Mono- and Bisadducts from the Addition of Thianthrene Cation Radical Salts to Cycloalkenes and Alkenes

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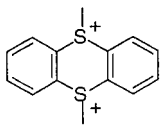
Thianthrene cation radical salts, $Th^{\bullet+}$ X^-(X^- = **a**, ClO_4^-; **b**, PF_6^-; **c**, SbF_6^-), add to cycloalkenes (C_5−C_8) in acetonitrile (MeCN) to form 1,2-bis(5-thianthreniumyl)cycloalkane salts and 1,2-(5,10-thianthreniumdiyl)cycloalkane salts, most of which have now been isolated and characterized. These are called bis- (**3**, **6**, **9**, **12**) and monoadducts (**4**, **7**, **10**, **13**). The proportional amount of the monoadduct obtained in the initial stage of the reaction varied with the cycloalkene in the order $C_6 \ll C_5 < C_7 \ll C_8$. Thus, the ratio bis:mono for C_5 and C_7 was, respectively, about 80/20 and 50/50. In contrast, only about 5% of the C_6 monoadduct (**7a**) and none of **7b**,**c** was obtained, while for C_8 none of the bisadducts **12a**−**c** was found. Bisadducts **3** and **9** lost thianthrene (Th) slowly in MeCN solution and changed into monoadducts **4** and **10**. A comparable change from **6a** into **7a** was not observed. The monoadducts, themselves, lost a proton slowly in dry MeCN and opened into 1-(5-thianthreniumyl)cycloalkenes (**5**, **8**, **11**, **14**). With **3** and **9**, particularly, it was possible to follow with NMR spectroscopy the succession of changes, for example, **3** to **4** to **5**. The opening of a monoadduct was made faster by adding a small amount of water to the solution. The bisadducts of 4-methylcyclohexene (**15a**) and 1,5-cyclooctadiene (**17a**) were isolated and characterized. Although a small amount of monodduct (**16a**) of 4-methylcyclohexene was found with NMR spectroscopy, it could not be isolated. Bis- and monoadducts were obtained also in additions of $Th^{\bullet+}$ ClO_4^- to acyclic alkenes, in relative amounts that, again, varied with the alkene. From *cis*-2-butene the dominant product was the bisadduct (**18**), while the monoaduct (**19**) was characterized with NMR spectroscopy but could not be isolated. In contrast, *trans*-3-hexene gave mainly the monoadduct (**21**), while the bis adduct (**20**) could not be isolated. With 4-methyl-*cis*-2-pentene, both bis- (**22**) and monoadduct (**23**) were isolated, the former being dominant. The conversion of **18** into **19** was characterized with NMR spectroscopy. In all cycloalkene bisadducts, the configurational relationship of the two thianthrenium groups was *trans*, while in the monoadducts, the bonds to the single thianthrene dication were (necessarily) *cis*. In both bis- and monoadducts of acyclic alkenes, the configuration of the alkene was retained. The mechanisms of addition with retention of configuration, of conversion of a bis- into a monoadduct, and of opening of a monoadduct are discussed. Products were identified with a combination of NMR spectroscopy, X-ray crystallography, elemental analysis, and (for cycloalkene adducts) reaction with thiophenoxide ion.

It was reported recently from these laboratories[1] that, contrary to earlier understanding,[2−4] thianthrene cation radical could form not only bis- but also monoadducts in its reactions with cycloalkenes. We showed that the aromatic portion of the ^1H NMR spectrum of a monoadduct was akin to that of a thianthrene dication (**1**), while in a bisadduct, each of the thianthrenium units, which may or may not be equivalent, had the character of a



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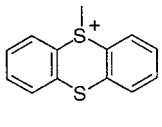

2

thianthrenium ion (**2**). At that time, we were not able to separate and isolate each pair of mono- and bisadducts of the C_5−C_8 cycloalkenes, except for the monoadducts of cyclooctene (**13a**−**d**), which are formed without accompaniment of bisadducts, and a bisadduct (**3c**) of cyclopentene. We were restricted to identifying the remaining members of the pairs of adducts from the NMR spectra of their mixtures. We return now to the adducts of the cycloalkenes, having been able to separate and study all pairs of the adducts to the C_5−C_7 cycloalkenes. Further, we have found that bis- and monoadducts can also be formed with acyclic alkenes, and we report here those of *cis*-2-butene (**18** and **19**), *trans*-3-hexene (**20** and **21**), and 4-methyl-*cis*-2-pentene (**22** and **23**), Scheme 2, their structures, and a proposed mechanism of their

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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.
(2) Shine, H. J.; Bandlish, B. K.; Mani, S. R.; Padilla, A. G. *J. Org. Chem.* **1979**, *44*, 915−917.
(3) Iwai, K.; Shine, H. J. *J. Org. Chem.* **1981**, *46*, 271−276.
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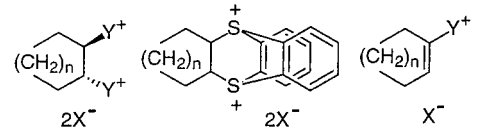
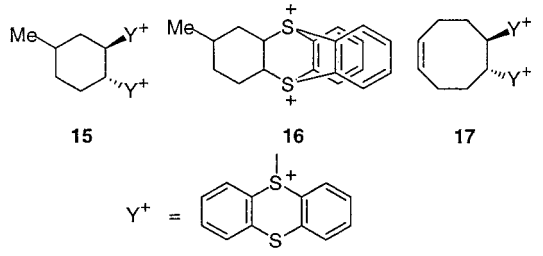
Scheme 1



