Structure and Thermal Decomposition of Some 5-(Cyclohexyloxy)thianthreniumyl Perchlorates

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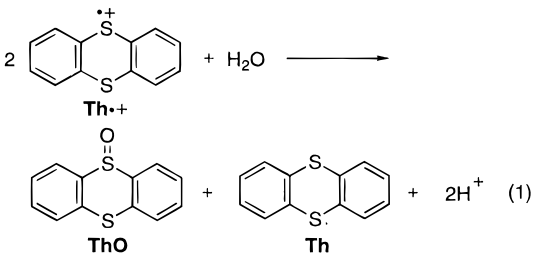
Five sets of *cis*- and *trans*-substituted cyclohexanols were used for reaction with thianthrene cation radical perchlorate, namely, *cis*- and *trans*-cyclohexane-1,2-diol, *cis*- and *trans*-2-methyl-, 3-methyl-, and 4-methylcyclohexanol, and *cis*,*cis*- and *trans*,*trans*-3,5-dimethylcyclohexanol. Reaction in CH_2Cl_2 solution and precipitation with ether gave the corresponding crystalline 5-(cyclohexyloxy)thianthreniumyl perchlorate salts. The configuration of each salt in $CDCl_3$ was shown by ^1H and ^{13}C NMR spectroscopy to correspond with the configuration of the cyclohexanol from which it was made. X-ray Ortep diagrams of four of the salts confirmed the structure deduced from NMR spectroscopy. In the NMR, inequivalence of the ^1H and ^{13}C signals from the thianthreniumyl 4- and 6-, 1- and 9-, 2- and 8-, and 3- and 7-positions was found when the 1′-position of the cyclohexyl ring was stereogenic. In the four Ortep diagrams, the orientation of the S−O bond was psuedoaxial. Thermal decomposition of the salts made from the monosubstituted cyclohexanols at 100 °C in CH_3CN solution gave products consistent with the assigned structures.

Introduction

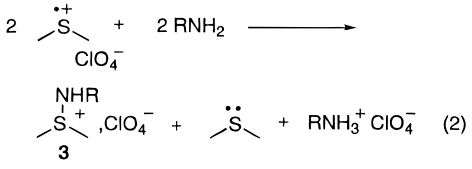
One of the simplest and best-known reactions of organosulfur cation radicals is that with water, which gives equal amounts of the parent organosulfur compound and its oxide. The reaction has been studied in much mechanistic detail with the thianthrene cation radical ($Th^{\bullet+}$), shown stoichiometrically in eq 1. Studies of this reaction, particularly, and of the similar phenothiazine cation radical reaction, have a very long history.[1] It is evident that, regardless of mechanistic nuances, the oxygen atom of the water molecule becomes the oxygen atom of the sulfoxide.



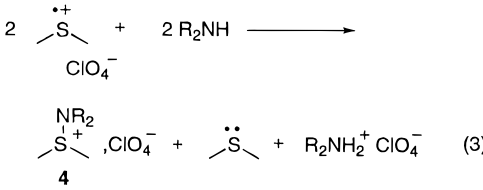
(1)

An analogous reaction of $Th^{\bullet+}$ [2] and of the phenoxathiin cation radical[3] with ammonia was discovered about 20 years ago. That reaction is illustrated in Scheme 1 with phenoxathiin cation radical, from which both the sulfiliminium perchlorate (**1**) and sulfilimine (**2**) were isolated.[3]

In that period also, reactions of $Th^{\bullet+}$ and of *N*-methyl- and *N*-phenylphenothiazine cation radicals with primary and secondary alkylamines were reported. Those reactions gave *N*-alkylsulfiliminium- (**3**) and *N*,*N*-dialkylsulfiliminium perchlorates (**4**), as shown in abbreviated form in eqs 2 and 3.[4]



(2)



(3)

In contrast with these reactions, particularly of the organosulfur cation radicals with alkylamines, no studies were reported, in the earlier years of cation radical chemistry, of reactions of organosulfur cation radicals with alcohols. It was known in our own laboratory that $Th^{\bullet+}$, for example, was unstable in solutions containing methanol and ethanol. Reactions at the root of this instability were known to be relatively slow, because methanol was used routinely to trap alkyl cations formed in some of our (faster) oxidations of azoalkanes by $Th^{\bullet+}$.[5] Furthermore, we were aware some 20 years ago that 5-(alkyloxy)thianthreniumyl perchlorates may be formed in reactions of $Th^{\bullet+}$ with alcohols, but were not able to pursue the work.[6]

Recently, we began investigations of the reactions of $Th^{\bullet+}$ with alcohols[7] and diols[8] in CH_3CN solutions. Reaction with alcohols gave alkenes, ethers, and, in some cases, *N*-alkylacetamides. Initially, it was thought that

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(1) (a) Shine, H. J. In *Organosulfur Chemistry*; Janssen, M. J., Ed.; Interscience Publishers: New York, 1967; pp 93−117. (b) Shine, H. J. In *Organic Free Radicals*; ACS Symposium Series No. 69; Pryor, W. A., Ed.; American Chemical Society: Washington, D.C., 1978; pp 359−375. (c) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 229. (d) Shine, H. J. In *The Chemistry of the Sulfonium Group*; Stirling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981; pp 523−570. (e) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, pp 55−157.

(2) Shine, H. J.; Silber, J. J. *J. Am. Chem. Soc.* **1972**, *94*, 1026.

(3) Mani, S. R.; Shine, H. J. *J. Org. Chem.* **1975**, *40*, 2756.

(4) (a) Kim, K.; Shine, H. J. *Tetrahedron Lett.* **1974**, 99. *J. Org. Chem.* **1974**, *39*, 2537. (b) Bandlish, B. K.; Padilla, A. G.; Shine, H. J. *J. Org. Chem.* **1975**, *40*, 2590.

(5) Engel, P. S.; Robertson, D. T.; Scholz, J. N.; Shine, H. J. *J. Org. Chem.* **1992**, *57*, 6178.

(6) (a) Unpublished work of Dr. K. Kim. (b) Bard, A. J.; Ledwith, A.; Shine, H. J. In *Advances Physical Organic Chemistry*; Gold, V., Bethell, D., Eds.; Academic Press: London, 1976; Vol. 13, p 232.

(7) (a) Shine, H. J.; Yueh, W. *Tetrahedron Lett.* **1992**, *33*, 6583. (b) Shine, H. J.; Yueh, W. *J. Org. Chem.* **1994**, *59*, 9, 3553.

(8) Han, D. S.; Shine, H. J. *J. Org. Chem.* **1996**, *61*, 1, 3977.

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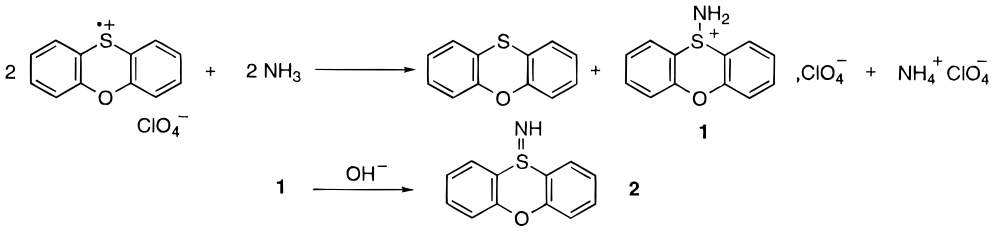
Scheme 1



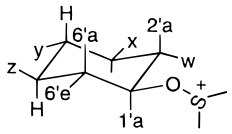
these products were formed in solution from reactions of the primary but labile products, 5-(alkyloxy)thianthreniumyl perchlorates.[7] In time, however, it was found that these primary products were quite stable in CH_3CN and that the secondary products that had been characterized and assayed by gas chromatography (GC) were being formed, in fact, for the most part by thermal decomposition on the GC column. Thus, 5-(cyclohexyloxy)thianthreniumyl perchlorate (**5a**) was isolated from the reaction of $Th^{\bullet+}ClO_4^-$ with cyclohexanol in CH_2Cl_2 solution and was shown to decompose not only on a GC column but also in CH_3CN at 100 °C to cyclohexene and ThO.[9]

We have now isolated thianthreniumyloxy perchlorates **5b**−**l** from reactions of $Th^{\bullet+}$ ClO_4^- with *cis*-and *trans*-cyclohexane-1,2-diol, *cis*- and *trans*-2-methylcyclohexanol, *cis*- and *trans*-3-methylcyclohexanol, and *cis*- and *trans*-4-methylcyclohexanol, *cis*,*cis*- and *trans*,*trans*-3,5-dimethylcyclohexanol, and methanol. We report here the ^1H NMR characterization of and structure of 10 of these 11 perchlorate salts, the ^{13}C NMR spectra of 7 of them (among which the 5-methoxy salt, **5l**, served as a model), and the structure of 4 of them as determined by X-ray crystallography (Ortep diagrams). We report also the products of decomposition of salts **5b**−**i** in CH_3CN at 100 °C.

