-C(11)	106(3)
C(1)-C(11)-C(10)	114(3)

EXPERIMENTAL

The nmr spectra were recorded, unless otherwise stated, as solutions in deuteriochloroform on a Bruker AC300 MHz instrument and chemical shifts are quoted downfield from TMS. Accurate mass measurements were recorded in either c.i. or e.i. modes on a VG70/250S instrument. Microanalyses were carried out by the Micro-analytical Laboratories, University of Otago. Melting points are uncorrected.

N-Pentenylpiperidine.

n-Pentanal (40.0 g, 0.47 mole) was added dropwise with vigorous stirring to a mixture of 86.0 g (1.0 mole) of piperidine and 35 g of anhydrous potassium carbonate at *ca* 0°. The suspension was stirred an additional 2-3 hours in an ice-bath and for *ca* 1 hour while warming to ambient temperature. The inorganic material was removed by filtration and washed with ether (2 x 100 ml) and the combined organic phases concentrated and distilled to give 60.0 g (83%) of *N*-pentenylpiperidine as a colourless, homogeneous liquid, bp 88-92°/25 mm; ^{1}H-nmr: δ 0.88 (t, J = 7.4 Hz, 3H), 1.34 (m, 2H), 1.54 (m, 6H), 1.94 (m, 4H) 2.74 (m, 4H), 4.38 (m, 1H), 5.80 (d, J = 14.0 Hz, 1H); ^{13}C-nmr: 13.6 (CH_3), 24.5 (CH_2), 25.6 (CH_2), 32.9 (CH_2), 50.2 (CH_2), 101.2 (CH), 140.5 (CH).

Anal. Calcd. for $C_{10}H_{20}N$: MH^+ m/z 154.1596. Found: MH^+ m/z 154.1586.

3-Piperidino-2-*n*-propylthietane 1,1-Dioxide (**3**).

To a stirred solution of 60.0 g (0.40 mole) of *N*-pentenylpiperidine, 43.6 g (0.44 mole) of triethylamine in 1 ℓ of anhydrous ether maintained at *ca* -5° under an atmosphere of nitrogen was added dropwise 51.0 g (0.44 mole) of methanesulphonyl chloride, the temperature being maintained below 0° throughout the addition. The mixture was stirred overnight at room temperature then filtered through celite to remove the precipitate and concentrated to 77.0 g (83%) of an homogeneous orange oil. A sample of this product was purified by flash chromatography to give 3-piperidino-2-*n*-propylthietane 1,1-dioxide **3** as a colourless oil; ^{1}H-nmr: δ 0.98 (t, J = 7.2 Hz, 3H), 1.37-1.64 (m, 8H), 1.72 and 2.13 (2 x m, 2H), 2.38 (bd s, 4H), 2.78 (q, J = 7.3 Hz, 1H), 3.93 (dABq, J = 12.6 Hz, J_{cis} or J_{trans} = 8.7 or 7.2 Hz, 2H), 4.18 (m, 1H); ^{13}C-nmr: 13.7 (CH_3), 20.9 (CH_2), 23.8 (CH_2), 25.5 (2 x CH_2), 31.8 (CH_2), 52.1 (2 x CH_2), 53.6 (CH), 65.3 (CH_2), 80.5 (CH).

Anal. Calcd. for $C_{11}H_{22}NO_2S$: MH^+ m/z 232.1371. Found: MH^+ m/z 232.1369.

4-*n*-Propylthiete 1,1-Dioxide (**5**).

