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Adducts of Phenoxathiin and Thianthrene Cation Radicals with Alkenes and Cycloalkenes

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Phenoxathiin cation radical perchlorate ($PO^{\bullet+}ClO_4^-$) added stereospecifically to cyclopentene, cyclohexene, cycloheptene, and 1,5-cyclooctadiene to give 1,2-bis(5-phenoxathiiniumyl)cycloalkane diperchlorates (**4**−**7**) in good yield. The diaxial configuration of the PO^+ groups was confirmed with X-ray crystallography. Unlike additions of thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) to these cycloalkenes, no evidence for formation of monoadducts was found in the reactions of $PO^{\bullet+}ClO_4^-$. This difference is discussed. Addition of $Th^{\bullet+}ClO_4^-$ to five trans alkenes (2-butene, 2-pentene, 4-methyl-2-pentene, 3-octene, 5-decene) and four cis alkenes (2-pentene, 2-hexene, 2-heptene, 5-decene) gave in each case a mixture of mono- and bisadducts in which the configuration of the alkene was retained. Thus, cis alkenes gave erythro monoadducts and threo bisadducts, whereas trans alkenes gave threo monoadducts and erythro bisadducts. In these additions to alkenes, cis alkenes gave predominantly bisadducts, while trans alkenes (except for *trans*-2-butene) gave predominantly monoadducts. This difference is explained. 1,2-Bis(5-phenoxathiiniumyl)-cycloalkanes (**4**−**7**) and 1,2-bis(5-thianthreniumyl)cycloalkanes underwent fast elimination reactions on activated alumina forming, respectively, 1-(5-phenoxathiiniumyl)cycloalkenes (**8**−**11**) and 1-(5-thianthreniumyl)cycloalkenes (**12**−**16**). Among adducts of $Th^{\bullet+}ClO_4^-$ and alkenes, monoadducts underwent fast ring opening on alumina to give (5-thianthreniumyl)alkenes, while bisadducts underwent fast eliminations of H^+ and thianthrene (Th) to give (5-thianthreniumyl)alkenes also. Ring opening of monoadducts was a stereospecific reaction in which the configuration of the original alkene was retained. Thus, erythro monoadducts (from cis alkenes) gave (*E*)-(5-thianthreniumyl)-alkenes and threo monoadducts (from trans alkenes) gave (*Z*)-(5-thianthreniumyl)alkenes. Among bisadducts, elimination of a proton and Th occurred and was more complex, giving both (*E*)- and (*Z*)-(5-thianthreniumyl)alkenes. These results are explained. Configurations of adducts and (5-thianthreniumyl)alkenes were deduced with the aid of X-ray crystallography and ^1H and ^{13}C NMR spectroscopy. In the NMR spectra of (*E*)- and (*Z*)-(5-thianthreniumyl)alkenes, the alkenyl proton of *Z* isomers always appeared at a lower field (0.8−1.0 ppm) than that of *E* isomers.

Introduction

Recent work in these laboratories has shown that the thianthrene cation radical ($Th^{\bullet+}$) reacts with cycloalkenes and alkenes to form mono- and bisadducts, stereospecifically.[1,2] This work followed a gap of over 20 years after the first reports that $Th^{\bullet+}$ and phenoxathiin cation radical ($PO^{\bullet+}$) gave bisadducts in reaction with cyclopentene, cyclohexene, and 1-octene.[3,4] At that early time, very little information on the configuration of the adducts was presented. It was deduced from reactions with nucleophiles that the thianthrenium groups in 1,2-bis(5-thianthreniumyl)cyclohexane diperchlorate were diaxial a relationship that was confirmed later with X-ray crystallography.[5] In the work of Qian et al.,[2] it was subsequently shown that the thianthrenium groups in the bisadducts of two other cycloalkenes (cyclopentene and cycloheptene) were also diaxial, and that in the monoadducts of these cycloalkenes and of cyclooctene, the two sulfonium linkages were necessarily cis related. Additions to three alkenes were also studied by Qian et al., namely, *cis*-2-butene, *trans*-3-hexene, and 4-methyl-*cis*-2-pentene. With these, the configuration of the alkenes was retained in both mono- and bisadducts. To explain the stereospecificity of additions to both cycloalkenes and alkenes, the proposal was made that, initially, cycloaddition between the alkene and cation radical occurred, giving a cyclic cation radical intermediate (**1**, Scheme 1). Reaction of the intermediate with a second $Th^{\bullet+}$ followed in either of two

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(1) Lee, W. K.; Liu, B.; Park, C. W.; Shine, H. J.; Guzman-Jimenez, I. Y.; Whitmire, K. H. *J. Org. Chem.* **1999**, *64*, 9206−9210.
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(3) Shine, H. J.; Bandlish, B. K.; Mani, S. R.; Padilla, A. G. *J. Org. Chem.* **1979**, *44*, 915−917.
(4) Iwai, K.; Shine, H. J. *J. Org. Chem.* **1981**, *46*, 271−276
(5) Houman, A.; Shukla, D.; Kraatz, H. B.; Wayner, D. D. M. *J. Org. Chem.* **1999**, *64*, 3342−3345.

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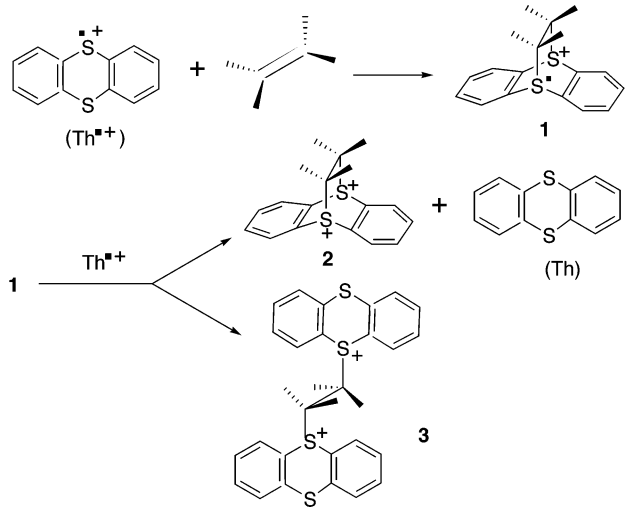
SCHEME 1



ways, oxidation to form a monoadduct (**2**) and thianthrene (Th) or displacement to form a bisadduct (**3**). It was shown with adducts of cycloheptene that reaction between a monoadduct (**2**) and Th to give a bisadduct (**3**) did not occur.[2] Whether a mono- or bisadduct was formed varied with the cycloalkene and alkene. Thus, cyclohexene gave mainly a bisadduct, while cyclooctene gave only a monoadduct. Among the three alkenes, each of which gave both mono- and bisadducts, the cis alkenes gave predominantly bisadducts, while the trans alkene gave mainly a monoadduct.