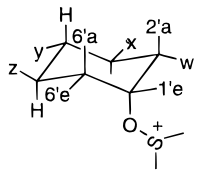
Results and Discussion

Structure of 5b−k. The structure we refer to here means the position (axial or equatorial) occupied by the thianthreniumyloxy group on the cyclohexyl ring. Initially, we felt that in all of these compounds the large thianthreniumyloxy group would have an equatorial orientation. ^1H NMR spectroscopy and X-ray crystallography (of four of the perchlorate salts) show, however, that this group has the same orientation in the cyclohexyl ring as the OH group had in the cyclohexanol from which the salt was prepared. This can be deduced from the splitting pattern in the NMR signal for the 1′-H atom of the cyclohexyl ring. That is, where the thianthreniumyloxy group is equatorial the 1′-H atom must be axial and show the splitting pattern of an axial H coupling with nearby protons. Correspondingly, where the thianthreniumyloxy group is in the axial position, the 1′-H atom must be equatorial and show the splitting pattern of an equatorial H. Our NMR results show that **5b**,**d**,**f**,**h**,**j** have (predominantly) an axial 1′-H atom whereas **5c**,**e**,**g**,**i**,**k** have (predominantly) an equatorial 1′-H atom (Scheme 2). The NMR data are particularly instructive in the cases of **5b** and **5c**, because in these cases the splitting pattern of not only the 1′-H but also of the 2′-H atom was discernible. In **5b** both of these H atoms are axial and their NMR signals were triplets of doublets.

Scheme 2



	w	x	y	z
5a	H	H	H	H
5b	OH	H	H	H
5d	Me	H	H	H
5f	H	H	H	Me
5h	H	H	Me	H
5j	H	Me	H	Me



	w	x	y	z
5c	OH	H	H	H
5e	Me	H	H	H
5g	H	H	H	Me
5i	H	H	Me	H
5k	H	Me	H	Me

For H-1′a we have *J*-1′a (2′a,6′a) 10.0 Hz, and *J*-1′a (6′e) 4.91 Hz. For H-2′a we have *J*-2′a (1′a,3′a) 10.1 Hz and *J*-2′a (3′e) 4.87 Hz. In contrast, in the isomer **5c** the 1′-H atom is equatorial and gave a broad and partly resolved singlet NMR signal diagnostic of an equatorial H atom. The 2′-H atom is axial and showed coupling with another axial H (3′-H) and two inequivalent equatorial H atoms at positions 1′ and 3′. That is, *J*-2′a (3′a) was 11.2 Hz, *J*-2′a (1′e) 2.37 Hz, and *J*-2′a (3′e) 4.40 Hz. We deduce that *J*-2′a (1′e) is the smaller coupling from the general rule that when an electron-attracting group (here the thianthreniumyloxy) is antiperiplanar to one of the coupling H atoms, *J* is diminished by 1−2 Hz.[10]

The orientations of the thianthreniumyloxy and OH groups in **5b** and **5c**, deduced from NMR spectra, are supported by the X-ray crystal patterns of these two salts (Figures 1a and 2a in the Supporting Information). The Ortep diagrams show clearly that the large thianthreniumyloxy group is axial in **5c**, and the NMR data show that this orientation is maintained in $CDCl_3$ solution. Correspondingly, the Ortep diagram for **5b** shows clearly that each substituent is in the equatorial position.

The 1′-H signals in the NMR spectra for **5d** and **5e** are equally diagnostic. In the trans isomer **5d**, the axial proton H-1′a gave rise to a triplet of doublets, *J*-1′a (2′a,6′a) 10.1 Hz and *J*-1′a (6′e) 4.61 Hz. This compares well with the NMR of the corresponding axial proton in *trans*-2-methylcyclohexanol, $J = 9.71$ and 4.27 Hz. The chemical shifts (Table 1) for these axial protons reflect also the nearby positive charge in **5d** ($\delta = 4.186$) as compared with $\delta = 3.121$ in the alcohol. Correspondingly, the NMR for H-1′e in **5e** is a doublet of triplets, with *J*-1′e (6′e) 4.90 Hz and *J*-1′e (2′a,6′a) 2.44 Hz. These data and assignments also comply with the general rule about the influence of an attached electronegative atom.[10] A similar multiplet is seen in *cis*-2-methylcyclohexanol,

(9) Zhao, W.; Shine, H. J. *Tetrahedron Lett.* **1996**, *37*, 1749. The numbering of protons (H_1 and H_4) in this report is incorrect and should be interchanged.

(10) Eliel, E. E.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; pp 712, 713.

Table 1. ^{1}H Chemical Shifts (δ)[a] for 5b−k and Thianthrene 5-Oxide (ThO)

	δ										
H[b]	**5b**	**5c**	**5d**	**5e**	**5f**	**5g**	**5h**	**5i**	**5j**	**5k**	**ThO**[c]
4	8.737	8.727	8.766	8.735	8.719	8.719	8.677	8.693	8.703	8.713	7.91
6	8.697	8.630	8.698	8.699	8.711	8.710					
1	7.921	7.928	7.920	7.933	7.907	7.928	7.923	7.939	7.914	7.929	7.60
9	7.911	7.920	7.913								
2	7.834	7.820	7.840	7.845	7.830	7.837	7.847	7.850	7.836	7.836	7.53
8	7.822	7.813	7.832		7.826	7.832					
3	7.738	7.732	7.744	7.743	7.743	7.742	7.730	7.740	7.740	7.734	7.40
7	7.720	7.708	7.735		7.738	7.736					
1′	4.581	5.146	4.186	4.773	4.646	5.063	4.579	4.933	4.674	5.107	
2′	3.288	3.953									

[a] In $CDCl_3$ solution with TMS as reference for **5b**−**k**. [b] Listed in order of decreasing δ. [c] In $CDCl_3$ solution with $CHCl_3$ as reference at 7.26 ppm, ref 13.