A suspension containing 93.0 g (0.4 mole) of dry silver oxide [freshly prepared from sodium hydroxide and silver nitrate and dried, after washing, at 80°], 200 g of anhydrous calcium sulphate and 129 g (0.35 mole) of the methiodide salt **4** in 1 ℓ of anhydrous tetrahydrofuran was refluxed with vigorous stirring for 2-3 hours. After cooling the solvent was removed by rotary evaporation and the resulting solids heated on a steam bath for 4 hours. After cooling the solids were extracted repeatedly (5 x) with ether and the combined extracts concentrated prior to filtration with ether through a plug of silica. Concentration of the eluate furnished 53 g (36%) of a light yellow liquid, a sample of which was purified by Kugelröhr distillation (*ca* 120°/0.5 mm) to give 4-*n*-propylthiete 1,1-dioxide **5** as a colourless liquid; ^{1}H-nmr: δ 0.98 (t, J = 7.2 Hz, 3H), 1.54 (m, 2H), 1.86 and 2.02 (2 x m, 2H), 4.79 (m, 1H), 6.82 (d, J = 5.1 Hz, 1H), 7.04 (m, 1H); ^{13}C-nmr: 13.7 (CH_3), 20.4 (CH_2), 30.6 (CH_2), 85.1 (CH), 141.4 (CH), 145.7 (CH).

The thiete 1,1-dioxide was obtained in like manner by using a five molar excess of lead monoxide instead of silver oxide. Yields were quantitative but low (~40%).

Anal. Calcd. for $C_6H_{14}NO_2S$: MNH_4^+ m/z 164.0745. Found: MNH_4^+ m/z 164.0738.

3-Piperidino-2-*n*-propylthietane 1,1-Dioxide, Methiodide Salt (**4**).

A sample of 90.0 g (0.39 mole) of the crude piperidinothietane 1,1-dioxide **3** was dissolved in 500 ml of dry acetone and refluxed while 83.0 g (0.58 mole) of methyl iodide was added dropwise. An additional portion of 50.0 g of methyl iodide was added similarly and the whole refluxed overnight. After cooling in ice the precipitated salt was removed by filtration, washed with cold acetone and dried to give 99 g (68%) of 3-piperidino-2-*n*-propylthietane 1,1-dioxide, methiodide salt **4** as a pale yellow solid which was used as such in subsequent reactions; ^{1}H-nmr (d_6-DMSO): δ 0.93 (t, J = 7.3 Hz, 3H), 1.31-2.10 (m, 10H), 3.22 (s, 3H), 3.26-3.60 (m, 4H), 4.48 (m, 1H), 4.61 and 5.01 (ABq, J_{AB} = 15.2 Hz, 2H), 5.22 (m, 2H); ^{13}C-nmr: 15.1 (CH_3), 20.5 (CH_2), 21.2 (CH_2), 21.4 (CH_2), 33.2 (CH_2), 43.6 (CH_3), 60.3 (CH_2), 60.6 (CH + CH_2), 63.3 (CH_2), 78.2 (CH).

Anal. Calcd. for $C_{12}H_{24}NO_2SI$: C, 38.61; H, 6.43; N, 3.75. Found: C, 38.74; H, 6.53; N, 3.92.

In like manner the methyl piperidinium bromide salt was obtained by the slow entrainment of methyl bromide through a refluxing solution of the piperidinothietane 1,1-dioxide in acetone, however, because of the consistently lower yields (~40%) the reaction was not pursued further.

2-*n*-Propylthietane 1,1-Dioxide (**6**).

A sample of 10 g (0.07 mole) of 4-*n*-propylthiete 1,1-dioxide was dissolved in 200 ml of ethanol containing 1.0 g of 10% palladium on charcoal and reduced at 50 psi for 24 hours. The catalyst was removed by filtration and the filtrate concentrated to a light yellow oil, a sample of which was purified by Kugelröhr distillation (*ca* 120°/0.5 mm) to give 2-*n*-propylthietane 1,1-dioxide **6** as a colourless liquid; ^{1}H-nmr: δ 0.98 (2 x overlapping t, J = 7.3 Hz, 3H), 1.45 (m, 2H), 1.75 and 2.05 (2 x m, 2H), 1.75 and 2.24 (2 x m, 2H), 3.94 (m, 2H), 4.35 (m, 1H); ^{13}C-nmr: 13.5 (CH_3), 14.0 (CH_2), 20.1 (CH_2), 31.3 (CH_2), 61.9 (CH_2), 78.5 (CH).