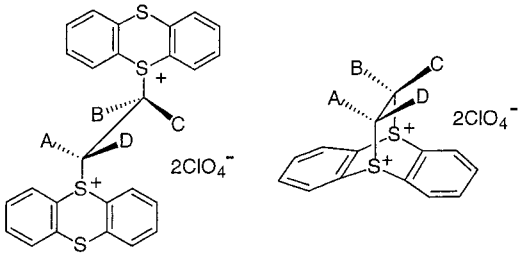
n	Compound		
1	**3**	**4**	**5**
2	**6**	**7**	**8**
3	**9**	**10**	**11**
4	**12**	**13**	**14**

X^- = **a**, ClO_4^-; **b**, PF_6^-; **c**, SbF_6^-; **d**, BF_4^-



15 **16** **17**

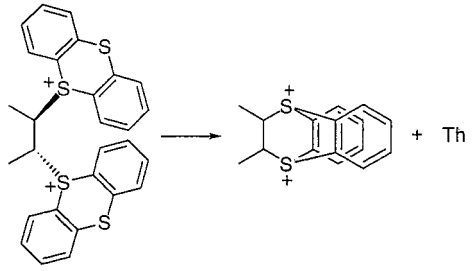
Scheme 2



18, 20, 22 **19, 21, 23**

	A	B	C	D
18, 19	Me	Me	H	H
20, 21	Et	H	Et	H
22, 23	Me	iPr	H	H

Scheme 3

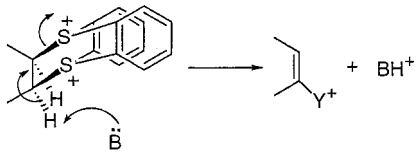


formation. We report, also, as shown in Scheme 3, that in acetonitrile (MeCN) solution, bisadducts **3**, **9**, **18**, **20** slowly lost thianthrene (Th) and became converted into monoadducts **4**, **10**, **19**, **21**. Even more slowly, the monoadducts **4**, **7**, **10**, **13** opened with the loss of a proton into the corresponding 1-(5-thianthreniumyl)cycloalkenes **5**, **8**, **11**, **14** (Scheme 4). Last, we report the reactions of some of the cyclic adducts with thiophenoxide ion, these reactions having a bearing on the structure of the adducts

Results and Discussion

Adducts and Their Structures. The adducts of cycloalkenes are listed in Scheme 1. They comprise (**3**−**14**) the bis- and monoadducts of the C_5−C_8 cycloalkenes, and the 1-(5-thianthreniumyl)cycloalkenes, the adducts (**15**, **16**) of 4-methylcyclohexene and (**17**) of 1,5-cyclooctadiene. Not all of the cycloalkenes gave a complete set of adducts. From cyclohexene, the only monoadduct that could be obtained was **7a**, and in only about 5% conversion as compared with 95% of the bisadduct **6a**. Monoadducts **7b**,**c** were not found. Although the bisadduct (**12**) of cyclooctene is listed, none could be found in any of the reactions of cyclooctene with thianthrenium salts. Between these extremes, the percentage ratio **3**:**4** of the cyclopentene adducts, obtained in preparative experiments, was about 80/20 for all salts (**a**−**c**), while for **9**:**10** from cycloheptene it was about 50/50. Having found now that in MeCN solution the bis adducts **3** and **9** slowly lost Th and were converted into monoadducts **4** and **10**, we felt that, possibly, a cyclooctene bisadduct (**12**) was being missed because of its rapid conversion into **13**. Therefore, reaction of $Th^{\bullet+}$ with cyclooctene was monitored with NMR spectroscopy as soon as it was instrumentally possible (15 min), but no sign of a bisadduct could be found. Further, reaction was carried out on a larger scale than was customary in order to search for a small amount of bisadduct in the product, but again, none could be found. In addition, in seeking information on the timing of formation of bis- and monoadducts, we examined the effect of time on the reaction of cycloheptene with $Th^{\bullet+}ClO_4^-$ and found the ratio bis:mono to be 70/30 after 5 and 70 min.

Scheme 4



A similar circumstance was found with the acyclic alkenes, whose adducts (**18**−**23**) are listed in Scheme 2. The major product from the addition of $Th^{\bullet+}ClO_4^-$ to *cis*-2-butene was the bisadduct (**18**). A small amount of monoadduct (**19**) was found in the NMR spectrum of the crude product, the percentage ratio **18**:**19** being about 95/5. In contrast, the major product from *trans*-3-hexene was the monoadduct (**21**) with a small amount of bisadduct (**20**), the NMR ratio **20**:**21** being about 5/95. Between these two extremes was the reaction with 4-methyl-*cis*-2-pentene, in which the bis:mono ratio was 75/25. Again, a search was made, this time with **20** and **21**, by monitoring the formation of adducts, to find if a bis- was being converted rapidly into the monoadduct. The NMR spectrum of the reaction mixture of $Th^{\bullet+}ClO_4^-$ with *trans*-3-hexene was recorded as soon as experimentally feasible (35 min) and while the presence of a small amount of $Th^{\bullet+}$ was inferred by its light pink color and by the broadening it caused in the NMR peaks of Th in the mixture. The relative amounts of mono- and bisadduct were measured from their methyl-group signals, and the ratio mono:bis remained the same (90/10) over a period of 3 h.

Thus, formation of bis- and monoadducts from both cyclic and acyclic alkenes appears to occur initially not successively but in parallel.

In all cycloalkene bisadducts the two thianthrenium groups are *trans* to each other. This relationship was deduced for **6a** from its chemical reactions some time ago[3]

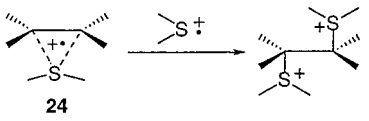
and was demonstrated with X-ray crystallography later by Wayner.[4] We have now characterized the bisadducts **9a**, **15a**, **17a**, **18**, and **22** with X-ray crystallography and the *trans*-relationship of their thianthrenium groups is evident in each of their Ortep diagrams (Figures F1, F3−5, and F7). The bisadduct **22** was reported earlier by Wayner, but a commitment on structure was not made.[4] Growth of single crystals of the other bisadducts reported here, suitable for X-ray crystallography, was unsuccessful.