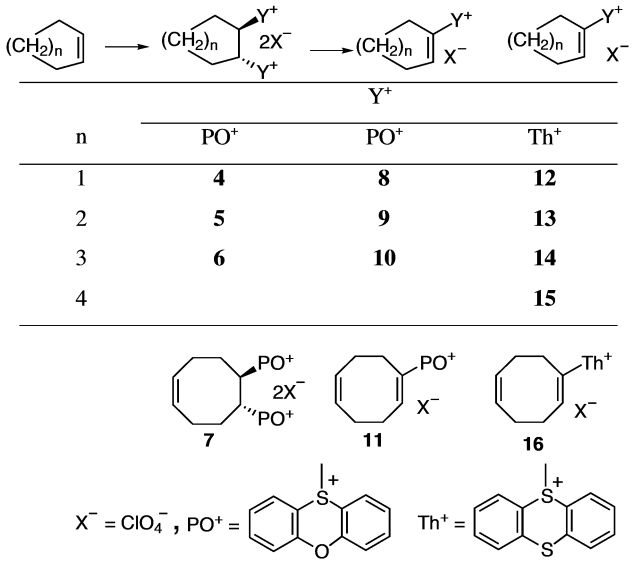
We have now studied the reactions of PO$^{\bullet+}$$ClO_4^-$ with cycloalkenes and those of Th$^{\bullet+}$$ClO_4^-$ with 13 alkenes. Our objectives were to study the stereochemistry of PO$^{\bullet+}$$ClO_4^-$ additions[3] and to probe further the effect of alkene configuration on mono- and bisadduct formation. In the course of the work, the ring opening of monoadducts and elimination in bisadducts on activated alumina were discovered.

Results

Adducts of PO$^{\bullet+}$$ClO_4^-$ and Cycloalkenes. Reactions of PO$^{\bullet+}$$ClO_4^-$ with cycloalkenes and 1,5-cyclooctadiene occurred readily, with the formation of bisadducts (**4**−**7**, Scheme 2). Reactions with alkenes were very slow, and further study was discontinued. This observation is analogous to that made earlier with 1-octene, from which a bisadduct dihydrate was obtained.[3] No evidence for monoadduct formation was found in any of the reactions with cycloalkenes. Two of the bisadduct diperchlorates (**4**, **5**) were reported earlier but were characterized only with elemental analyses.[3] In the present work, single crystals of **4**−**7** were grown successfully for X-ray crystallography (Supporting Information, Figures S1−S4), with which the diaxial configurations of the two phenoxathiiniumyl groups were disclosed. The adducts **4**−**7** were characterized also with ^{1}H and ^{13}C NMR spectroscopy.

Adducts of Th$^{\bullet+}$$ClO_4^-$ and Alkenes. Reaction of Th$^{\bullet+}$$ClO_4^-$ with 10 of 13 alkenes also occurred readily, in concordance with our earlier work.[2] In most cases, a mixture of mono- and bisadduct diperchlorates was obtained by precipitation from solvent acetonitrile (MeCN) with ether. In the 300-MHz NMR spectrum of each

SCHEME 2



n	Y$^+$ = PO$^+$	PO$^+$	Th$^+$
1	**4**	**8**	**12**
2	**5**	**9**	**13**
3	**6**	**10**	**14**
4			**15**

TABLE 1. Products of Addition of Th$^{\bullet+}$$ClO_4^-$ to Alkenes

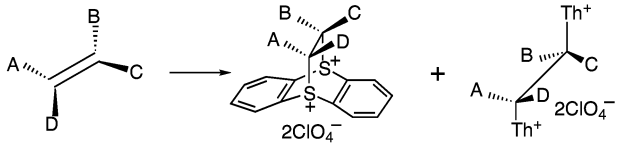
alkene	products (%)[a] mono	bis	Th[b]	sum
trans-2-butene	**17**, 19	**18**, 63	24	106
trans-2-pentene	**19**, 19	**20**, 25	49	93
cis-2-pentene	**21**, 7	**22**, 56	31	94
2-Me-2-butene	**23**, 33	**24**	64	97
cis-2-hexene	**25**, 15	**26**, 51	30	96
trans-4-Me-2-pentene	**27**, 30	**28**, 7	53	90
cis-2-heptene	**29**, 13	**30**, 47	31	91
trans-3-octene	**31**, 41	**32**, 8	48	97
cis-5-decene	**33**, 19	**34**, 39	40	98
trans-5-decene	**35**, 45	**36**, 2	55	102

[a] The percentage of original Th$^{\bullet+}$ units in each compound; 50% in a monoadduct would represent complete conversion of Th$^{\bullet+}$ into that adduct and Th. Yields of adducts were measured with 300 MHz NMR spectroscopy. [b] Measured with GC and includes the amount of Th equivalent to the amount of monoadduct. The remainder represents unprecipitated mono- and bisadduct that decomposed in the GC inlet.

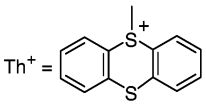
mixture, portions of the monoadduct signals were sufficiently separated from portions of the bisadduct signals to enable assay of the relative amounts of the adducts. These, and the originating alkenes, are listed in Table 1, while the structures of the adducts (**17**−**36**) themselves are listed in Scheme 3. Each of the 10 monoadducts was isolated and recrystallized by reprecipitations from MeCN for ^{1}H and ^{13}C NMR spectroscopy. One of the monoadducts (**23**) was unstable in CD_3CN solution and could not be characterized satisfactorily with NMR spectroscopy. When freshly made, however, it was convertible readily into an identifiable (X-ray crystallography) (5-thianthreniumyl)alkene (**38**). It was possible to grow crystals of four monoadducts (**17**, **27**, **33**, and **35**) for X-ray crystallography, and their Ortep diagrams confirmed their designated structures. Those Ortep diagrams are included here (Supporting Information, Figure S5, **17**; Figure S6, **27**; Figure S7, **33**; and Figure S8, **35**). Elemental analyses of two of the monoadducts (**25** and **29**) were obtained.