Anal. Calcd. for $C_6H_{16}NO_2S$: MNH_4^+ m/z 166.0902. Found: MNH_4^+ m/z 166.0897.

2-*n*-Propylthietane (**1**).

A sample of 17.0 g (0.115 mole) of 4-*n*-propylthietane 1,1-dioxide **5** in 30 ml of ether was added dropwise to stirred, cooled suspension of 14.0 g (0.37 mole) lithium aluminium hydride in 30 ml of ether. After refluxing overnight the mixture was cooled in ice and worked-up in the standard manner. The inorganic material was removed by filtration and the filtrate concentrated by slow distillation through a Vigreux column to give 8.0 g (60%) of 2-*n*-propylthietane, a sample of which was purified by distillation (80°/95 mm) to give the thietane **1** as a colourless liquid. The nmr data were consistent with that previously published [21].

In precisely the same manner, reduction of the thiete 1,1-dioxide **5** afforded the same thietane in comparable yields.

3-Piperidino-2-*n*-propylthietane *N*,1,1-Trioxide (**11**).

To a vigorously stirred sample of 4.8 g (0.021 mole) of piperidinothietane 1,1-dioxide **3** was added dropwise 10 ml (30%, 0.088 mole) of hydrogen peroxide and the mixture stirred overnight. The resulting solid was removed by filtration and washed with a minimum volume of iced-water and dried firstly by suction and secondly under vacuum at 0.2 mm to give 3.5 g (65%) of 3-piperidino-2-*n*-propylthietane *N*,1,1-trioxide **11** as a white solid mp 90-115° dec; ^{1}H-nmr (d_6-DMSO): δ 0.88 (t, J = 7.3 Hz, 3H), 1.32-1.58 (m, 8H), 1.78 and 1.88 (2 x 1H, m), 2.30 (bd s, 4H), 2.63 (m, 1H), 3.87 and 4.06 (2 x 1H, m), 4.24 (m, 1H); ^{13}C-nmr: 14.8 (CH_3), 21.4 (CH_2), 24.8 (CH_2), 26.4 (CH_2), 32.6 (CH_2), 52.4 (CH_2), 53.9 (CH), 66.3 (CH_2), 80.8 (CH).

Anal. Calcd. for $C_{11}H_{23}NO_4S$: C, 49.81; H, 8.68; N, 5.28. Found: C, 49.61; H, 8.40; N, 5.16.

Thermolysis of the Amine Oxide **11**.

A stirred sample of 10.0 g (0.039 mole) of the *N*-oxide **11** was placed in a small flask and prepared for distillation under vacuum (25 mm). The temperature was raised to *ca* 90° at which point an ebullient decomposition occurred and a distillate was collected. After obvious cessation (*ca* 5 minutes) the cooled residue was triturated with ether and the resulting solid recovered by filtration and recrystallised from ether to give 3.9 g (58%) of 2-*n*-propylthiete 1,1-dioxide **12** as large colourless prisms, mp 73°; ^{1}H-nmr: δ 1.02 (t, J = 7.4 Hz, t, 3H), 1.67 (m, 2H), 2.40 (m, 2H), 4.35 (bd s, 2H), 6.63 (bd s, 1H); ^{13}C-nmr: 13.9 (CH_3), 19.9 (CH_2), 28.1 (CH_2), 28.1 (CH_2), 69.0 (CH_2), 127.9 (CH), 163.5 (C_q).

Anal. Calcd. for $C_6H_{10}O_2S$: C, 49.32; H, 6.85; S, 21.92. Found: C, 49.44; H, 7.09; S, 21.98.

The distillate was acidified with 2*M* hydrochloric acid and extracted with ether. After neutralisation of the aqueous phase with saturated aqueous sodium bicarbonate and supersaturation with salt the aqueous phase was extracted with ether (2 x) and the combined ether phases concentrated to give 1.8 g (46%) of *N*-hydroxypiperidine as a viscous, light yellow oil that slowly solidified. This was shown to be identical to a sample prepared according to a published procedure [22]; ^{13}C-nmr: 23.8 (CH_2), 25.9 (2 x CH_2), 59.7 (2 x CH_2).