Apart from X-ray crystallography, the NMR spectrum of each bisadduct was consistent with its structure. In **6a**, the two Th^+ groups are equivalent, and the aromatic ^1H NMR spectrum consequently consists of two dd (two sets of 4,6- and 1,9-protons) and two td (the two sets of 2,8- and 3,7-protons).[1,4] Equivalence of the two Th^+ groups was also found in **18** with ^1H and ^{13}C NMR data. In all the other bisadducts the two Th^+ groups were not magnetically equivalent. Thus, the spectrum of **9a** had four dd attributable to the 4,6-, 4',6'-, 1,9-, and 1',9'-protons, three td attributable (arbitrarily) to the 2,8-, 2',8'− and 3,7-protons, and one ddd attributable to the 3',7'-protons and indicating a lack of equivalence even within one Th^+ group.

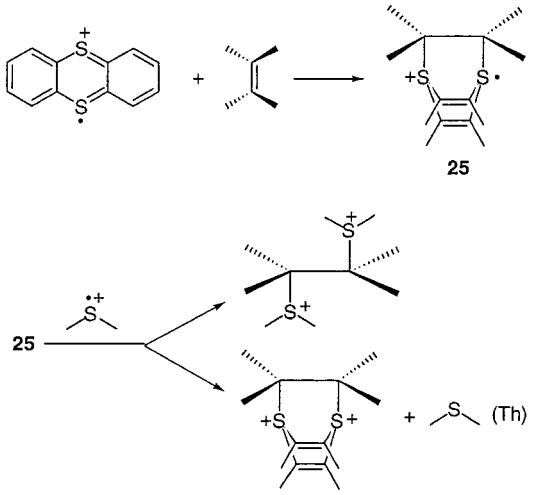
Most striking among structures of bisadducts are those of **18** and **22**. In each of these, the configuration of the alkene has been retained in the alkane. These bisadducts are *threo*-stereoisomers. This can be seen in the Ortep diagrams of **18** and **22** (Figures F5 and F7), in which the relationships of the staggered *threo* configuration are clearly seen. Insofar as **22** is concerned, its structure can be compared with those of *threo*-2,3-dibromo- and *threo*-2,3-dichloro-4-methylpentane, reported by Kingsbury and Best.[5] In the NMR spectrum of **22** the small coupling (1.75 Hz) between the C_2 and C_3 methine protons is diagnostic of a *threo*- rather than an *erythro*-isomer.[5] Thus, the bisadducts **18** and **22** have been formed in a *trans*-addition, without allowing for or entailing rotation about the erstwhile double bond. Addition was stereospecific. *Trans*-addition of the two Th^+ groups to the cycloalkenes is assumed to follow the same path.

Each of the newly isolated monoadducts from the cycloalkenes (**4b**, **7a**, **10a**) had the aromatic ^1H NMR spectrum of four sets of dd, as reported earlier for **13**.[1] Single-crystal X-ray crystallography was achievable with only one of the new cyclic monoadducts, **4b** (Figure F2). Among the monoadducts of the acyclic alkenes, only one (**21**), from *trans*-3-hexene, could be characterized with X-ray crystallography. The Ortep diagram (Figure F6) shows that the adduct has a *threo* structure in which the configuration of the *trans*-3-hexene is retained. Despite its apparent symmetry, **21** had a complex ^1H NMR spectrum, indicative of long-range,virtual coupling among alkyl H atoms.[6] The aromatic proton signals were not grouped in four separate dd, but were overlapped in two multiplets, each of 4H. Nevertheless, the ^{13}C spectrum of six aromatic and three alkyl signals was as predicted for the structure. That the alkene configuration was retained in the monoadduct **23** is deducible from its ^1H NMR spectrum. Coupling between the methine protons on atoms C_2 and C_3 was relatively large (7−8 Hz), a property attributable to an *erythro* configuration[5] and to *cis*-related protons as in comparable rigid structures,[7] particularly such as those in dibenzo[2.2.2]cyclooctadienes.[8] Monoadduct **19** could not be isolated. It was identifiable only from its aromatic ^1H (four sets of dd) and ^{13}C (six peaks) NMR spectra, which were clearly discernible in the NMR spectra of its mixture with bisadduct **18**. We assume, in analogy with adducts **21** and **23**, and guided by the retention of *cis*-2-butene's configuration in bisadduct **18** (Figure F5), that monoadduct **19** has an *erythro* structure, too, arising from retention of alkene configuration.