Only three of the bisadducts (**18**, **26**, and **30**) could be isolated, all of which showed the presence of a small amount of the monoadduct and Th in their NMR spectra.

SCHEME 3



Mono No.	A	B	C	D	Bis No.
17	H	Me	H	Me	**18**
19	H	Me	H	Et	**20**
21	Et	Me	H	H	**22**
23	Me	Me	H	Me	**24**
25	Pr	Me	H	H	**26**
27	H	Me	H	iPr	**28**
29	Bu	Me	H	H	**30**
31	H	Et	H	Bu	**32**
33	Bu	Bu	H	H	**34**
35	H	Bu	H	Bu	**36**



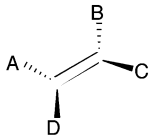
Nevertheless, it was possible to obtain ^{1}H and ^{13}C NMR data for these adducts after allowance for signals from the monoadducts. The difficulty in isolating pure bisadducts is attributed to their slow conversion into monoadducts in solution, as was demonstrated earlier.[2]

Three alkenes, (*E*)- and (*Z*)-3-methyl-2-pentene and 2,3-dimethyl-2-butene, failed to yield adducts with $Th^{\bullet+}ClO_4^-$. Nevertheless, the $Th^{\bullet+}$ was reduced to Th. These reactions are being pursued.

Reactions of Adducts on Alumina. When a solution of a bis(5-phenoxathiiniumyl)adduct diperchlorate in MeCN was deposited on activated alumina for a short time, elimination of a proton and phenoxathiin occurred and a 1-(5-phenoxathiiniumyl)cycloalkene was formed in good yield. Thus, adducts **4**−**7** gave products **8**−**11** (Scheme 2), three of which (**9**−**11**) have been characterized with X-ray crystallography (Supporting Information, Figures S9−S11). The known[2] 1,2-bis(5-thianthreniumyl)adducts of cyclopentene, cyclohexene, cycloheptene, and 1,5-cyclooctadiene and the monoadduct, 1,2-(5,10-thianthreniumdiyl)cyclooctane, behaved similarly on alumina and gave the products **12**−**16**. The 1-(5-thianthreniumyl)cycloalkenes **12**−**15** were obtained earlier in very slow reactions of the monoadducts in wet MeCN. They were then characterized with ^{1}H NMR spectroscopy, elemental analysis (**14**, **15**), and X-ray crystallography (**13**). In the present work, they and **16** have been further characterized with ^{13}C NMR spectroscopy.

Formation of (5-thianthreniumyl)alkenes also occurred readily with the adducts listed in Scheme 3. The products are listed in Table 2. All of the products in Table 2 were obtained from monoadducts, except for **43**, **44**, **49**, and **50**, which were obtained from bisadducts (**26** and **30**). In these reactions, a single (5-thianthreniumyl)alkene was obtained from each of the symmetrical adducts, namely, **37** from **17**, **53** from **33**, and **54** from **35**. In all other cases,

TABLE 2. (5-Thianthreniumyl)alkenes



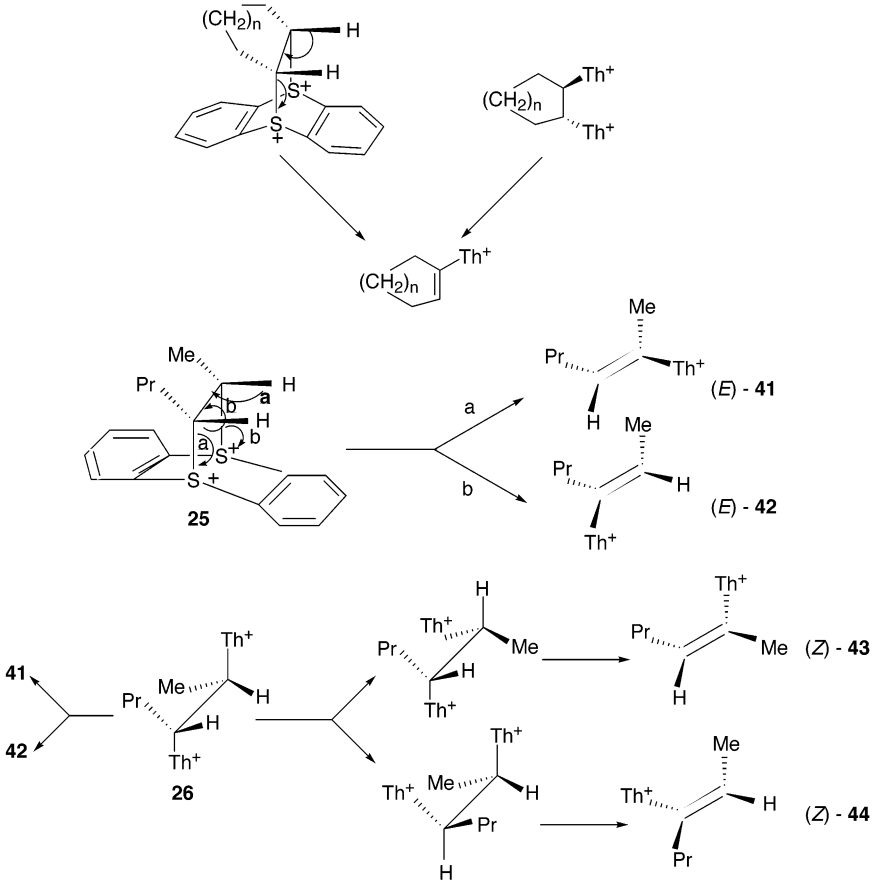
compd	A	B	C	D	confign
37	Me	Th^+	Me	H	*Z*
38	Me	Th^+	Me	Me	
39	Et	Th^+	Me	H	*Z*
40	Et	H	Me	Th^+	*Z*
41	H	Th^+	Me	Pr	*E*
42	Th^+	H	Me	Pr	*E*
43	H	Me	Th^+	Pr	*Z*
44	Th^+	Me	H	Pr	*Z*
45	iPr	Th^+	Me	H	*Z*
46	iPr	H	Me	Th^+	*Z*
47	H	Th^+	Me	Bu	*E*
48	Th^+	H	Me	Bu	*E*
49	H	Me	Th^+	Bu	*Z*
50	Th^+	Me	H	Bu	*Z*
51	Bu	Th^+	Et	H	*Z*
52	Bu	H	Et	Th^+	*Z*
53	Bu	Bu	Th^+	H	*E*
54	H	Bu	Th^+	Bu	*Z*