The trituration liquors from the pyrolysis were subjected to flash chromatography with 20% ethyl acetate-hexane and, in addition to the thiete 1,1-dioxide **12** (0.6 g) a further three compounds were isolated. The most mobile of these was obtained (0.8 g) as a viscous colourless liquid and assigned as 3-(*N*-piperidinyloxy)-2-*n*-propylthietane 1,1-dioxide **19**; ^{1}H-nmr: δ 1.01 (t, J = 7.2 Hz, 3H), 1.27 (m, 1H), 1.42-1.66 (m, 6H), 1.66-1.93 (m, 3H), 2.02 (m, 1H), 2.40 (m, 2H), 3.19 (m, 2H), 3.97 (m, 1H), 4.06-4.30 (m, 3H); ^{13}C-nmr: 13.6 (CH_3), 20.1 (CH_2), 23.3 (CH_2), 25.3 (2 x CH_2), 30.0 (CH_2), 57.3 (2 x CH_2), 66.1 (CH), 67.2 (CH_2), 82.2 (CH).

Anal. Calcd. for $C_{11}H_{22}NO_3S$: MH^+ m/z 248.1320. Found: MH^+ m/z 248.1323.

The remaining two compounds were isolated in low yields as solids and crystallised from pentane to give fine colourless needles; each was shown to have a stoichiometry consistent with retention of the piperidine moiety. The lesser mobile of the two isomeric species was shown by single crystal X-ray diffraction to be *exo*-7-aza-6-oxa-4-*n*-propyl-3-thiatricyclo[5.4.$1^{1,7}$.$1^{2,5}$]undecane 3,3-dioxide **17a**, mp 120°; ^{1}H-nmr: δ 0.98 (t, J = 7.3 Hz, 3H), 1.27-1.57 (m, 6H), 1.58-1.78 (m, 3H), 1.89 and 2.12 (m, 2 x 1H), 3.13 and 3.42 (m, 2 x 1H), 3.80 (m, 1H), 4.27 (m, 1H), 4.66 (m, 1H), 4.78 (m, 1H); ^{13}C-nmr: 13.8 (CH_3), 19.6, 20.9, 22.3, 24.1, 24.7, 50.1 (6 x CH_2), 59.4, 64.9, 82.5, 89.7 (4 x CH).

Anal. Calcd. for $C_{11}H_{19}NO_3S$: C, 53.88; H, 7.76; N, 5.71. Found: C, 54.16; H, 7.52; N, 5.82.

The more mobile species of this isomeric pair, tentatively assigned as *endo*-7-aza-6-oxa-4-*n*-propyl-3-thiatricyclo[5.4.$1^{1,7}$.$1^{2,5}$]-

undecane 3,3-dioxide **17b**, was obtained as fine colourless needles, mp 65°; ^{1}H-nmr: δ 0.99 (t, J = 7.2 Hz, 3H), 1.30-1.60 (m, 6H), 1.60-1.93 (m, 3H), 2.03 (m, 1H), 3.19 and 3.47 (m, 2 x 1H), 3.82 (m, 1H), 4.33-4.48 (m, 2H), 4.52 (d, J = 7.0 Hz, 1H); ^{13}C-nmr: 13.6 (CH_3), 19.7, 20.2, 22.5, 24.2, 29.5, 50.3 (6 x CH_2), 58.9, 68.8, 83.2, 87.6 (4 x CH).

Anal. Calcd. for $C_{11}H_{19}NO_3S$: C, 53.88; H, 7.76; S, 13.06. Found: C, 53.79; H, 8.05; S, 13.28.

Cycloaddition of 3,4,5,6-Tetrahydropyridine *N*-Oxide to 4-*n*-Propylthiete 1,1-Dioxide (**5**).