J = 5.06 and 2.51 Hz, while the chemical shifts of the two related protons are δ = 4.773 for **5e** and 3.78 for the alcohol, again reflecting the positive charge in **5e**. **5f**, prepared from *cis*-3-methylcyclohexanol, has an axial 1′-H, whose NMR signal was a triplet of triplets, δ = 4.646. The alcohol, itself, had a similar NMR multiplet, δ = 3.563. Isomeric **5g** and the corresponding *trans*-3-methylcyclohexanol had equatorial 1′-H, broad and poorly resolved multiplets, centered at δ = 5.063 and 4.061, respectively. **5h**, prepared from *trans*-4-methylcyclohexanol, has an axial 1′-H whose NMR signal was a triplet of triplets with J-1′a (2′a,6′a) 10.9 Hz and J-1′a (2′e,6′e) 4.51 Hz. The NMR of the related proton in *trans*-4-methylcyclohexanol itself was also a triplet of triplets with J = 10.7 and 4.36 Hz, with δ = 3.544 as compared with 4.58 for **5h**. In the cis isomer **5i** the axial orientation of the thianthreniumyloxy group is deducible from the NMR spectrum of H-1′e and supported by the Ortep diagram from X-ray crystallography (Figure 3a in the Supporting Information). The NMR spectrum of H-1′e was a poorly resolved multiplet, satisfiable with J approximately 4.7 and 2.9 Hz. In the case of **5k**, the axial orientation of the thianthreniumyloxy group is deduced from the equatorial orientation of H-1′, a broad, unresolved singlet, δ = 5.107. The isomer **5j** had, in contrast, for H-1′, a triplet of triplets, J = 11.2 and 4.65 Hz, centered at δ = 4.674, diagnostic of an equatorial thianthreniumyloxy group, and this is seen clearly, also, in the Ortep projection of Figure 4a in the Supporting Information. Similar patterns for H-1′ were found in the corresponding alcohols.

Insofar as structure is concerned, then, the *cis*-cyclohexanols gave cis salts (**5c**,**e**,**f**,**i**,**j**) and the *trans*-cyclohexanols gave trans salts (**5b**,**d**,**g**,**h**,**k**). The cis salts did not undergo the ring flipping in solution that would have placed the large thianthreniumyloxy group predominantly in the equatorial position. This was a surprise to us. Brown, in a similar finding years ago, found that group size and conformational disposition were not necessarily related and invoked the (opposing) contributions of van der Waals and covalent radii of the group.[11] He noted, for example, the report of Berlin and Jensen[12] that, contrary to expectation (based on group size), the amount of axial conformer increased in the series chloro-, bromo-, and iodocyclohexane. It seems, analogously, that in **5c**,**e**,**g**,**i**,**k** the large thianthreniumyl group must be far enough away from the ring (Brown's covalent radius) as to not cause the 1,3-diaxial interactions that would result in ring flipping. Ring flipping, which would place the large group in the equatorial position would then, in fact, place a group with, presumably, a larger effective covalent radius (Me, OH) in the less sterically suitable axial position. It is remarkable, in fact, that when *cis*-cyclohexane-1,2-diol reacts with $Th^{\bullet+}$, the axial OH group becomes thianthreniumyloxy (**5c**). In **5b**, ring flipping, which is proposed (later) to account for the thermal decomposition of **5b**, is inhibited at room temperature because that would place the remaining OH group in the axial position, too. It is notable that only one of the OH groups in these cyclohexane diols reacted with $Th^{\bullet+}$.

Insofar as a preferred configuration of the thianthreniumyloxy group is concerned, it is, in fact, equatorial in **5a**, just as is the hydroxyl group in cyclohexanol. This is deduced again from the ^{1}H NMR patterns for the 1′-hydrogen. In **5a**, this was an overlapping triplet of triplets with J-1′a (2′a,6′a) 8.62 and J-1′a (2′e,6′e) 4.31 Hz, while in cyclohexanol the corresponding J were 9.03 and 4.45 Hz. The relevant chemical shifts were 4.691 and 3.611 ppm.

The NMR spectra of compounds **5b**−**k** also had well-defined signals from the aromatic ring protons. The data on chemical shifts and coupling constants are given in Tables 1 and 2. We can relate the NMR spectra of **5b**−**k** to the spectrum of thianthrene 5-oxide (ThO). ThO is a symmetrical molecule with four sets of equivalent protons, H-1,9; H-2,8; H-3,7; and H-4,6. Chemical shifts for ThO have been reported by Lam,[13] in Ternay's laboratory, and go from low to high field in the order 4,6; 1,9; 2,8; 3,7. The same order in chemical shifts occurs in **5b**−**k**, as deduced from comparison with ThO, from splitting patterns and from COSY spectra of **5i**. **5i** was chosen for COSY spectroscopy because of the simplicity of its aromatic-region NMR spectrum. That is, the signals were for four sets of equivalent protons, as in ThO, and were not complicated with overlapping. The spectrum consisted of doublets of doublets for H-4,6 and H-1,9 and triplets of doublets for H-2,8 and H-3,7. The spectrum from the trans isomer **5h** also had the simplicity of splitting patterns with the exception that a small coupling (J = 0.637) was found in the spectrum of H-1,9 and may have been caused by *para* coupling J-1(4),9(6).

In contrast with the simplicity of the aromatic ^{1}H NMR spectra of **5h**,**i** caused by sets of equivalent protons, the spectra of **5b**−**g** were more complex, because of the inequivalency of the protons in each set. The spectra of **5b**,**c** exhibited this complexity most clearly. The multiplet attributable to each of the eight aromatic protons

(11) Brown, H. C.; Klimisch, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 1425.
(12) Berlin, A. J.; Jensen, F. R. *Chem. Ind. (London)* **1960**, 998.

(13) Lam, W. W. *The Synthesis and Multinuclear Magnetic Resonance Studies of Pharmacologically Important Sulfur-Containing Compounds*. Dissertation; University of Texas at Arlington, 1989, p 234.

Table 2. Coupling Constants (*J*) for Aromatic H in 5b−k and Thianthrene 5-Oxide (ThO)

	J[b]										
coupling[a]	**5b**	**5c**	**5d**	**5e**	**5f**	**5g**	**5h**	**5i**	**5j**	**5k**	ThO
4(3)	7.73	7.62	7.83	7.08[d]	7.81	7.59	7.86	7.88	7.61	7.78	7.66
6(7)	*c*	7.75	*c*	7.26[d]	7.70	7.73					
4(2)	1.66	1.65	1.56	1.50	2.03		1.36	1.40	*f*	1.44	1.39
6(8)	1.57	1.55	1.50	*e*	1.74	1.84					
4(1)	0.638	0.632	*e*	*e*	*e*	*e*	*e*	*e*	*e*	*e*	*e*
6(9)	*e*	*e*	*e*	*e*	0.758	*e*	*e*	*e*	*e*	*e*	*e*
1(2)	7.21	7.84	7.83	7.82	7.83	7.64	7.98	7.98	7.74	7.82	7.56
9(8)	7.89	7.68	7.84								
1(3)	1.64	1.43	1.68	1.55	1.89	1.79	1.76	1.52	1.79	1.55	1.26
9(7)	1.51	1.65	1.28								
1(4)	0.638	0.730	*e*	*e*	*e*	*e*	0.636	*e*	*e*	*e*	*e*
9(6)	*e*	*e*	*e*	*e*	*e*	*e*					
2(1,3)	7.53	7.51	7.62	7.51	7.62	7.66	7.49	7.67	7.46	7.54	7.55
8(7,9)	7.39	7.85	7.63		7.62	7.29					
2(4)	1.69	1.56	1.71	1.55	1.77	1.46	1.48	1.42	1.52	1.57	1.31
8(6)	1.56	1.39	1.74		1.78	1.51					
3(2,4)	7.42	7.43	7.22	7.48	7.32	7.54	7.73	7.62	7.43	7.49	7.47
7(6,8)	7.48	7.49	7.37		7.45	7.51					
3(1)	1.72	1.63	1.74	1.63	1.64	1.11[d]	1.61	1.36	1.85	1.62	1.47
7(9)	1.68	1.54	1.82		1.84	1.44					

[a] Protons are listed in order of decreasing δ. For example, H-4 (before H-6) coupling with H-3, a doublet; and H-2 (before H-8) coupling with H-8 and H-3, a triplet. [b] In Hz; coupling constants are averages when more than one value was measured. For example (**5b**), the coupling pattern for H-4 was a dd, so that coupling with H-2 gave two doublets with averaged $J = 1.66$ Hz. [c] Overlap made measurement uncertain. [d] Low value attributed to poor resolution. [e] Coupling not evident. [f] Coupling unresolved.