two (5-thianthreniumyl)alkenes were formed from each unsymmetrical monoadduct (e.g., **39** and **40** from **19**). No attempt was made to separate the pairs of products. Their structures were deduced from coupling patterns in the NMR spectrum of their mixture, and the relative amounts of the positional isomers were measured with integrations of particular NMR signals. Elemental analyses were obtained for some of these mixtures of isomers, namely, **39** and **40**, **41** and **42**, **45** and **46**, and **51** and **52**; elemental analysis of the single isomer **54** was also obtained. All but one (**38**) of the (5-thianthreniumyl)-alkenes had either *E* or *Z* configurations, those configurations being controlled by the structure of the originating adduct. This was demonstrated with X-ray crystallography, for example, for (*Z*)-**37**, formed from *threo*-**17**, the adduct of *trans*-2-butene (Supporting Information, Figure S12). X-ray crystallography was used also to characterize **38**, formed from **23**, the adduct of 2-methyl-2-butene (Supporting Information, Figure S13). Furthermore, *erythro*-**33** from *cis*-5-decene and *threo*-**35** from *trans*-5-decene, whose structures were confirmed with X-ray crystallography, gave, respectively, the corresponding (*E*)-**53** and (*Z*)-**54**.

Thus, erythro monoadducts gave *E* isomers and threo monoadducts gave *Z* isomers.

In contrast with a pair of mono- and bis(5-thianthreniumyl)adducts of a cycloalkene, which on alumina gave necessarily the same 1-(5-thianthreniumyl)cycloalkene, a pair of configurationally distinct mono- and bisadducts of an alkene behaved differently from each other on alumina (Scheme 4). This was found with adducts **29** (mono) and **30** (bis) of *cis*-2-heptene and also with adducts **25** (mono) and **26** (bis) of *cis*-2-hexene. That is, **29** gave only (*E*)-2- (**47**) and (*E*)-3-(5-thianthreniumyl)-2-heptene (**48**), whereas **30** gave a mixture of four isomers, namely, **47** and **48** as well as (*Z*)-2- (**49**) and (*Z*)-3-(5-thianthreniumyl)-2-heptene (**50**), in which **49** and **50** were dominant. The presence of small signals from **47** and **48** in the NMR spectrum of the mixture was deducible with the aid of their spectra recorded with the use of **29** alone.

SCHEME 4



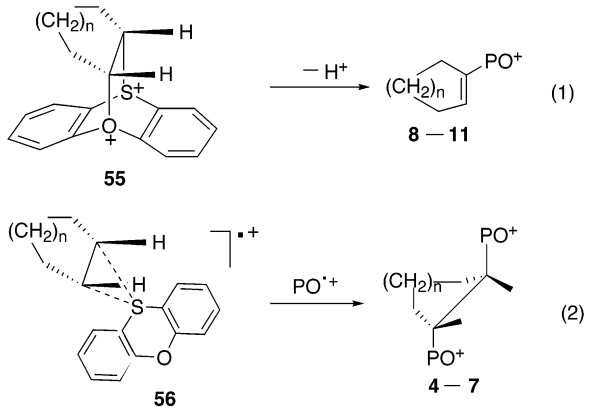
On the basis of integrations of the cleanly separated triplet signals of the four C-7 methyl groups, the ratio of *Z* to *E* isomers was 2.9/1. Once again, no attempt was made to separate positional isomers (**49** and **50**), so that their structures were deduced from coupling patterns in the NMR spectrum of their mixture. The relative amounts of isomers was again measured with integrations of particular NMR signals, such as of the alkenyl and terminal methyl groups. In addition, guidance about relative amounts of isomers was given by peak intensities in the ^{13}C NMR spectra.

Similarly, **25** (mono) gave only (*E*)-2- (**41**) and (*E*)-3-(5-thianthreniumyl)-2-hexene (**42**). From **26** (bis), which contained a small amount of **25**, a mixture was obtained containing **41** and **42** and both (*Z*)-2- (**43**) and (*Z*)-3-(5-thianthreniumyl)-2-hexene (**44**). The compounds **43** and **44** were dominant in this mixture, while the amounts of **41** and **42** were larger than could be attributed to the small amount of **25** that was present at the start. On the basis of methyl-group triplets, the ratio (*Z*)-**43**/(*Z*)-**44** was 1/2, and the ratio of *Z* to *E* isomers was 3.2/1. Here, then, threo bisadducts (**26**, **30**) gave mainly (*Z*)-(5-thianthreniumyl)alkenes.

Discussion

Structures and Formation of Adducts. Ortep diagrams (Figures S1−S4) leave no question that the PO$^+$ groups in 1,2-bis(5-phenoxathiiniumyl)cycloalkanes are diaxial. The formation of both mono- and bisadducts in reactions of Th$^{\bullet+}$ with the same cycloalkenes led us to propose that the first step in reaction is the cycloaddition of Th$^{\bullet+}$ and the alkene (Scheme 1). Having found no evidence of monoadducts in reactions of PO$^{\bullet+}$ with the cycloalkenes, we conclude that an intermediate analogous to **1** is not formed or, if formed, reacts with a second PO$^{\bullet+}$ only to give a bisadduct. A cyclic monoadduct, e.g., **55**, eq 1, apparently cannot be formed. Had such an adduct been formed but not remained intact, it would certainly have opened into a recognizable 1-(phenoxathiiniumyl)-cycloalkene, four of which (**8**−**11**) we have isolated, but from eliminations in bisadducts on alumina. It may be argued that **55** *is* formed but reacts completely with PO to give bisadducts (**4**−**7**). That possible route to bisadducts was found to be invalid in thianthrene chemistry,[2] so that there is no basis to believe that it would be valid in phenoxathiin chemistry. Consequently, to account for the stereospecific formation of 1,2-diaxial adducts **4**−**7**, we suggest that an episulfonium cation radical (**56**) is formed and undergoes opening in reaction with a second PO$^{\bullet+}$, eq 2.