To a stirred, cooled (0°) mixture of 0.35 g (4.3 mmoles) of piperidine and 0.02 g (0.2 mmole) of selenium dioxide in 8 ml of acetone was added dropwise 1.02 g (30%, 9.0 mmoles) of hydrogen peroxide. After stirring for 3 hours the acetone was removed under vacuum (0.5 mm) and to the remaining liquid a solution of 0.5 g (3.4 mmoles) of the thiete 1,1-dioxide **5** in 5 ml of dioxane was added in a single portion. After 0.5 hours at room temperature the solution was warmed to 70° for 2 hours before being cooled, concentrated and the residue extracted with ether. The resulting product, which contained no starting material, was subjected to flash chromatography with 20% ethyl acetate/hexane and three compounds were isolated. The most mobile of these was recrystallised from hexane to give 0.19 g (23%) of the cycloadduct **17b**, mp 65°. All spectral data recorded for this compound were identical to those observed previously for **17b**. The major components, easily identified as 2-*n*-propylthiete 1,1-dioxide **12** and 3-piperidino-2-*n*-propylthietane 1,1-dioxide **3**, were isolated as a mixture; the former could be recovered from this mixture in low yield by trituration with ether.

In like manner, this reaction was repeated on the same scale with the isomeric 2-*n*-propylthiete 1,1-dioxide **12**. Only this starting material was recovered and no evidence of nitrone/thiete 1,1-dioxide cycloaddition was obtained. Furthermore, none of the piperidine-derived Michael adduct, **3**, was observed.

Reaction of Methiodide Salt **4** with Base.

(i) Sodium Methoxide.

To a suspension of 2.45 g (6.6 mmoles) of the methiodide salt **4** in 20 ml cold (0°) anhydrous methanol was added dropwise by syringe 1.42 ml (25 wt%, 0.6 mmole) of a methanolic solution of sodium methoxide. The resulting solution was stirred at 0° for 0.5 hour then at ambient temperature overnight. After dilution with methylene chloride and water the organic phase was separated, washed with water and dried before being concentrated. Purification of the resulting liquid either by flash chromatography or by Kügelrohr distillation (80-100°/25 mm) furnished 0.94 g (81%) of 3-methoxy-2-*n*-propylthietane 1,1-dioxide **16** in quantitative yield as a colourless liquid; ^{1}H-nmr: δ 1.00 (t, J = 7.1 Hz, 3H), 1.93 (m, 2H), 1.82 and 2.06 (2 x 1H m), 3.36 (s, 3H), 3.77 (m, 1H), 3.93 and 4.18 (2 x 1H m), 4.22 (m, 1H); ^{13}C-nmr: 13.6 (CH_3), 20.2 (CH_2), 30.2 (CH_2), 57.5 (CH_3), 67.6 (CH_2 + CH), 83.3 (CH).

Anal. Calcd. for $C_7H_{15}O_3S$: MH^+ m/z 179.0742. Found: MH^+ m/z 179.0738.

The same reaction, when repeated in anhydrous THF and quenched several minutes after completion of the addition gave a mixture (1:2) of thiete 1,1-dioxide **5** and **16**, respectively.

(ii) *n*-Butyllithium.

To a stirred suspension of 1.0 g (2.7 mmoles) of the methiodide salt **4** in 30 ml of anhydrous THF was added at -78° dropwise by syringe 2.7 ml (1.2 *M*, 3.2 mmoles) of a solution of *n*-butyllithium in hexane and the resulting solution stirred at -78° for 2 hours. After warming to ambient temperature the solution was quenched with water and extracted with ether. The ether phase was washed with brine, dried and concentrated to a homogeneous liquid that was purified by Kügelrohr distillation (*ca* 100°/25 mm) to give 0.2 g (52%) 4-*n*-propylthiete 1,1-dioxide **5**. All spectral data were identical to those previously recorded for **5**.