Table 3. Aromatic ^{13}C Chemical Shifts (δ)[a]

	compound and δ						
position	**5a**	**5d**	**5f**	**5i**	**5j**	**5k**	**5l**[b]
4	135.824	135.744	135.779	135.815	135.809	135.984	136.427
6		135.664					
4a	135.660	135.541	135.668	135.645	135.643	135.709	135.715
5a		135.508					
1	135.403	134.950	135.517	134.493	134.501	134.339	135.527
9		134.486					
2	129.352	129.539	129.394	129.381	129.402	129.334	129.446
8		129.277					
3	129.097	128.928	129.063	129.123	129.079	129.264	128.947
7		128.863					
9a	121.741	122.255	121.961	121.856	121.920	121.756	119.241
10a		121.453	121.886				

[a] In ppm with respect to TMS as internal standard. [b] 5-(Methoxy)thianthreniumyl perchlorate.

was readily assignable, but an arbitrary choice had to be made as to which proton of each pair would be assigned the downfield shift. The choice was made, as seen in Table 1, to assign the lower-field shift to the lower numbered proton, e.g., H-4 rather than H-6. Coupling constants for most of the proton−proton interactions were measurable. Only in a few cases were splittings not distinct enough for measurement or too small to be seen. The data are given in Table 2.

Inequivalency of protons in a pair of protons was seen fairly well in **5d**,**f**,**g** and to a small extent in **5e**. The chemical shifts and coupling constants are listed in Tables 1 and 2. The inequivalency of protons in the rings of **5b**−**g** is attributable to the presence of a stereogenic center at position C-1′ in the cyclohexyl ring. That is, regardless of the conformation of the cyclohexyl ring in **5b**−**g**, and regardless of the cyclohexyloxy's spatial orientation (whether pseudoaxial or equatorial at the sulfur atom) and the possiblity of rotation about the S−O and O−cyclohexyl axes, the protons on the separated aromatic rings of thianthrenium apparently experience different environments and respond with different chemical shifts.[14a] This effect is absent in **5h**,**i**.[14b]

The possibility must be addressed that inequivalency in ^{1}H signals may have been caused not by the presence of a stereogenic center in **5b**−**g** but by restriction to rotation of the cyclohexyl moiety about its S−O bond. To test this possibility, **5j** and **5k** were prepared, the premise being that if rotation were restricted in, say, **5f** and **5g**, the 3-methylcyclohexyloxy salts, it should be even more restricted in the 3,5-dimethylcyclohexyloxy salts, **5j** and **5k**, and give rise in them to inequivalent NMR signals. In the event, each of the two astereogenic salts, **5j** and **5k**, gave aromatic NMR spectra with no sign of inequivalent chemical shifts, supporting the interpretation that inequivalency in **5b**−**g** is caused by the presence of a stereogenic center in them.

The inequivalency in δ seen in the ^{1}H NMR spectra was also seen in the aromatic ^{13}C spectra. Thus, **5a** showed the expected six aromatic ^{13}C peaks of a symmetrical 5-(alkyloxy)thianthreniumyl ion (Table 3). The same complement of peaks was obtained with **5i**, **5j**, and **5k**, and with 5-methoxythianthreniumyl perchlorate, **5l**. On the other hand, **5d** showed 12 aromatic ^{13}C peaks,

(14) (a) For a discussion of this effect, see Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: Oxford, 1987; pp 299−302. (b) The same effect is seen in simpler 5-(alkyloxy)thianthreniumyl perchlorates in which the alkyl group has a stereogenic center attached to oxygen, such as 2-pentyl and 2-hexyl. The effect is absent where the alkyl group is, for example, methyl, ethyl, isopropyl. Unpublished work of W. Zhao.

concordant with its full set of inequivalent ^{1}H peaks. The 12 peaks are listed in Table 3 with assignments of δ based on the assignments made to the ^{1}H signals of **5d**. On the basis of inequivalency in ^{1}H shifts in **5f**, we expected to find the analogous inequivalency in its ^{13}C spectrum. However, only seven ^{13}C peaks were found. We deduce that overlapping of ^{13}C peaks occurred for all signals except those from C-9a and C-10a. The difference in results between **5d** and **5f** can be accommodated by examining the δ data in their ^{1}H spectra. The differences ($\Delta\delta$, ppm) in δ in **5d** for H-4 and H-6 (0.068), H-1 and H-9 (0.007), H-2 and H-8 (0.008), and H-3 and H-7 (0.009) are larger than for the corresponding shifts in **5f**. Those $\Delta\delta$, in the same sequence, are 0.008, 0.000, 0.004, and 0.005, indicating that the effect of the unsymmetrical alkyl group in **5d** is larger than in **5f**. This difference in effect shows up not only in the ^{1}H but also in the ^{13}C spectra.

Last, the effect of the positive charge on chemical shifts in **5b**−**k** can be seen by comparison with those in ThO (Table 1). The effect is most marked on the H-4,6 protons, with $\Delta\delta$ approximately 0.7 ppm, and falls off for the other sets of protons to approximately 0.3 ppm. The effect of the positive charge is apparently transmitted also to the cyclohexyl ring's H-1′, as seen by comparing the data for **5d**−**i** with those of the corresponding alcohols. That is, δ for H-1′ in *trans*-2-methyl-, *cis*-2-methyl-, *trans*-3-methyl-, *cis*-3-methyl-, *trans*-4-methyl-, and *cis*-4-methylcyclohexanol was 3.121, 3.779, 4.037, 3.563, 3.544, and 3.947, respectively, while for **5d**,**e**,**f**, **g**,**h**,**i**, δ was 4.186, 4.773, 4.646, 5.063, 4.579, and 4.933, respectively. Similarly, δ for H-1′ in **5j** and **5k** was, respectively, 4.674 and 5.107, as compared with 3.612 and 4.130 in the corresponding alcohols. The difference in δ between a compound **5** and its corresponding alcohol was thus approximately 1 ppm. It is notable that the equatorial H-1′ had a larger downfield shift than the axial H-1′ in each pair of salts and alcohols, in agreement with the generality that axial H generally resonates upfield of equatorial H.[10]

In the discussions above, the structures **5a**−**k** have been treated as if each cyclohexyl group had one identifiable conformation. That is, the H-1′ proton has been characterized as being axial in some cases and equatorial in others. The corresponding cyclohexanols have been treated similarly. We recognize that in each of the alcohols, however, we are identifying the major conformer of a two-conformer equilibrium. In that respect, Neikam and Dailey,[15a] using low-temperature NMR spectroscopy, found the equilibrium of conformers of cyclohexanol in CS_2 solution to contain 7.1% of the axial-OH conformer. Also, Bassindale[15b] has recorded that in *cis*-4-methylcyclohexanol, the conformer with axial-OH and equatorial-CH_3 is preferred to the extent of (our calculation) 88%. We were unable to detect the separated conformers of these alcohols in $CDCl_3$ at −50 °C. To go to lower temperatures with examples of **5** we turned to solvent CD_2Cl_2, mp −97 °C. With that, two unresolved but separate H-1′ peaks were detected in **5a** at −90 °C, at δ = 4.46 (axial-H, 81%) and 4.95 (equatorial-H, 19%). At 25 °C in this solvent one partly resolved multiplet was observed at δ = 4.63. These data show that the equatorial component of **5a** (i.e., with axial H-1′) dominates the equilibrated conformers at 25 °C to the extent, calculated from ΔG, of 71%. In contrast with **5a**, no change in the unresolved singlet NMR signal from H-1′ in **5i**, the salt made from *cis*-4-methylcyclohexanol, could be detected in going stepwise down to −90 °C. Thus, **5i** appeared to be in one conformation only. Low-temperature NMR spectroscopy was not carried out with any other examples of **5** or corresponding alcohols.