Scheme 5



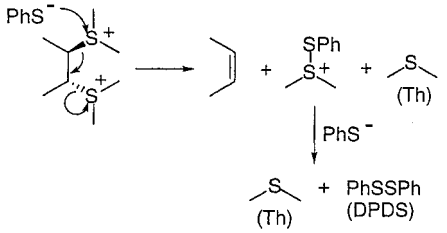
Scheme 6



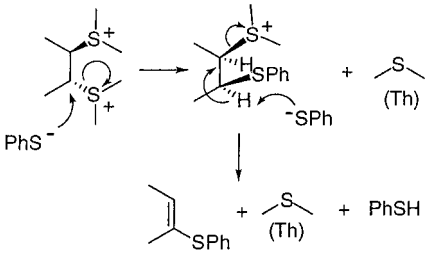
The pattern has emerged that both bis- and monoadducts are formed stereospecifically. Stereospecific *trans*-addition in bisadducts is readily interpretable if a thiirane-type radical ion intermediate (**24**) is formed and is opened by the attack of a second cation radical (Scheme 5). But, such an intermediate is not suited to stereospecific monoadduct formation, since, for that, front-side intramolecular attack on the thiirane ring by the remote sulfur atom would be needed. In a monoadduct, the two bonds from alkane carbon to thianthrenium sulfur are *cis*-related. Achieving that relationship stereospecifically from a thiirane-type intermediate would not be reasonable. Instead, we propose that monoadducts are formed in a concerted addition analogous to the [3 + 2] Diels−Alder cation-radical cycloadditions that have been characterized extensively by Bauld.[9] In monoadduct formation, however, cycloaddition is stoichiometric, not catalytic,[9] and the intermediate distonic, sulfuranyl cation radical adduct (**25**) serves not to propogate a chain but to reduce the second $Th^{\bullet+}$ (Scheme 6). In this proposal, the central ring of the cation radical, with high spin density on the

(5) Kingsbury, C. A.; Best, D. C.; *J. Org. Chem.* **1967**, *32*, 6−10.
(6) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed.; Wiley: New York, 1998; pp 179−183.
(7) Marchand, A, P. *Stereochemical Applications of NMR. Studies in Rigid and Bicyclic Systems. Methods of Stereochemical Analysis*; Verlag Chemie Intl.: Deerfield Beach, FL, 1982; Vol. 2, pp 143−144.
(8) Cristol, S. J.; Russell, T. W.; Mohrig, J. R.; Plorde, D. E. *J. Org. Chem.* **1966**, *31*, 581−584.
(9) (a) Bauld, N. L. In *Advances in Electron-Transfer Chemistry*; 1992; Vol. 2, pp 1−66. (b) Bauld, N. L. *Tetrahedron* **1989**, *45*, 5307−5363.

Scheme 7



Scheme 8

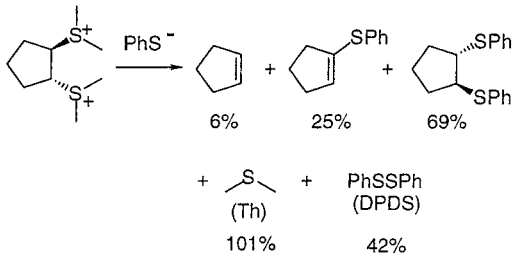


5,10-sulfur atoms,[10] serves as the diene-like cation radical in the cycloaddition.

The intermediate **25** could also serve as the source of stereospecific bisadduct formation. In that case, the competition between bis- and monoaddition amounts to bonding with or oxidizing **25** by the second $Th^{\bullet+}$ (Scheme 6). At this stage we do not know why bonding would be favored in one reaction (e.g., in cyclohexene's case) and oxidation in another (e.g., in cyclooctene's case). Nor do we know if *trans*-3-hexene favors monoaddition and the *cis*-alkenes favor bisaddition because of their geometric differences. It seems unlikely that differences in the oxidation potentials of the relevant distonic sulfuranyl cation radicals would be marked enough to control the pathways, suggesting that structural or conformational factors are in control. These perplexing questions await elucidation.

Isolation of all of the cycloalkene adducts (except **12**) allowed us to use an additional method of characterizing an adduct, namely, from the stoichiometry and products of its reaction with thiophenoxide ion, a technique we reported earlier.[1] This reaction was used with **3a**, **6a**, **9a**, **10a**, and **17a**. Reactions of **6a**, **9a**, and **17a** gave cyclohexene, cycloheptene, and 1,5-cyclooctadiene, respectively, along with Th and DPDS, according to the stoichiometry of the *trans*-elimination reaction shown in Scheme 7, in which thianthrene structures are shown in abbreviated form. Apart from this, the major route of reaction, a small amount of 1-(phenylthio)cycloalkene was formed from **6a** and **9a**, as is proposed in Scheme 8. Reaction of **10a** with thiophenoxide ion gave cycloheptene, 1-(phenylthio)cycloheptene, Th, and DPDS, analogously. A striking exception to the dominant pathway of Scheme 7 was in the reaction of **3a**, Scheme 9. We reported that reaction earlier, but were not then able to distinguish between 1- and 3-(phenylthio)cyclopentene as one of the products. That has now been settled. Thus, the dominant reaction (94%) of **3a** is substitution of Th^+ by PhS^-. The thiophilicity of PhS^-, which led to elimination with the other adducts, is suppressed or inhibited in **3a**, suggesting that access by PhS^- to the sulfonium sulfur atoms of the Th^+ groups in **3a** is sterically

Scheme 9



compromised. The reactions of all of these adducts with thiophenoxide ion are interpretable on the basis of the proposed structures of the adducts.

Ring-Opening in Monoadducts. When kept in MeCN solution, each of the monoadducts **4**, **7**, **10**, and **13** lost a proton and opened into a 1-(5-thianthreniumyl) cycloalkene (**5**, **8**, **11**, and **14**). These changes were slower (**4**, **10**, **13)** than those of the corresponding bis- into monoadducts, but we have not made quantitative comparisons among the four monoadducts. The conversion of **10b** into **11b**, for example, was followed with NMR spectroscopy, and 50 days elapsed before the spectrum of **10b** was no longer visible. In this and other monoadduct conversions, a small amount of Th was formed, indicative of an elimination reaction with, in the case of **10b**, formation of 1,3-cycloheptadiene, but that reaction was not explored. We found that deprotonation of a monoadduct was faster in wet than in dry MeCN. Some of the reactions were followed with NMR spectroscopy in CD_3CN containing D_2O. For example, whereas none of **11c** but a small amount of Th was formed from **10c** in CD_3CN in 3 days, addition of two drops of D_2O led to 35% of **11c** in the same period. Addition of a further 0.1 mL of D_2O caused complete loss of **10c** in 11 days. Analogously, **7a** in dry CD_3CN was converted completely into **8a** and Th in the ratio 35/65 in 13 days. A similar solution containing 0.1 mL of D_2O led completely in 18 h to **8a** and Th in the ratio 80/20 and allowed for the isolation and X-ray characterization of **8a** (Figure F8). In this reaction a small amount of 1,3-cyclohexadiene was found by GC but was not measured. These and similar experiences with **4a** and **13a** indicate that water served as a base (B in Scheme 4). A study of the comparative ease of deprotonation of the four monoadducts was not made nor was **21** studied in this way.