Reaction of 3-Piperidino-2-*n*-propylthietane 1,1-Dioxide (**3**) with *m*-Chloroperbenzoic Acid.

To a stirred solution of 1.35 g (5.8 mmoles) of the thietane 1,1-dioxide **3** in 20 ml of dichloromethane was added (1.33 g, 80%, 6.4 mmoles) *m*-chloroperbenzoic acid and the resulting solution stirred for 2 hours at ambient temperature. The solution was diluted with additional dichloromethane and washed with potassium hydroxide solution (1 *M*) and water before being dried and concentrated to give 0.25 g (30%) of 2-*n*-propylthiete 1,1-dioxide **12** as a highly crystalline solid. The nmr spectra were identical to those previously recorded for **12**. No attempt was made to establish the intermediacy (or otherwise) of the 4-*n*-propyl 1,1-dioxide **5** in this reaction.

Reaction of Thiete 1,1-Dioxide (**5**) with Sodium Borohydride.

A solution of 1.9 g (0.05 mole) of sodium borohydride in 5 ml (0.2%) of aqueous sodium hydroxide was added dropwise to a freshly prepared, stirred solution of 2.9 g (0.02 mole) of 1,1-dioxide **5** in 15 ml of ethanol at 0°. After an additional 0.5 hour, during which time the 1,1-dioxide was consumed, the solution was neutralised with dilute acid and extracted with ether (4 x 40 ml). The combined ether phase was washed with brine, dried and concentrated to a liquid that was subjected to flash chromatography (20% ethyl acetate/hexane) to give 1.0 g of 3-ethoxy-2-*n*-propylthietane 1,1-dioxide **27** as colourless liquid; ^{1}H-nmr: δ 0.99 (t, J = 7.3 Hz, 3H), 1.22 (t, J = 6.9 Hz, 3H), 1.49 (m, 2H), 1.80 and 2.03 (2 x 1H m), 3.46 (q, J = 6.9 Hz, 2H), 3.83 (m, 1H), 3.93 and 4.17 (2 x 1H m), 4.26 (m, 1H); ^{13}C-nmr: 13.8 (CH_3), 15.2 (CH_3), 20.6 (CH_2), 31.0 (CH_2), 66.1 (CH_2), 66.3 (CH), 68.1 (CH_2), 83.8 (CH).

Anal. Calcd. for $C_8H_{20}NO_3S$: MNH_4^+ m/z 210.1164. Found: MNH_4^+ m/z 210.1159.

Continued elution furnished 2-*n*-propylthietane 1,1-dioxide **6** as a colourless liquid for which ^{1}H- and ^{13}C-nmr data were identical to those previously recorded. This reaction, when performed by an inverse addition using only glyme as solvent and a similar workup, gave only the thietane 1,1-dioxide **6** in quantitative yield.

Reaction of Thiete 1,1-Dioxide **12** with Sodium Borohydride.

To a solution of 1.0 g (6.8 mmoles) of 1,1-dioxide **12** in 20 ml of dry glyme was added portionwise with stirring 0.5 g (13.2 mmoles) of sodium borohydride. After 4 hours the solution was neutralised with dilute acid and extracted with ether (4 x 40 ml). The combined ether phase was washed with brine then dried and concentrated to give 0.9 g (91%) of the thietane 1,1-dioxide **6** as a colourless oil. All spectral data were consistent with those previously recorded.

Reaction of Thiete 1,1-Dioxide **12** with Lithium Aluminium Hydride.