Our using NMR data to specify H-1′ as being either dominantly equatorial or axial appears to be justified. The aromatic ^{1}H NMR spectra of **5a** and **5i** at low temperatures showed no sign of inequivalence. As the temperature was lowered stepwise to −90 °C, the aromatic signals retained their dd (H-4,6 and H-1,9) and td (H-2,8 and H-3,7) character until at about −45 °C, when the smaller splittings began to disappear. At −90 °C, for example, the aromatic signals were doublets for H-4,6 and H-1,9, and triplets for H-2,8 and H-3,7. Our conclusion from these data is that the presence of two cyclohexyl conformers, as witnessed with **5a**, could not be the cause of the inequivalence in the aromatic NMR signals that we have noted in some of **5**.

A remaining feature of the structure of the salts **5** pertains to the orientation of the S−O bond, that is, as to whether it is pseudoaxial or pseudoequatorial. An analogous situation has been presented nicely with thianthreniumyl bis(ethoxycarbonyl)methylide by Ternay, and this ylide is in the pseudoequatorial conformation in the solid state.[16] In the four cases for which we have X-ray crystallographic data, **5b**, **5c**, **5i**, and **5j**, the orientation is clearly pseudoaxial, as can be seen in the projections of Figures 1b−4b in the Supporting Information. The orientation has some relevance to our analysis of NMR spectra in that it could be suggested that the inequivalency found in some of the aromatic ^{1}H and ^{13}C signals could be caused in solution by inversion of configuration at sulfur, leading to a mixture of conformers with different chemical shifts. However, we rule out this possibility in that it is not seen, for example, with **5i**, whose crystallographic orientation is no different from that of **5b**, **5c**, and **5j**.

Products of Thermal Decomposition. Products were obtained by heating **5** in CH_3CN solution at 100 °C for 30−40 min, and were identified and assayed with gas chromatography (GC). The product from **5b** (trans-isomer) was cyclohexene oxide (**6**, 96%), whereas **5c** (cis) gave mainly cyclohexanone (**7**, 96%) and only a small amount of **6**. From **5d** (trans-isomer) were obtained 1-methyl- (**8**, 45%) and 3-methylcyclohexene (**9**, 34%) and some *N*-(2-methylcyclohexyl)acetamide (**10**, 14%). The cis-isomer **5e** gave 93% of **8** and 2.7% of **9**; none of **10** was obtained. Decomposition of both cis (**5f**) and trans (**5g**) isomers gave mixtures of 3-methyl- (**9**) and 4-methylcyclohexene (**11**), which could not be separated on our GC columns. They are reported as a mixture (Table 6). Small amounts of 1-methylcyclohexene (**8**) were also obtained from **5f** and **5g**. 4-Methylcyclohexene (**11**) was obtained from the decomposition of both (trans) **5h** (87%) and (cis) **5i** (81%) isomers of the 4-methylcyclohexyloxy salt (Table 7).

In the first reports of reactions of $Th^{\bullet+}ClO_4^-$ with alcohols it was mistakenly thought that the primary products, 5-(alkyloxy)thianthreniumyl perchlorates, were short-lived in solutions containing DTBMP, and that the

(15) (a) Neikam, W. C.; Dailey, B. P. *J. Chem. Phys.* **1963**, *38*, 445. (b) Bassindale. A. *The Third Dimension in Organic Chemistry*; John Wiley & Sons: New York, 1984; p 90.

(16) Ternay, A. L., Jr.; Baack, J.; Lam, W. W. *Phosphorus, Sulfur Silicon* **1992**, *70*, 19, and references therein.

Table 4. Products of Decomposition of 5b and 5c in CH_3CN Solution Containing DTBMP[a]

run	proc[b]	reactant, mmol × 10^2	products,[c] mmol × 10^2					ratio:[e] products/ ThO
			6	**7**	diol[d]	Th	ThO	
1	a	**5b**, 16.2	10.3	2.0	3.8	4.4	11.6	
	b		10.8	1.9	4.4	4.0	22.9	
	c		0	0	16.4	0.43	15.0	1.09
2	a	**5b**, 9.6	8.4	1.4	0	1.5	8.0	
	d		8.8	0.25	0	0.50	9.0	1.00
	b		9.2	0	0	0.20	9.2	1.00
	c		9.2	0	0	0.19	9.7	0.95
3	a	**5c**, 9.9	1.2	8.6	0	1.5	8.0	
	d		0.77	9.5	0	0.60	9.0	1.14
	b		0.68	9.0	0	0.51	9.1	1.06
	c		0.65	9.5	0	0.45	9.3	1.09

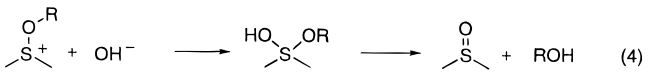
[a] Each solution contained DTBMP in small excess over the amount of **5**. [b] (a) Unheated solution stirred for 75 min and injected onto column. (b) Preceding solution stirred with 0.4 mL of 2 M K_2CO_3 solution for 5 min and again injected onto column. (c) Preceding solution containing K_2CO_3 stirred for 18 h (run 1), 20 h (run 2), 23 h (run 3) and injected onto column. (d) Preceding solution heated at 100 °C for 30 min, cooled, and injected onto column. [c] Columns used were C for **6**, **7**, and diol, and A for Th and ThO. [d] *cis*- (run 3) or tr*a*ns- (runs 1, 2) cyclohexane-1,2-diol. [e] (Sum of **6**, **7** and diol)/ThO.

Table 5. Products of Decomposition of 5d and 5e in CH_3CN Solution Containing DTBMP[a]

run	proc[b]	reactant, mmol × 10^2	products,[c] mmol × 10^2						ratio:[f] products/ ThO
			8	**9**	amide[d]	ROH[e]	Th	ThO	
4	a	**5d**, 10.1	5.2	4.3	0	0	0.65	10.4	0.93
	b		0	0	0	9.4	0.35	9.8	0.96
5	a	**5d**, 10.5	5.8	4.6		0	0.88	10.3	1.01
	c		4.8	3.6	2.4	0	0.68	10.1	1.07
	b		4.6	3.4	1.4	0	0.40	9.8	0.96
6	a	**5e**, 9.8	9.0	0.56	0	0	0.65	10.2	0.94
	b		2.8	0	0	6.9	0.47	9.8	0.99
	d		2.6	0	0	7.2	0.61	10.0	0.98
7	a	**5e**, 10.1	9.3	0.57	0	0	0.72	10.0	0.99
	c		9.2	0.29	0	0	0.65	10.6	0.90
	b		9.4	0.27	0	0	0.58	9.9	0.98
	d		8.5	0.27	0	0	0.49	10.1	0.87

[a] Each solution contained DTBMP in a small excess over the amount of **5**. [b] (a) Unheated solution stirred for 40 min (runs 5, 6), 70 min (run 4), 85 min (run 7), and injected onto column. (b) Preceding solution stirred with 0.4 mL of 2 M K_2CO_3 solution for 15 min (runs 4, 5), 5 min (run 6), 10 min (run 7), and again injected onto column. (c) Preceding solution heated at 100 °C for 30 min (run 7), 40 min (run 5), cooled, and injected onto column. (d) Preceding solution containing K_2CO_3 stirred for 24 h and injected onto column. [c] Columns used were B for **8** and **9** and C for all other products. [d] *N*-(2-Methylcyclohexyl)acetamide. [e] *cis*- (runs 6, 7) or *trans*- (runs 4, 5) 2-Methylcyclohexanol. [f] (Sum of **8**, **9**, amide, and ROH)/ThO.

secondary products, e.g., alkenes, were formed in solution at room temperature.[7] Only later was it recognized that the primary products were quite stable at room temperature and that the secondary products had been formed by thermal decomposition of the primary either in the GC inlet or on the GC column. Consequently, in the present work we adopted an experimental procedure to ensure that the products obtained were indeed formed by heating compounds **5** in solution and were not formed from **5** during GC assay. Two experimental protocols were used. In the first, with each of **5b**−**i**, the solution of **5** in CH_3CN was first shown to decompose into secondary products on the GC column, i.e., as in our earlier report.[7] The unheated solution was then treated, usually briefly (20−30 min), with a small amount of aqueous K_2CO_3 and shown to give on GC assay none of the secondary products but only ThO and the alcohol from which **5** had been made. This part of the protocol was based on an earlier finding that **5a** reacted very readily with aqueous K_2CO_3 to give ThO and cyclohexanol.[9] Next, a new solution of **5** was heated at 100 °C and after cooling it to room temperature secondary products were assayed by GC. Aqueous K_2CO_3 was next added to the solution and GC assay was repeated, showing this time that only the secondary products were detectable. That is, that **5** had not survived the heating in solution, for had it done so it would have been hydrolyzed into ThO and the appropriate alcohol, as shown schematically in eq 4. Data for this protocol are given in Tables 4−7.