Conversion of Bis- into Monoadducts. When left in MeCN solution, all bisadducts slowly changed into the corresponding monoadducts, except for **6** whose conversion into **7** was too slow to follow. The conversion was studied mostly of **9** into **10**, because both **9** and **10** were readily isolable and characterizable, the conversion could be followed daily, and the further conversion of **10** into **11** was too slow to interfere. In contrast, for example, although the conversion of the cyclopentene adducts, **3** into **4**, could be followed with NMR spectroscopy, the spectra became complicated eventually by the concomitant conversion of **4** into **5**.

Conversion of the bisadduct (**18**) of *cis*-2-butene into **19** was very slow but was followed with NMR spectroscopy.

The conversion of **9** into **10** occurred cleanly in CD_3CN solutions that were shielded from light. When such solutions were exposed to daylight or fluorescent light, the thianthrene cation radical was formed in low

(10) Shine, H. J. In *The Chemistry of the Sulfonium Group*; Stirling, C. J. M.; Patai, S., Eds.; Wiley: New York, 1981; pp 523−569.

concentration, as was shown with absorption and esr spectroscopy. Nevertheless, conversion could be followed with NMR spectroscopy. Our discussion, then, is of shielded solutions first and of unshielded solutions next.

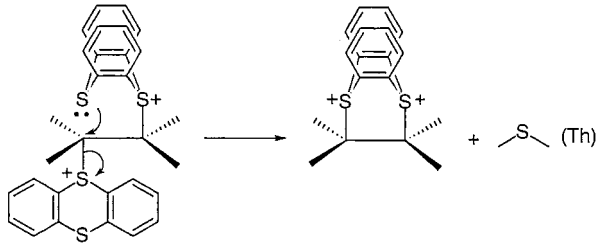
Both **9a** and **9c** were used in NMR tubes shielded with foil except when in the NMR probe. The relative amounts of **9** and **10** were measured from the integrations of their aromatic proton signals and also their methine proton signals daily over a period of 6 to10 days. At all times, the integration of the most downfield 4H dd of **10** was equal to those of the two sets of 4H dd of Th, showing that conversion was stoichiometrically correct. Rates of conversion were calculated from the initial concentration of **9** and the concentrations obtained from the ratios **9**:**10** at timed intervals. Reasonably good first-order rate plots were obtained. The rate of conversion of **9c** ($k = 9.6 \pm 0.5 \times 10^{-3}$ h^{-1}) was not affected by the presence of added Th ($k = 9.3 \pm 0.4 \times 10^{-3}$ h^{-1}). That is, conversion was irreversible. Irreversibility was confirmed with the unchanging NMR spectrum of a solution of **10a** containing added Th; no sign of **9a** was found over a period of 6 d, when the experiment was stopped. The lack of effect of Th on the formation of **9** and **10** was confirmed also by measuring the ratio **9a**:**10a** in the addition of $Th^{\bullet+}ClO_4^-$ to cycloheptene in the absence and presence of added Th. That is, the ratio **9a**:**10a** was measured in their mixture that was precipitated as soon as addition was complete and was found to be unaffected by having added Th to the solution. The results of the several approaches show that in shielded solutions **9** is converted cleanly and irreversibly into **10**. Solutions remained colorless throughout the conversion and, in this way, failed to show the presence of $Th^{\bullet+}$.

The effect of light on solutions of **9** was investigated with a solution of **9c** comparable to those that had been shielded from light. The solution was kept under laboratory daylight and fluorescent light and soon became light pink in color. The color intensified during exposure and diminished during darkness. NMR measurements of the amounts of **9c** and **10c** were made in the usual way, but the signals from Th were broad and shallow. The rate of conversion was a little faster ($k = 11.5 \pm 0.18 \times 10^{-3}$ h^{-1}) than in the shielded solution. Gradually, small NMR signals from ThO were detected overlapping the upfield aromatic signals from **9c**. Thus, $Th^{\bullet+}$ was formed in the presence of light and was hydrolyzed to ThO (and Th) by the water remaining in the solvent. The formation of $Th^{\bullet+}$ under laboratory illumination was confirmed in separate experiments with absorption and esr spectroscopy. Absorbances of the bands characteristic of $Th^{\bullet+}$ at 539, 915, and 1032 nm showed that the concentrations of $Th^{\bullet+}$ amounted to 1−3% of the initial amount of **9c**. The esr spectrum was identical with that of $Th^{\bullet+}PF_6^-$. $Th^{\bullet+}$ was not found in a solution of **10a** or of Th that was exposed to light.

The effect of $Th^{\bullet+}$ on the conversion was also investigated with the addition of $Th^{\bullet+}ClO_4^-$ (0.0085 mmol) to a solution of **9a** (0.0106 mmol). The rate of conversion ($8.2 \pm 0.67 \times 10^{-3}$ h^{-1}), was unchanged from that ($8.0 \pm 0.3 \times 10^{-3}$ h^{-1}) in the absence of added $Th^{\bullet+}ClO_4^-$. The spectrum of Th that was formed, however, was again broadened by exchange with $Th^{\bullet+}$, and the gradual formation of ThO was pronounced.