The structures of the monoadducts in Scheme 3 have been designated with the help of similar structures in our earlier work,[2] with X-ray crystallography where possible (**17**, **27**, **33**, **35**) and with NMR spectroscopy. Ideally, the aromatic ^{1}H NMR spectra of these monoadducts would be two sets of dd with *J* close to 6 and 3 Hz, akin to Th itself. Thianthrenium monoadducts of cycloalkenes have this character.[1,2] Furthermore, the ^{13}C NMR spectra would have six peaks. In total, the ^{1}H and ^{13}C spectra would result ideally from a symmetrical



aromatic system. These NMR patterns are borne out only in two of the present cases, however, namely, **17** and **33**. Other monoadducts had six ^{13}C peaks but not the expected ^{1}H patterns (**35**), while others had two sets of complex 4 H multiplets but 12 ^{13}C peaks (**19**, **21**, **25**, **27**, **29**). These results indicate that the lack of symmetry in most of the adducts is responsible for the nonclassical monoadduct NMR spectra. We had hoped, furthermore, that the methine H atoms from the erstwhile double bond would show diagnostically large coupling constants in erythro isomers (cis) and, correspondingly, small coupling constants in threo isomers (trans).[2,6−8] Unfortunately, the signals from these protons were too complex from other couplings to be deciphered in many of the adducts (**17**, **19**, **31**, **33**, **35**). *J* was diagnostically large (8.5−10.8) in *erythro*-**25** and -**29** and smaller (6.0 Hz) in *threo*-**27**.

The structures of the bisadducts of Scheme 3 are designated principally deductively. That is, if we accept the structures of the monoadducts and the way in which bisadducts are formed (Scheme 1), the structures of the bisadducts must fall in place. The NMR spectra of only three bisadducts could be recorded. The complex ^{1}H NMR spectrum of **18** (from *trans*-2-butene) did not allow for diagnosis of the proposed erythro structure. On the other hand, the small sizes (1.0−1.3 Hz) of *J* for the protons on C-2 and C-3 of **26** (from *cis*-2-hexene) and of **30** (from *cis*-2-heptene) support the proposed threo structure of those adducts.

The mono- and bisadduct pairs **25** and **26** (from *cis*-2-hexene) and **29** and **30** (from *cis*-2-heptene) provide nice confirmation of erythro/threo patterns and validation of the assigned structures. In each of the monoadducts (**25** and **29**), coupling between the C-2 and C-3 protons is large (8.5−9.0 Hz), attesting to an erythro configuration. In each of the bis adducts (**26** and **30**), the coupling is small (1.3 Hz), attesting to a threo configuration. These configurations in turn validate the proposed modes of formation of mono- and bisadducts, and, as is shown later, validate also the assignments to the respective (5-thianthreniumyl)alkenes obtained from these adducts.

Ratios of Mono- and Bisadducts. With the exception of *trans*-2-butene, additions to the alkenes in Table 1 confirm our earlier results;[2] cis alkenes gave more bis- than monoadduct, whereas the reverse describes addition to trans alkenes. A 50% yield of monoadducts, as expressed in Table 1, would mean that all of the $Th^{\bullet+}$ is converted into monoadduct. This is almost reached with *trans*-3-octene and *trans*-5-decene. With two of the remaining trans alkenes (*trans*-2-pentene and *trans*-4-methyl-2-pentene), more of the $Th^{\bullet+}$ was converted into mono- than bisadduct. In contrast, the bisadduct was dominant with *cis*-2-pentene, *cis*-2-hexene, *cis*-2-heptene, and *cis*-5-decene. The results suggest that the trans configuration of alkyl groups in intermediate **1** inhibits displacement by the second $Th^{\bullet+}$ to give a bisadduct and promotes electron transfer to give a monoadduct. With *trans*-2-butene, it appears that the small size of the methyl groups allows for displacement in **1**.

In principle, the yields of monoadduct and Th should be the same. The excesses of Th listed in Table 1 are attributed to decomposition in the GC inlet of unprecipitated mono- and bisadducts remaining in the reaction solution at the time of the assay of Th. These decompositions were demonstrated independently in this and earlier work.[2] It is probable, of course, that the amounts of adducts remaining in solution will affect the yields of adducts in Table 1. The observed trends in yields appear to be self-consistent and acceptable.

Formation of Substituted Alkenes 8−16 and 37−54. In our earlier work, we reported that when a thianthrenium monoadduct of a cycloalkene was left in MeCN solution, it slowly opened into a 1-(5-thianthreniumyl)cycloalkene. The ring opening was faster when small amounts of water were added to the solution. Ring opening was attributed to base-promoted (H_2O) deprotonation of the adduct. In the present work, rapid ring opening in monoadducts and elimination in bisadducts on activated alumina has been achieved with high yields. Thianthrenium mono- and bisadducts of cycloalkenes gave the same 1-(5-thianthreniumyl)cycloalkene (Scheme 4). Thus, in the earlier work, the products **12**−**14** were obtained from monoadducts.[2] In the present work, bisadducts were used. The constraints on ring geometry prevent any other cycloalkenyl product from being formed. This behavior has not been observed with the mono- and bisadducts of alkenes. In this group, monoadducts gave (5-thianthreniumyl)alkenes in which the configuration of the adducts was retained, resulting from a pseudocis ring-opening loss of a proton. Retention of configuration is confirmed with the formation of **37** (*Z*) from **17** (threo), whose Ortep diagrams certify their structures. This case serves as the foundation of our assignments of *E* and *Z* configurations in all other cases, and upon that foundation is added the auxiliary evidence of the numbers and types of products formed and the NMR couplings within them. Thus the symmetrical **33** (erythro) and **35** (threo), whose Ortep diagrams certify their structures, gave each only one product, **53** and **54**, and, with **37** as an analogy, it is reasonable to assign a *Z* configuration to **54** and thus the *E* configuration to **53**. Where an unsymmetrical erythro monoadduct (e.g., **25**) gave two alkenyl products, it is reasonable, again, to assign *E* configurations to them. Where an unsymmetrical bisadduct (e.g., **26**) gave four products, there is no question that two of them had to be *E* isomers and two had to be *Z* isomers. In the case of