(4)

An example of data from this protocol can be seen most easily in Table 7 with the decomposition of **5h**. Entry 8a shows that injection of a solution of **5h** onto the GC column gave 4-methylcyclohexene (**11**, 99%). However, addition of 0.3 mL of 2 M aqueous K_2CO_3 to the unheated solution followed by GC assay gave, entry 8b, none of **11** but only *trans*-4-methylcyclohexanol (99%). These two experiments show that **5h** decomposed on the GC column. In contrast, run 9, Table 7, shows that when heated in solution at 100 °C for 30 min, **5h** gave **11** (entry c) and that, after heating, none of **5h** survived for later conversion into 4-methylcyclohexanol with K_2CO_3, entries 9b and 9d. Similar data for **5i** are found in Table 7 and for the other compounds **5b**−**g** in Tables 4−6.

When decomposition of **5** occurs and gives one of the products **6**−**11**, or when **5** is hydrolyzed to the corresponding alcohol, an equal amount of ThO must be formed. Therefore, the amount of ThO that was formed in the various reactions was assayed and is listed in each entry in the tables. In principle, the amount of ThO should equal the sum of the amounts of products in each reaction. That is, the ratio of products/ThO should be 1.00. This ratio is listed in the last column of each table and is seen for the most part to be close to unity. Thianthrene (Th) was also formed in every reaction, usually in small amounts which are listed in the tables. We do not know the way(s) in which Th was formed.

As an example of the pumping protocol, an unheated solution of **5h** was evaporated to dryness at room temperature, and the volatile material, collected in liquid N_2, was found to contain only a small amount of **11**. The residue was redissolved in CH_3CN and that solution was heated at 100 °C for 30 min, and again evaporated to dryness at room temperature. The volatile material now gave 76% of the **11** available in **5h**. The residue from the second evaporation was dissolved in CH_3CN, and after treatment with K_2CO_3 the solution was injected into the GC column, giving a trace of **11** and 18% of *N*-(4-methylcyclohexyl)acetamide. These results show that **5h** decomposed when heated in solution almost completely into **11** and the amide.

The products of thermal decomposition are related to the structures of **5b**−**i**. Thus **5b** (trans) gave mainly cyclohexene oxide (**6**) whereas **5c** (cis) gave mainly cyclohexanone (**7**). We attribute formation of **6** to the inversion of configuration of **5b**, placing the substituents in the diaxial configuration, eq 5. Inversions of this kind prior to product formation have been proposed by others, for example, to account for the formation of 3-methylcy-

(17) Brown, H. C.; Klimisch, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 1430.

Table 6. Products of Decomposition of 5f and 5g in CH_3CN Solution Containing DTBMP[a]

run	proc[b]	reactant, mmol × 10^2	products,[c] mmol × 10^2						ratio:[f] products/ThO
			8	(**9** + **11**)[d]	amide	ROH[e]	Th	ThO	
1	a	**5f**, 10.1	0.26	6.64	0	1.37	0.91	9.13	0.91
	b		0	0.18	0	10.2	0.19	9.9	1.05
	c		0	0.12	0	9.6	0.17	9.9	0.99
2	a	**5f**, 10.0	0.44	6.6	0	1.42	0.77	9.3	0.91
	d		1.1	8.3	1.24	0	0.19	10.0	1.06
	b		1.1	8.1	tr	0	0.19	9.9	0.93
3	a	**5g**, 10.0	0	9.4	0	0.63	0.68	8.9	1.13
	b		0	0.3	0	9.93	0.15	9.5	1.08
4	a	**5g**, 10.5	0	9.73	0	0.83	0.82	9.6	1.10
	d		0.94	9.6	tr	0	0.15	10.2	1.03
	b		0.94	9.3	tr		0.16	10.3	0.99

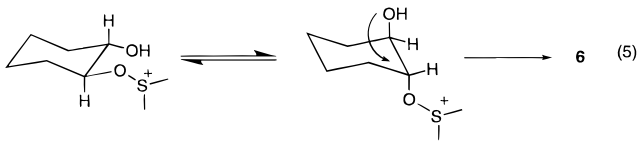
[a] Each solution contained DTBMP in small excess over the amount of **5**. [b] (a) Unheated solution stirred for 5 h and injected onto column. (b) Preceding solution stirred with 0.4 mL of 2 M K_2CO_3 10 min (run 1), 60 min (run 2), 90 min (run 3), 120 min (run 4), and again injected onto column. (c) Preceding solution containing K_2CO_3 stirred for 90 min, and injected onto column. (d) Preceding solution heated at 100 °C for 30 min, cooled and injected onto column. [c] Columns used were B for **8**, **9**, and **11**; and A for other products. [d] **9** and **11** could not be separated. [e] *cis*- (from **5f**) or *trans*-3-Methylcyclohexanol (from **5g**). [f] (Sum of **8**, **9**, **11**, amide, and ROH)/ThO.

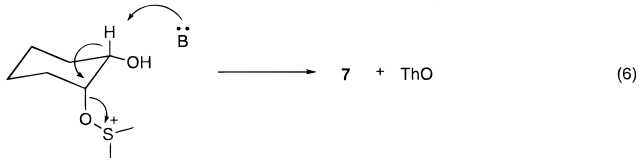
Table 7. Products of Decomposition of 5h and 5i in CH_3CN Solution Containing DTBMP[a]

run	proc[b]	reactant, mmol × 10^2	products,[c] mmol × 10^2					ratio: products/ ThO
			11	amide[d]	ROH[e]	Th	ThO	
8	a	**5h**, 10.0	9.9	0	0	0.32	10.2	0.97
	b		0	0	9.9	0.12	9.8	1.01
9	a	**5h**, 10.4	9.8	0	0	0.58	10.2	0.96
	c		9.6	2.6	0	0.16	10.1	1.20
	b		9.1	1.6	0	0.09	9.2	1.16
	d		9.0	1.6	0	0.10	10.3	1.03
10	a	**5i**, 9.84	9.6	0	0	0.24	10.2	0.94
	b		0.21	0	8.7	0.85	10.2	0.87
	d		tr	0	8.9	tr	9.9	0.89
11	a	**5i**, 10.5	9.8	0	0	0.45	10.2	0.96
	c		9.6	*f*	0	0.15	10.1	0.95
	b		8.2	*f*	0	0.08	9.7	0.85
	d		8.8	*f*	0	tr	10.5	0.84

[a] Each solution contained DTBMP in small excess over the amount of **5**. [b] (a) Unheated solution stirred for 45 min (runs 8, 10), 70 min (runs 9, 11), and injected onto column. (b) Preceding solution stirred with 0.3 mL of 2 M K_2CO_3 solution for 15 min (run 8), 20 min (runs 9−11), and again injected onto column. (c) Preceding solution heated at 100 °C for 30 min, cooled, and injected onto column. (d) Preceding solution containing K_2CO_3 stirred for 23 h (run 9), 27 h (run 10), 28 h (run 11), and injected onto column. [c] Columns used were B for **11** and A for all other products. [d] *N*-(4-Methylcyclohexyl)acetamide. [e] *cis*- (runs 10, 11) or *trans*- (runs 8, 9) 4-methylcyclohexanol. [f] GC peaks were small and broad and could not be integrated.

clohexene in the relatively slow elimination reactions of *trans*-2-methylcyclohexyl tosylate.[17−19] The formation of *trans*-2-(ethyloxy)cyclohexanol from the solvolysis of *trans*-2-hydroxycyclohexyl tosylate has been attributed, also, to neighboring-group participation (i.e., backside attack) of the hydroxyl group in the tosylate.[20] The preferred formation of **7** from **5c** (eq 6) is also understandable.