To a stirred suspension of 0.8 g (21.1 mmoles) of lithium aluminium hydride in 40 ml of anhydrous ether that was cooled to -78° under dry argon was added dropwise a solution of 1.5 g (10.3 mmoles) of 2-*n*-propylthiete 1,1-dioxide **12** in ether. After stirring for 1 hour at this temperature the mixture was allowed to

warm to ambient temperature before being quenched in the usual manner. Removal of the inorganic material by filtration and concentration of the ether phase by slow distillation gave 0.8 g of a mobile liquid that was shown by gc-ms [Hewlett-Packard MSD, 25 m DB5, 60° (1 minute) <7°/minute <200°] to comprise two components only. These were shown to be 2-*n*-propylthietane **1** (*ca* 30%, as the lesser mobile species) and a mercaptohexane (*ca* 70%). The mixture was purified by Kügelrohr distillation at 140 mm to give a colourless liquid, the composition of which was unchanged. An examination of the ^{13}C-nmr spectrum, in particular, and of the EPA-NIH Mass Spectral Data Base lead to the assignment of the major product as 3-mercaptohexane **26**.

Anal. Calcd. for $C_6H_{15}S$: MH^+ m/z 119.0895. Found: MH^+ m/z 119.0890.

X-Ray Crystallographic Data for *exo*-7-Aza-6-oxa-4-*n*-propyl-3-thiatricyclo[5.4.$1^{1,7}$.$1^{2,5}$]undecane 3,3-Dioxide (**17a**).

Formula is $C_{11}H_{19}NO_3S$: M_r = 245.3, monoclinic, $P2_1/n$; a = 13.490(5), b = 5.149(3), c = 18.229(8) Å, β = 100.38(3)°; V = 1246(1) $Å^3$; Z = 4, D_c = 1.31 Mg m^{-3}, λ(MoKα) = .71073 A, μ = 0.23 mm^{-1}, F(000) = 528, T = 193°K, final R = 0.11 for 304 uniquely observed reflections. The molecular structure, shown in Figure 2, was determined from a needle-like crystal of dimensions 0.50 x 0.12 x 0.03 mm that was mounted on Nicolet R3M diffractometer. Cell dimensions were determined using 25 reflections (6.9 <2θ <20.2 degrees) centred automatically using graphite-monochromated MoKα radiation. A total of 1732 reflections (h = -14 to 14, k 0 to 5, ℓ 0 to 19) including three standards were measured within the limits 2 <2θ <45 degrees at 193°K by conventional omega scan mode with fixed background time and scanning speed. Equivalent reflections were averaged (R_{int} .033), with profile fitting utilized in processing the data [23] and the 304 reflections with intensities 2.5 times their standard deviations (from counting statistics) were corrected for Lorentz and polarization factors. No absorption correction was applied.

The structure was solved by direct methods [24] and successive difference Fourier syntheses. Refinement [25] was *via* full matrix least-squares minimizing wD^2, where $D = |F_O| - |F_C|$ and $w = 1\sigma(F_O)^{-2}$ and $|F_O|F_C|$ are the calculated and observed structure factors. Lack of significant observations restricted the refinement of hydrogen atom positions and thermal parameters. All non-hydrogen atoms were refined isotropically in groups. Hydrogen atoms were included in calculated positions (C-H 1.08 Å) except for H(141) which was located from the difference map. Hydrogens H(81)-H(112) were refined with one common isotropic thermal parameter; remaining hydrogens were fixed at U values of their host atom plus 0.010 $Å^3$. No features of significance were noted in the final difference map, highest peak 0.78 e $Å^{-3}$. Scattering factors for non-hydrogen and hydrogen atoms were taken from conventional sources [26,27]. Final residuals R, R_W were 0.11, 0.05 respectively.

Figures 1 and 2 are computer-generated diagrams [25] illustrating the independent molecules and the atom labelling schemes with 30% probability ellipsoids. Tables 1-3 list the atomic and thermal parameters for **17a**. The thietane ring is planar within experimental error (mean deviation 0.02(5) Å) and the fused five membered ring is in an envelope conformation with the flap atom N7 0.72(5) Å from the plane. The fused piperidine ring is in a chair conformation with N7 and C10 0.40(5) and -0.73(5) Å from the chair plane. All data for **11** are reported elsewhere [28]. Crystals of **17b** were determined by a Weissenberg film study to be orthorhombic with a = 21.3(2), b = 5.2(2) and c = 10.9(2) Å; insufficient diffracted intensity precluded further study.

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