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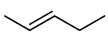
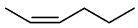
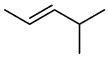
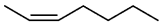
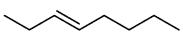
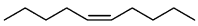
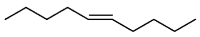
TABLE 3. ^{1}H Chemical Shifts in (5-Thianthreniumyl)Alkenes

Original Alkene	Compd. No.	Compd. Confign.	δ	Position H	Position Th$^+$	Multiplet[a]
	**37**	*Z*	6.63	C-2	C-3	qd
	**39**	*Z*	6.55	C-3	C-2	td
	40	*Z*	6.60	C-2	C-3	qt
	**41**	*E*	5.76	C-3	C-2	t
	42	*E*	5.61	C-2	C-3	q
	43	*Z*	6.58	C-3	C-2	t
	44	*Z*	6.59	C-2	C-3	q
	**45**	*Z*	6.39	C-3	C-2	d
	46	*Z*	6.69	C-2	C-3	q
	**47**	*E*	5.77	C-3	C-2	td
	48	*E*	5.59	C-2	C-3	q
	49	*Z*	6.62[b]	C-3	C-2	t
	50	*Z*	6.62[b]	C-2	C-3	q
	**51**	*Z*	6.48	C-4	C-3	t
	52	*Z*	6.52	C-3	C-4	t
	**53**	*E*	5.46	C-6	C-5	t
	**54**	*Z*	6.50	C-6	C-5	t

[a] NMR multiplet of the proton. [b] Overlapping multiplets.

26, then, the two *E* isomers were those also obtained from **25** and the two remaining isomers must be *Z* isomers. A similar argument is made for **47** and **48**, *E* isomers, from **29** (erythro) and the four products (**47**, **48**, **49**, **50**) from **30** (threo). The summation is that monoadducts are destined to give ring-opening products of fixed configuration. Bisadducts, on the other hand, can not only eliminate in a pseudocis way and give the same alkenes as from the monoadduct but also rotate into conformations suitable to the common anti-periplanar eliminations. That rotation results in alkenes with configuration opposite from that of the original alkene. This is set out in Scheme 4.

The ^{1}H NMR data reveal interesting features in the (5-thianthreniumyl)alkenes. The chemical shift of the alkenyl proton of *Z* isomers is always at lower field than that of *E* isomers. The data are listed in Table 3. Particular comparisons can be made of compounds originating from the same alkene, namely, of **41** and **42** with **43** and **44** (all from adducts of *cis*-2-hexene) and of **47** and **48** with **49** and **50** (all from adducts of *cis*-2-heptene). The signal from the C-3 proton in **49** overlapped with the signal from the C-2 proton in **50**, however, so that the chemical shift of the multiplet of these compounds is given. Comparisons can also be made of **53** (from the adduct *cis*-5-decene) with **54** (from the adduct of *trans*-5-decene). The differences in chemical shift between *E* and *Z* isomers of these compounds is about 0.8−1.0 ppm.

Whereas the alkenyl proton signals of our *Z* isomers were always at a lower field than those of the *E* isomers, the opposite has been reported for (*E*)- and (*Z*)-2-methyl-2-pentenoic acid, -ester, and -alcohol.[9] A similar finding was made for (*E*)-2-methyl-2-butenal (δ = 6.60) and its *Z* isomer (δ = 6.53).[10] Thus, it appears that a generalization about chemical shifts cannot be made to cover all classes of trisubstituted *E* and *Z* isomers.

The dramatic effect on chemical shift of the oxygen atom in 1-(5-phenoxathiiniumyl)cycloalkenes as compared with 1-(5-thianthreniumyl)cycloalkenes can be seen in the data in Table 4. Downfield shifts of 0.9−1.5 ppm can be seen. The cause of this difference may possibly be attributable to the oxygen atom's inductive effect.

Experimental Section

Thianthrene (Th$^{\bullet+}$) and phenoxathiin cation radical perchlorates (PO$^{\bullet+}$ClO$_4^-$) were prepared as described earlier.[11,12] The *potential explosiveness* of Th$^{\bullet+}$ClO$_4^-$ should be noted.[11]

Preparation of Bis-1,2-(5-phenoxathiiniumyl)cycloalkane Diperchlorates (4−7). An example is given with **5**. To a stirred suspension of 260 mg (0.868 mmol) of phenoxathiin cation radical perchlorate (PO$^{\bullet+}$ClO$_4^-$) in 5 mL of MeCN was added 1 mL of cyclohexene. The purple color of PO$^{\bullet+}$ClO$_4^-$ was discharged within 2 min, and a white precipitate formed. Dry ether was added until further precipitation ceased. The

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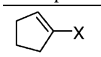
(10) Vogeli, U.; von Philipsborn, W. *Org. Magn. Reson.* **1975**, *7*, 617−627.
(11) Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368−3372.
(12) Mani, S. R.; Shine, H. J. *J. Org. Chem.* **1975**, *40*, 2756−2758.