Bisadduct **18** also lost Th and changed into **19** cleanly in the dark. We used **18** because in principle it could give two monoadducts if a dissociative pathway of conversion was involved that allowed for rotation of the alkyl chain. However, only one monoadduct (**19**) was found in the changing NMR spectrum. The conversion of **18** into **19** was slower ($k = 2.6 \pm 0.14 \times 10^{-3}$ h^{-1}) than that of **9** into **10**. When exposed to light, a solution of **18** behaved analogously to one of **9**, but the rate of conversion into **19** ($k = 2.6 \pm 0.14 \times 10^{-3}$ h^{-1}) was unaffected by illumination. Small peaks of a new multiplet at 5.45 ppm and doublet at 1.57 ppm had appeared, too. These changes were not followed further.

Scheme 10



Our overall view of these conversions is that the effect of light encountered here is coincidental to the conversion and does not affect it substantially. It is noteworthy, however, that the bis- and monoadducts are colorless and the light-induced formation of $Th^{\bullet+}$ occurred in Pyrex vessels. **9a**, for example, has absorption bands at 237 and 310 nm, with extinction coefficients 41000 and 7400; there is no measurable absorption above 360 nm. Further study is planned. The shielded conversion itself appears to be intramolecular and the result of displacement of one Th^+ group by the distant S atom of the other (Scheme 10). In **9** and other cycloalkane adducts, rotation about the pertinent cycloalkane C−C bond during conversion is not possible. In the acyclic adduct (**18**), where in principle rotation and a change in configuration could occur, it does not, attesting to the concerted nature of the displacement.

Experimental Section

Solvent acetonitrile (MeCN) was dried by distillation from P_2O_5 followed by distillation from CaH_2. Alkenes, cycloalkenes, and cycloalkanones were from commercial sources. Two GC columns were used: Column A, 10% OV-101 on 80−100 mesh Chrom-WHP, 4 ft x 1/8 in stainless steel (ss), and column B, 20% BEEA on 60−80 mesh Chrom-PAW, 8 ft x 1/8 in ss. Thianthrene cation radical salts ($Th^{\bullet+}ClO_4^-$, $Th^{\bullet+}PF_6^-$, and $Th^{\bullet+}SbF_6^-$) were prepared as described earlier.[1] The *potential explosiveness* of $Th^{\bullet+}ClO_4^-$ should be noted.[11] NMR spectra list δ (J) in ppm and Hz. Elemental analyses were by Desert Analytics, Tucson, AZ. Mass spectra were provided by Dr. Terry Marriott, Rice University.

Preparation and Separation of Bis- and Monoadducts. A detailed example is given with **1,2-bis(5-thianthrenium-yl)cycloheptane diperchlorate** (**9a**) and **1,2-(5,10-thianthreniumdiyl)cycloheptane diperchlorate** (**10a**). A solution of 1.78 g (18.5 mmol) of cycloheptene in 2 mL of MeCN was added dropwise to a stirred suspension of 1.00 g (3.17 mmol) of $Th^{\bullet+}ClO_4^-$ in 8 mL of MeCN at room temperature. The purple color of the solution faded to pink, and a white precipitate formed after the addition of the cycloalkene was finished. The mixture was stirred overnight (20 h), after which the solution was slightly yellow and the precipitate slightly pink. Dried ether was added and produced more precipitate, which was filtered, washed with ether, and dried under vacuum to give 870 mg of product. The aromatic portion of the ^1H NMR spectrum showed that the product was a mixture of

(11) Shine, H. J.; Yeuh, W. *J. Org. Chem.* **1994**, *59*, 3553−3359.

bis- and monoadducts of $Th^{\bullet+}ClO_4^-$ to cycloheptene and the ratio of the adducts, from the integrated low-field and high-field signals,[1] was, for **9a**:**10a**, 60/40. These data showed that the total yield of adducts was 86%, namely 50% of **9a** and 36% of **10a**. The product was dissolved in 20 mL of MeCN. Ether was added dropwise until the solution became turbid. After several minutes, a mixture of needlelike and denser, powdery crystals deposited. Addition of ether to the clear supernatant solution, causing further precipitation, was continued until precipitation stopped. The mixture was swirled, allowing for the decantation and filtration of the lighter, needlelike crystals, which were washed with ether and dried to give 350 mg of solid, A. The remaining solids, a mixture of powdery and needlelike crystals was filtered and treated similarly to give 390 mg of solid, B. The filtrate was concentrated to give a precipitate, which was dissolved in a small amount of MeCN to which ether was added, giving 60 mg of solid, C. Again, the filtrate was concentrated and gave 80 mg of thianthrene (Th). Each of the solids, A, B, and C was again subjected to fractional precipitation, and each time the precipitates of needlelike and powdery crystals were combined, separately. Finally, 301 mg of needles (solid D) and 212 mg of powdery solid (E) were obtained. ^{1}H NMR spectroscopy showed that D was a mixture of **9a** and **10a** in the ratio 5/95, that is, mainly the monoadduct, and that E was a mixture of **9a** and **10a** in the ratio 95/5, that is mainly the bisadduct. These products were again recrystallized from MeCN/ether to give 206 mg of pure **9a**, mp 142.5−143 °C dec, from E, and 257 mg of pure **10a**, mp 146−146.2 °C dec, from D. It is notable that, although the initial mixture of **9a** and **10a** contained more of **9a**, the amount of **9a** decreased and the amount of **10a** increased during the numerous fractional precipitations. In fact, when all of the powdery fractions and all of the needlelike fractions were combined, the pure, powdery **9a** amounted to 206 mg and the impure, needlelike **10a** amounted to 480 mg. The reason for this change in relative amounts of **9a** and **10a** is, as is shown later, the slow conversion of **9a** into **10a** and Th, accounting also for the Th that began showing up in the reprecipitations. Single crystals of **9a** and **10a** were grown for X-ray crystallography. An Ortep diagram for **9a** was obtained and is reported here (Figure F1), but the crystals of **10a** were too slender to diffract. ^{1}H NMR, CD_3CN, 500 MHz: (**9a**): 8.125 (8.0, 1.0, 1.0), dd, 2H; 8.112 (7.5, 1.0, 1.0), dd, 2H; 7.924 (8.0, 7.5, 1.0, 1.5, 1.0), td, 2H; 7.894 (8.0, 1.0, 1.0), dd, 2H; 7.850 (7.5, 8.0, 1.0, 1.5, 1.5), td, 2H; 7.810 (8.0, 8.0, 1.5, 1.0, 1.5), td, 2H; 7.723 (7.5, 8.0, 1.5, 1.5, 8.0, 1.0, 1.0), overlapping ddd, 2H; 7.661 (8.0, 1.0, 1.0), dd, 2H; 4.78, m, 2H; 2.173, m (overlap with solvent water); 1.986, m, 2H; 1.848, m, 4H; 1.630 (6.5, 8.0), t, 1H; 1.600 (8.0, 7.5), t, 1H. (**10a**): 8.618 (6.0, 3.5, 3.5), dd, 2H; 8.554 (6.0, 3.5, 3.5), dd, 2H; 8.208 (5.5, 3.5, 3.0), dd, 2H; 8.144 (5.5, 3.0, 3.5), dd, 2H; 4.692 (8.0, 2.5, 2.5), dd, 2H; 2.595, m, 2H; 2.042, m, 2H; 1.672, m, 1H; 1.325, m, 4H; 1.134, m, 1H. Anal. Calcd for $C_{19}H_{20}S_2Cl_2O_8$ (**9a**): C, 44.6; H, 3.94; S, 12.5; Cl, 13.9. Found: C, 44.3; H, 3.64; S, 12.3; Cl, 14.1.