Our work with **5d** (trans) and **5e** (cis) can be compared with reactions of *cis*- and *trans*-2-methylcyclohexanol and their tosylates that are reported in the literature. Under purely E2-like conditions, the sulfurane from *trans*-2-methylcyclohexanol[21] and *trans*-2-methylcyclohexyl tosylate gave 99−100% of 3-methylcyclohexene (**9**).[17,18,22] Thermal decomposition of the *trans*-tosylate in dimethyl sulfoxide (DMSO), however, gave 70% of 1-methylcyclohexene (**8**) and only 30% of **9**, and the decomposition was said to have, therefore, carbonium-ion-pair character.[19] The reaction of *trans*-2-methylcyclohexanol with $Th^{\bullet+}ClO_4^-$, reported earlier,[7] gave **8** and **9** in the ratio 66:34, that is, akin to the ratio reported by Hatch for the tosylate.[19] We know now that our earlier results were from the (then unrecognized) decomposition of **5d** on GC column. That corresponds with our present finding that **5d** decomposed at 100 °C in solution to give **8** and **9** in the ratio 57:43. Thus, decomposition of **5d** is thermal and E1- rather than E2-like in character. In contrast with **5d**, the cis-isomer **5e** gave mainly **8** and a small amount of **9** (run 7a, Table 5), a result that conforms with either E1- or E2-like elimination. The decompositions of cis (**5f**) and trans (**5g**) salts, from *cis*- and *trans*-3-methylcyclohexanol, could not be distinguished from each other. Each gave an inseparable mixture of 3- and 4-methylcyclohexene (**9** and **11**), and also each gave a small amount of 1-methylcyclohexene (**8**), Table 6. The formation of **8** suggests the participation of a rearranging carbonium ion in the decomposition and would be consistent with an E1-like formation of **9** and **11**. Analogously (Table 7), decomposition of **5i** (*cis*) and **5h** (*trans*) gave only 4-methylcyclohexene (**11**), accompanied, in the case of **5i**, by a small amount of amide, a result indicative of carbonium ion involvement.

In contrast with **5b**−**i**, and with **5a** reported earlier,[7] cyclohexyl tosylate decomposed only to a small extent when heated in CH_3CN at 100 °C for 30 min. It did not react in CH_3CN with K_2CO_3 at room temperature. Cyclohexyl tosylate did decompose to cyclohexene when injected onto the GC column, however. These conclusions are based on experimental sequences similar to those described in Tables 4−7, and on a pumping protocol, the results of which are in the Experimental Section. Hatch and co-workers heated the tosylate under reflux in DMS0

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(19) Hatch, L. F.; Matar, M. S.; Garvisch, A. *Indian J. Chem.* **1974**, *12*, 583.
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(95−100 °C) for 3 h in order to complete the formation of **8** and **9**. The difference between cyclohexyl tosylate and **5a**−**i** lies in the remarkably good leaving group (ThO) in the **5** compounds.

Experimental Section

Acetonitrile (Eastman, HPLC grade) was dried by distillation from CaH_2 and again from P_2O_5, each under N_2. Dichloromethane was dried by distillation from P_2O_5. *cis*- and *trans*-Cyclohexane-1,2-diol and all authentic products except 3-methylcyclohexene (from Lancaster Syntheses, Inc.) were from Aldrich Chemical Co. *cis*- and *trans*-3-Methylcyclohexanol, *cis*,*cis*- and *trans*,*trans*-3,5-dimethylcyclohexanol were from ChemSampCo (earlier, Wiley Organics),[23] while *cis*- and *trans*-4-methylcyclohexanol were from TCI America. Quantitative gas chromatographic (GC) assays were made with a Varian Associates Model 3700 instrument attached to a Spectra-Physics Model 4290 recorder-integrator. Three columns were used: A, 10% OV-101 on 80−100 mesh Chrom-WHP, 4 ft × 1/8 in. stainless steel (ss); B, 10% Carbowax 20M on Chrom-WHP, 6 ft × 1/8 in. ss; and C, 10% OV-17 on 80−100 mesh Chrom-Q11, 6 ft × 1/8 in. ss. Assays were made with the use of predetermined concentration factors for authentic compounds, and internal standards: either naphthalene or biphenyl with column A, 2-butanone with column B, and biphenyl with column C. Columns were heated and ramped as follows: A and C, injector at 250 °C, detector at 300 °C, oven at 50 °C for 2 min and then 12 °C/min to 250 °C; B, initially similar settings, but ramped only to 100 °C.

Preparation of 5b−l. Approximately 0.80 mmol of $Th^{\bullet+}ClO_4^-$ was weighed into a 50-mL flask containing a magnetic stirrer, and to this was added 15 mL of CH_2Cl_2. The flask was capped with a septum through which was added, after 5 min of stirring, an excess (1.2−3 mmol) of the appropriate alcohol in 5 mL of CH_2Cl_2. Stirring was continued at room temperature until the color of $Th^{\bullet+}$ had disappeared, the time for which depended on the amount of alcohol that was used, namely 2−3 h for approximately 3 mmol and 30 h for 1.2 mmol. The (usually yellow) solution was concentrated to about 5 mL in a rotary evaporator and was diluted with 25 mL of dry ether. The white precipitate of **5** was filtered and washed three times with ether. In most cases, preparation was also successful if the reaction solution was stirred in an ice bath rather than at room temperature. In the preparation of **5g**, all procedures were conducted in an ice bath prior to concentration and dilution with ether, because very little of **5g** could be obtained from reaction at room temperature. Reaction of $Th^{\bullet+}ClO_4^-$ with *cis*,*cis*-3,5-dimethylcyclohexanol in an ice bath was complete within 140 min. However, similar reaction with *trans*,*trans*-3,5-dimethylcyclohexanol was incomplete even after 4 d and could be completed only after stirring at room tempereature for 5 h. Yields (%) and mp (°C, dec): **5b**, 90, 89−90; **5c**, 73, 82−85; **5d**, 80, 94−96; **5e**, 37, 68−70; **5f**, 68, 93−96; **5g**, 37, 81−82; **5h**, 80, 104−107; **5i**, 74, 90−91; **5j**, 60, 98−100; **5k**, 48, 102−104.

For obtaining single crystals for X-ray crystallography (**5b**,**c**,**i**), the solid was dissolved in 2 mL of CH_2Cl_2 in a 5-mL vial. The vial was placed in a larger bottle containing 10 mL of ether, and the bottle was capped. The bottle was left (2−14 d) either at room temperature or in the freezer until crystals appeared in the vial, and these were filtered and washed with ether. In the case of **5j**, 10 mL of pentane was used instead of ether, and the bottle was kept in the freezer.