TABLE 4. ^{1}H Chemical Shifts (δ)[a] in 8−16

Compd.	X^b, δ PO^+	Th^+	$\Delta\delta$
	**8**, 7.12	**12**, 6.18[c]	0.94
	**9**, 7.23	**13**, 6.02[c]	1.21
	**10**, 7.36	**14**, 5.90[c]	1.46
	**11**, 7.21	**16**, 5.80	1.41

[a] Solvent CD_3CN in all cases. [b] PO^+ = 5-phenoxathiiniumyl, Th^+ = 5-thianthreniumyl. [c] Reference 2.

precipitate was filtered, washed with ether, and dried under vacuum to give 240 mg (0.352 mmol, 81%) of **5**, mp 155−156 °C (dec). Literature mp 156−157 °C.[3]

Analogous preparations gave **4**, mp 154−155 °C (dec), 87% from cyclopentene; **6**, mp 125−126 °C (dec), 70% from cycloheptene; and **7**, mp 93−94 °C (dec), 33% from 1,5-cyclooctadiene. Single crystals for X-ray crystallography were grown successfully for **4** (Figure S1), **5** (Figure S2), **6** (Figure S3), and **7** (Figure S4).

Preparation of 1-(5-Phenoxathiiniumyl)cycloalkene Perchlorates (8−11). An example is given with **9**. A solution of 70 mg (0.103 mmol) of **5** in 5 mL of MeCN was poured onto 26 g of activated alumina held in a fritted glass funnel. The mixture was washed with MeCN, and the filtrate was evaporated to give a solid residue. Assay of a sample with ^{1}H NMR showed that it contained phenoxathiin and **9** in the ratio 45/55. The residue contained no **5**. It was washed three times with ether to remove phenoxathiin**,** leaving 31 mg (0.081 mmol, 79%) of **9**, mp 177−175 °C (dec), after reprecipitation from MeCN with ether. Analogous preparations gave 1-(5-phenoxathiiniumyl)cyclopentene perchlorate (**8**, 88%), mp 145−146 °C from **4**; 1-(5-phenoxthinumyl)cycloheptene perchlorate (**10**, 92%), mp 155−156 °C, from **6**; and 1-(5-phenoxathiiniumyl)-1,5-cyclooctadiene perchlorate (**11**, 87%), mp 183.5−184 °C, from **7**.

Single crystals for X-ray crystallography were grown successfully for **9** (Figure S9), **10** (Figure S10), and **11** (Figure S11).

Preparation of 1-(5-Thianthreniumyl)cycloalkene Perchlorates (12−16). An example is given with 1-(5-thianthreniumyl)cyclohexene perchlorate (**13**). A solution of 109 mg of 1,2-bis(5-thianthreniumyl)cyclohexane diperchlorate[2] in 4 mL of MeCN was poured onto 23 g of activated alumina as described above. The mixture was washed with MeCN/CH_2Cl_2 (1/2) and MeCN. Evaporation of the solvent gave a mixture of **13** and Th (55/45), which was washed with ether, leaving 57 mg (0.144 mmol, 94%) of **13**, mp 228−229 °C (dec).

Similar treatment of the 1,2-bisadduct of cyclopentene[2] gave **12**, 97%, mp 241−242 °C (dec); of the 1,2-bisadduct of cycloheptene[2] gave **14**, 100%, mp 174−174.5 °C (dec); and of the 1,2-bisadduct of 1,5-cyclooctadiene[2] gave **16**, 66%, mp 138−139 °C (dec). Because the bisadduct of cyclooctene has eluded preparation, the monoadduct, 1,2-(5,10-thianthreniumdiyl)-cyclooctane diperchlorate,[2] was used and gave **15**, 94%, mp 172−173 °C (dec).

The ^{1}H NMR spectra of **12**−**15** were reported earlier.[2] Here (Supporting Information), we report their ^{13}C NMR spectra and complete data for **16**, all in CD_3CN.

Addition of $Th^{\bullet+}ClO_4^-$ to Alkenes: Mono- and Bisadducts (17−36). An example is given with *trans*-2-butene. *trans*-2-Butene was bubbled slowly for 40 min into a suspension of 334 mg (1.06 mmol) of $Th^{\bullet+}ClO_4^-$ in 8 mL of MeCN, stirred under argon. A white solid deposited from the light-pink solution. Dropwise addition of ether caused further precipitation. Workup gave 273 mg of product that was shown with NMR spectroscopy to be a mixture of *threo*-2,3-(5,10-thianthreniumdiyl)butane diperchlorate (**17**) and *erythro*-2,3-bis(5-thianthreniumyl)butane diperchlorate (**18**) in the ratio 40/60. These data correspond with the conversion of 36% of $Th^{\bullet+}ClO_4^-$ to **17** and 50% to **18**. GC assay of the filtrate gave 0.306 mmol of Th, 0.192 mmol of which corresponds with formation of **17**. Thus, the filtrate yielded an additional 0.114 mmol of Th, attributable to decomposition of unprecipitated adducts in the GC inlet. The recovery of thianthrenium units thus totaled 1.028 mmol, 97% of the initial $Th^{\bullet+}ClO_4^-$. Repeated fractional crystallization of the mixture of **17** and **18** gave 51 mg of pure **17**, mp 182−183 °C (dec). A sample of pure **18** could not be obtained. **18** was isolated containing a small amount of **17**. The NMR signals for **18** could be distinguished from the smaller signals of **17**.

Similar reactions were carried out with 9 other alkenes. Nine of the 10 alkenes gave mixtures of mono- and bisadducts, and one gave only a monoadduct. The yields of adducts are listed in Table 1. Also listed in the table is the amount of Th assayed with GC after compensation for the amount corresponding with the formation of the monoadduct. In all cases, a pure monoadduct was isolated. Although only one pure bisadduct (**30**) could be isolated by fractional crystallization, its NMR solution showed the developing presence of **29** and Th. NMR spectra were obtainable in this and other bisadduct cases from the mixture of mono- and bisadducts. The following adducts were isolated: **19** (from *trans*-2-pentene), mp 150−151 °C (dec). **21** (from *cis*-2-pentene), mp 135−135.5 °C (dec). **25** (from *cis*-2-hexene), mp 134−135 °C (dec). Anal. Calcd for $C_{18}H_{20}S_2Cl_2O_8$ (**25**): C, 43.3; H, 4.04; S, 12.8; Cl, 14.2. Found: C, 43.0; H, 3.78; S, 12.7; Cl, 14.0. **26** (from *cis*-2-hexene), mp 125−126 °C (dec). The NMR solution contained a small amount of **25** and Th. The NMR signals of **26** were distinguishable from the smaller signals of **25**. **27** (from *trans*-4-methyl-2-pentene), mp 114−115 °C (dec). **29** (from *cis*-2-heptene), mp 133−134 °C (dec). Anal. Calcd for $C_{19}H_{22}S_2Cl_2O_8$ (**29**): C, 44.5; H, 4.32; S, 12.5. Found: C, 44.4; H, 4.36; S, 12.3. **30** (from *cis*-2-heptene), mp 93−94 °C (dec). When first isolated, **30** was free of **29** and some of it was used immediately for conversion into **49** and **50** on alumina. During acquisition of NMR data, however, **29** and Th appeared in the solution of **30**. The NMR spectrum of **30** was deduced after allowance for the smaller signals from **29** and Th. **31** (from *trans*-3-octene), mp 152−153 °C (dec). **33** (from *cis*-5-decene), mp 134−135 °C (dec). **35** (from *trans*-5-decene), mp 139−139.5 °C (dec).