Similar reactions of cycloheptene with $Th^{\bullet+}PF_6^-$ and $Th^{\bullet+}SbF_6^-$ were carried out, the objective being to obtain single crystals of monoadduct that, with larger anions, might diffract successfully. In this way, we obtained 430 mg of a mixture of PF_6^- salts **9b** and **10b** in the ration 65/35. These data represent a total yield of products of 83%, amounting to 53% of **9b** and 30% of **10b**. Fractional precipitation and crystallization gave **9b** free of **10b** (by NMR), mp 155.2−156.5 °C dec, and **10b** free of **9b**, mp 159.5−161 °C dec. Use of $Th^{\bullet+}SbF_6^-$ gave 590 mg of a mixture of **9c** and **10c** in the ratio 50/50, representing a total yield of 80%. Separation gave **9c**, mp 182−183.5 °C dec, and **10c**, mp 195−195.5 °C dec. Each of these four products had a satisfacory ^{1}H NMR spectrum, similar to those reported for **9a** and **10a**. Unfortunately, single crystals of **10b** and **10c** suitable for X-ray crystallography could not be obtained.

1,2-Bis(5-thianthreniumyl)cyclopentane Diperchlorate (3a) and 1,2-(5,10-Thianthreniumdiyl)cyclopentane Diperchlorate (4a). The reactants were 4.0 mL (45 mmol) of cyclopentene and 1.48 g (4.69 mmol) of $Th^{\bullet+}ClO_4^-$ in 20 mL of MeCN. Workup gave 1.26 g of a mixture of **3a** and **4a** in the ratio 90/10. This represents 79% recovery of $Th^{\bullet+}ClO_4^-$, with 71% as **3a** and 8% as **4a**. Separation and recrystallization gave **3a**, mp 165−167 °C dec, and **4a**, mp 177−178 °C dec. ^{1}H NMR, CD_3CN, 500 MHz (**3a**): 8.110 (8.0, 0.5, 0.5), dd, 4H; 7.919 (8.25, 1.5, 1.0), dd, 2H; 7.863 (7.25, 8.0, 1.0, 1.5, 1.5), td, 2H; 7.842 (7.5, 8.0, 1.5, 1.5, 1.5), td, 2H; 7.777 (7.75, 7.75, 1.0, 1.5, 1.0), td, 2H; 7.725 (7.75, 7.75, 1.5, 1.0, 1.5), td, 2H; 7.576 (8.0, 1.0, 1.0), dd, 2H; 4.879 (7.5, 2.5, 2.5), dd, 2H; 2.357 (7.7 ave), sext, 2H; 2.219 (7.13 ave), quint, 2H; 1.91, m (overlapping solvent). (**4a**): 8.622 (6.0, 3.5, 3.5), dd, 2H; 8.527 (5.5, 3.5, 3.5), dd, 2H; 8.200 (6.0, 3.5, 3.0), dd, 2H; 8.104 (6.0, 3.0, 3.5), dd, 2H; 4.873, m, 2H; 2.52−2.46, m, 2H; 1.78−1.69, m, 1H; 1.57−1.49, m, 2H; 1.43−1.36, m, 1H. Anal. Calcd for $C_{17}H_{16}S_2Cl_2O_8.CH_3CN$ (**4a**): C, 43.5; H, 3.65; S, 12.2; Cl, 13.5. Found: C, 43.0; H, 3.46; S, 12.4; Cl, 13.9. Single crystals of **4a** failed to diffract well.

Reaction of cyclopentene (8.0 mL, 91 mmol) with $Th^{\bullet+}PF_6^-$ (700 mg, 1.94 mmol) gave 650 mg of a mixture of **3b** and **4b** in the ratio 85/15, representing 82% recovery of $Th^{\bullet+}PF_6^-$ with 75% as **3b** and 7% as **4b**. Workup gave **3b**, mp 168.2−169 °C dec, and **4b**, mp 176−177.5 °C dec, each having an acceptable ^{1}H NMR spectrum. A single crystal of **4b** diffracted successfully to give the Ortep diagram of Figure F2.