Thermal Decomposition of 5b−i. The technique used is illustrated with **5i**. **Decomposition of 5-(*cis*-4-methylcyclohexyloxy)thianthreniumyl Perchlorate (5i) in MeCN. A. Without Heating.** See run 10, Table 7. A solution of 42.2 mg (0.0984 mmol) of **5i** and 34.6 mg (0.168 mmol) of DTBMP in 5 mL of MeCN containing both naphthalene and 2-butanone as GC standards was stirred for 45 min. GC assay with columns A and B gave (a) 4-methylcyclohexene (**11**, 0.096 mmol, 97.6%), DTBMP (0.156 mmol, 92.9%), and thianthrene 5-oxide (ThO, 0.102 mmol, 103%); 4-methylcyclohexanol was not detected. After 80 min of stirring, 0.3 mL of 2 M K_2CO_3 solution was injected through the septum. The mixture was sampled for GC assay after periods of stirring, giving, (b) after 20 min, 0.0021 mmol (2.13%) of **11**, 0.087 mmol (88.4%) of *cis*-4-methylcyclohexanol, 0.0085 mmol (8.64%) of Th, and 0.102 mmol (104%) of ThO. After (d) 27 h, assay gave only a trace of **11**, 0.089 mmol (90.4%) of *cis*-4-methylcyclohexanol, a trace of Th, and 0.099 mmol (101%) of ThO.

B. With Heating. See run 11, Table 7. In a similar way, a solution of 45.0 mg (0.105 mmol) of **5i** and 34.9 mg (0.170 mmol) of DTBMP was (a) sampled for GC assay after 70 min of stirrring. The solution was then (c) heated at 100 °C for 30 min, cooled, and again sampled for GC assay. To the cooled solution was added 0.3 mL of K_2CO_3 solution, and samples for GC assay were taken after (b) 20 min and (d) 28 h of stirring. The GC assays gave, in mmol, for assays a, c, b, d: **11**, 0.0984 (93.7%), 0.096 (91.4%), 0.082 (78.1%), and 0.088 (83.8%); DTBMP, 0.157 (92.4%), 0.164 (96.5%), 0.161 (94.7%), and 0.174 (102%); Th, 0.0045 (4.3%), 0.0015 (1.43%), 0.0008 (0.8%), and a trace; ThO, 0.102 (97.1%), 0.101 (96.2%), 0.097 (92.4%), and 0.105 (100%). *cis*-4-methylcyclohexanol was not observed in any of the assays. Small amounts of *N*-(4-methylcyclohexyl)acetamide were found in the heated solution, but were not assayed.

C. With Pumping Off Volatile Products. These data are not listed in Table 7. A solution of 48.2 mg (0.113 mmol) of **5i** and 35.4 mg (0.172 mmol) of DTBMP, containing only 2-butanone as standard, was stirred for 50 min and a sample (a) was withdrawn for GC assay. The solution was then evaporated at room temperature, the volatile materials being trapped in a receiver cooled in liquid N_2. The solution (b) of volatile materials, to which naphthalene standard was added, was used for GC assay. The solid residue left after evaporation was dissolved in 5 mL of MeCN containing 2-butanone as standard and (c) sampled for assay. The solution was then heated for 30 min at 100 °C, cooled and (d) again sampled for assay. The solution was evaporated as before and the collected distillate (e) was used for assay after addition of naphthalene as standard. The residue from this second evaporation was dissolved in 5 mL of MeCN containing both naphthalene and 2-butanone for (f) GC assay. To the solution was added 0.3 mL of K_2CO_3 solution, and after 10 min of stirring, GC assay (g) was carried out. DTBMP, Th, and ThO were not measured in assays a, c, and d. Assays a−d gave for (a), 0.112 mmol (99.1%) of **11**; (b) 0.0069 mmol (6.1%) of **11**, 0.039 mmol (22.7%) of DTBMP, no Th, and a trace of ThO; (c) 0.104 mmol (92.0%), and (d) 0.092 mmol (81.4%) of **11**. Assay e gave 0.064 mmol (56.6%) of **11** and 0.0086 mmol (5.0%) of DTBMP; (f) gave 0.0016 mmol of **11**, 0.005 mmol (4.42%) of *N*-(4-methylcyclohexyl)acetamide, 0.097 mmol (85.8%) of DTBMP, 0.0012 mmol (1.06%) of Th, and 0.110 mmol (97.3%) of ThO. The final assay (g) showed no **11**, the same amounts of the amide and Th, 0.096 mmol (85%) of DTBMP, and 0.111 mmol (98.2%) of ThO.

A control experiment was carried out with the evaporation of a solution of 0.0997 mmol of **11** and 0.224 mmol of 2-butanone in 5 mL of MeCN. GC assay (a) before and (b) after evaporation gave (a) 0.0973 mmol (97.6%) and (b) 0.088 mmol (88.3%) of **11**.

Preparation of Amides. *N*-Substituted amides were made by reaction of each of the methylcyclohexanols with an excess of concentrated sulfuric acid in MeCN. It was recognized that this procedure would probably give a mixture of

(23) There is some disagreement in the literature over the identity of these 3,5-dimethylcyclohexanols. When supplied to us, the solid alcohol was named as all *cis* and the liquid alcohol as *cis*,*trans*,*trans*. These assignments were consistent with data in earlier literature[24] in which the all *cis* isomer is said to have mp 40.0−40.3 °C, and the *trans*,*trans* isomer to be liquid at room temperature. However, our NMR data did not agree with the assigned configurations, in that the solid alcohol had $\delta = 4.12$ (equatorial H) and the liquid alcohol had $\delta = 3.61$ (axial H) for the C-1 H atom. That is, the solid alcohol had to be the *trans*-1,3-*cis*-3,5-*trans*-1,5 isomer (called *trans*,*trans* in the text), and the liquid alcohol had to be the all *cis* isomer (called *cis*,*cis* in the text). Our NMR data agree with those of Li and Allinger, namely $\delta = 4.02$ for the *trans*,*trans* and 3.48 for the all *cis* isomer.[25] Our assignments were confirmed, also, by the NMR data for **5j**,**k** and by Ortep data not only for **5j**, but also for the solid, *trans*,*trans* alcohol itself (see Figure 5 in the Supporting Information).

cis- and *trans*-isomers in each case, but this was deemed sufficient for assaying the small amounts of amide that were formed in decomposition of some of the **5** in MeCN. The low melting points of our products indicated indeed that they contained a mixture of isomers, but separation of isomers was not observed in the GC traces. Although *cis*- and *trans*-*N*-(2-methyl-,[26] *cis*- and *trans*-*N*-(3-methyl-,[27] and *cis*- and *trans*-*N*-(4-methylcyclohexyl)acetamide[28] are known, we did not attempt to use the tedious methods of their preparation.

Crystal Structure Determinations. Suitable crystals were attached to glass fibers. Data collections were performed at −100 °C for **5b**,**c**,**i**, and at ambient temperature for **5j** on a Siemens Model P4 automated diffractometer using Mo K_α radiation. Unit cell parameters were determined and refined by a least-squares fit of 24 high angle relections. Data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections based upon Ψ-scans were applied for **5b**,**c**,**j**. The space group determinations were based upon a check of Laue symmetry and systematic absences present and were confirmed by structure solution. The structures were determined by direct methods followed by successive cycles of full-matrix least squares refinement and difference Fourier analysis using the SHELXTL-IRIS software package provided by Siemens Analytical X-ray Instrument Inc. The parameters refined included the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms, with the exception of **5i** and **5j**, for which the thianthrene ring carbon atoms were refined with isotropic thermal parameters. Hydrogen atoms were placed in calculated positions but were not refined unless otherwise specified. ORTEP[29] drawings are shown with 30% probability ellipsoids. Full details for the structure determinations are available in the Supporting Information. The data for **5i**,**j** were weak and limited in number because of the poorer quality of the crystals, which did not allow for anisotropic refinement for all atoms. Consequently, the carbon atoms of the rigid thianthrene ring were refined isotropically and a number of ellipsoids for the remaining atoms are distorted.

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Supporting Information Available: Figures 1−4, Ortep diagrams of compounds **5b** (Figures 1a,b), **5c** (Figures 2a,b), **5i** (Figures 3a,b), and **5j** (Figures 4a,b). Figure 5, Ortep diagram of *trans*,*trans*-3,5-dimethylcyclohexanol; legends to the figures (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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