Single-crystal growth of **17** (Figure S5), **27** (Figure S6), **33** (Figure S7), and **35 (**Figure S8) for X-ray crystallography was successful.

Preparation of (5-Thianthreniumyl)alkenes (37−54). The method used, ring-opening of monoadducts on alumina, was as described for the preparation of substituted cycloalkenes (**8**−**16**). In contrast with those preparations, small amounts of Th were also formed when monoadducts of alkenes were placed on alumina. This indicates that the monoadducts were decomposing to a lesser extent in another, as yet unspecified, way. The following products were isolated: **37**, (*Z*)-2-(5-thianthreniumyl)butene perchlorate, mp 146−148 °C (dec), 88% from **17**. Single-crystal growth for X-ray crystallography was successful (Figure S12). **38**, 2-(5-thianthreniumyl)-3-methyl-2-butene perchlorate, mp 162−163 °C (dec), 69% from freshly prepared **23**. Single-crystal growth for X-ray crystallography was successful (Figure S13). **39** and **40**, (*Z*)-2- and (*Z*)-3-(5-thianthreniumyl)-2-pentene perchlorate, a mixture obtained in the ratio 3/2, mp 120−121 °C, 90% from **19**. Anal. Calcd for $C_{17}H_{17}S_2ClO_4$ (mixture of **39** and **40**): C, 53.1; H, 4.45; S, 16.2; Cl, 9.21. Found: C, 53.2; H, 4.25; S, 16.3; Cl, 9.11. **41** and **42**, (*E*)-2- and (*E*)-3-(5-thianthreniumyl)-2-hexene perchlorate, a mixture obtained in the ratio 3/1, mp 87−88 °C, 92% from **25**. Anal. Calcd for $C_{18}H_{19}S_2ClO_4$ (mixture of **41** and **42**): C, 54.2; H, 4.80; S, 16.1; Cl, 8.88. Found: C, 54.3; H, 4.70; S, 15.7; Cl, 8.64. **43** and **44**, (*Z*)-2- and (Z)-3-(5-

thianthreniumyl)-2-hexene perchlorate, a mixture in the ratio 1/2 obtained along with small amounts of **41** and **42** from a 1/9 mixture of **25** and **26**. The ^{1}H signals of **43** and **44** could be distinguished from the smaller signals of **41** and **42** from which they were separated for the most part. ^{1}H spectral assignments of alkyl signals were made on the basis of coupling patterns of particular protons, but aromatic signals could not be assigned with surety. **45** and **46**, (*Z*)-2- and (*Z*)-3-(5-thianthreniumyl)-4-methyl-2-pentene perchlorate, a mixture obtained in the ratio 3/2, mp 87−88 °C (dec), 118−123 °C (dec), 64% from **27**. Anal. Calcd for $C_{18}H_{19}S_2ClO_4$ (mixture of **45** and **46**): C, 54.2; H, 4.80; S, 16.1; Cl, 8.88. Found: C, 54.1; H, 4.85; S, 15.8; Cl, 8.77. **47** and **48**, (*E*)-2- and (*E*)-3-(5-thianthreniumyl)-2-heptene perchlorate, a mixture obtained in the ratio 3/1, sticky solid, 86% from **29**. **49** and **50**, (*Z*)-2- and (*Z*)-3-(5-thianthreniumyl)-2-heptene perchlorate, a mixture in the ratio 3/7 obtained along with smaller amounts of **47** and **48**, 99% from **30**. The ratio of *Z* to *E* isomers was 3/1, and within the two *E* isomers, the ratio of **47** to **48** was 3/2. **51** and **52**, (*Z*)-3- and (*Z*)-4-(5-thianthreniumyl)-3-octene perchlorate, a mixture obtained in the ratio 2/3, mp 80−82 °C, 68% from **31**. Anal. Calcd for $C_{20}H_{23}S_2ClO_4$ (mixture of **51** and **52**): C, 56.3; H, 5.43; S, 15.0; Cl, 8.30. Found: C, 56.4; H, 5.34; S, 14.7; Cl, 8.70. **53**, (*E*)-5-(5-thianthreniumyl)-5-decene perchlorate, mp 52−53 °C, 84% from **33**. **54**, (*Z*)-5-(5-thianthreniumyl)-5-decene perchlorate, mp 66−68 °C, 82% from **35**. Anal. Calcd for $C_{22}H_{27}S_2ClO_4$ (**54**): C, 58.1; H, 5.98; S, 14.1; Cl, 8.39. Found: C, 58.3; H, 5.82; S, 13.8; Cl, 8.39. X-ray crystallography was performed as described.[2]

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Supporting Information Available: General experimental procedures, ^{1}H and ^{13}C NMR data for compounds **4**−**19**, **21**, **25**−**27**, **33**, **35**, **37**−**54**. Figures S1−S13 (Ortep diagrams) and tables giving X-ray crystallographic data for compounds **4**−**7**, **9**−**11**, **17**, **27**, **33**, **35**, **37**, and **38**. Structures **17** and **35** are of limited accuracy because of disorder problems caused by the perchlorate ions. This information is available free of charge via the Internet at http://pubs.acs.org.

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