Reaction of cyclopentene (1.5 mL, 17 mmol) with $Th^{\bullet+}SbF_6^-$ (540 mg, 1.19 mmol) in 8 mL of MeCN gave 480 mg of a mixture of **3c** and **4c** in the ratio 90/10, representing 81% recovery of $Th^{\bullet+}SbF_6^-$ with 77% as **3c** and 4% as **4c**. Workup gave **3c**, mp 213.5−214.5 °C dec and **4c**, mp 211−212 °C dec. The ^{1}H NMR spectra were similar to those of **3a** and **4a**. The crystal structure of **3c** was reported earlier.[1] Anal. Calcd for $C_{17}H_{16}S_2Sb_2F_{12}.CH_3CN$ (**4c**): C, 28.6; H, 2.40; S, 8.05; F, 28.6. Found: C, 28.2; H, 2.37; S, 7.70; F, 27.8.

1,2-Bis(5-thianthreniumyl)cyclohexane Diperchlorate (6a) and 1,2-(5,10-thianthreniumdiyl)cyclohexane Diperchlorate (7a). A solution of 1.80 mL (17.8 mmol) of cyclohexene in 1.0 mL of MeCN and a suspension of 680 mg (2.15 mmol) of $Th^{\bullet+}ClO_4^-$ were used. After 4 h of stirring, 560 mg of precipitate was obtained and found with NMR spectroscopy to be solely **6a**. Addition of ether to the filtrate gave 150 mg of a mixture of **6a** and **7a**, which was separated with fractional precipitations and crystallization into 117 mg of **6a**, mp 149−149.2 °C dec, and 31 mg of **7a**, mp 127−128 °C dec. The ^{1}H NMR spectrum of **6a** agreed with that of an earlier report.[4] Single crystals of **7a** were too slender for successful X-ray diffraction. ^{1}H NMR, CD_3CN, 200 MHz (**7a**): 8.613 (5.81, 3.31, 3.40), dd, 2H; 8.526 (5.85, 3.47, 3.47), dd, 2H; 8.200 (5.77, 3.31, 3.43), dd, 2H; 8.145 (5.86, 3.26, 3.22), dd, 2H; 4.582, m, 2H; 2.310, br d, 2H; 1.768−1.665, m, 2H; 1.553, m, 2H; 1.319, m, 2H.

Reaction of cyclohexene with $Th^{\bullet+}PF_6^-$ gave only the bisadduct (**6b**), 90%, mp 144.5−145.5 °C dec. None of **7b** could be found. Similarly, reaction with $Th^{\bullet+}SbF_6^-$ gave only **6c**, 43%, mp 176.2−177 °C dec, and none of **7c**. Each of **6b** and **6c** had a satisfactory ^{1}H NMR spectrum.

1,2-Bis(5-thianthreniumyl)-4-methylcyclohexane Diperchlorate (15a). 4-Methylcyclohexene (1.0 mL, 8.3 mmol) and 390 mg (1.24 mmol) of $Th^{\bullet+}ClO_4^-$ were used in 5 mL of MeCN. Addition of ether after 5 h gave a yellow oil which solidified on rubbing, to give 450 mg of product. ^{1}H NMR spectroscopy showed the presence of **15a** and **16a** in the ratio 95/5, representing a recovery of 99% of $Th^{\bullet+}ClO_4^-$, with 95% as **15a** and 4% as **16a**. Attempts to separate and recover **16a** failed; only **15a** could be obtained, mp 112−113 °C dec. Growth of a single crystal for X-ray crystallography was successful (Figure F3). ^{1}H NMR, CD_3CN, 500 MHz (**15a**): 8.118−7.705, m, 16H; 4.284, br m, 2H; 2.323, m, 1H; 2.064−2.003, m, 1H; 1.996−1.948, m, 1H; 1.873, br d, 1H; 1.581−1.457, m, 2H; 1.317, m, 1H; 1.003 (6.5), d, 3H.

5,6-Bis(5-thianthreniumyl)cyclooctene Diperchlorate (17a). A solution of 2.72 g (25.1 mmol) of 1,5-cyclooctadiene in 8 mL of MeCN was added dropwise to a suspension of 910 mg (2.88 mmol) of $Th^{\bullet+}ClO_4^-$ in 10 mL of MeCN. After 20 min of stirring the yellow solution began depositing a white precipitate. Ether (80 mL) was added after 4.5 h of stirring. The solid was filtered, washed, and dried to give 930 mg (1.26

mmol, 88%) of **17a**. A monoadduct was not obtained. Crystallization from MeCN/ether gave mp 115−116 °C dec. Single-crystal growing was successful (Figure F4). ^{1}H NMR, CD_3CN, 500 MHz (**17a**): 8.096 (8.0, 1.0, 1.0), dd, 2H; 8.043−8.022, br dd, 2H; 7.933 (7.75, 7.75, 1.5, 1.0, 1.5), td, 2H; 7.881 (8.0, 1.25, 1.5, 0.5), ddd, 2H; 7.851 (7.0, 8.25, 1.0, 1.0, 1.0), td, 2H; 7.786 (7.5, 8.8, 1.0, 1.0, 1.0), td, 2H; overlapping dd, 7.748 (7.75, 2.0, 1.5), dd, 1H; 7.734 (8.0, 2.0, 2.0), dd, 1H; 7.685 (8.0, 1.0, 1.0), dd, 2H; 5.973 (4.0, 4.0), br t, 2H; 4.442 (5.75, 6.0), br t, 2H; 2.840 (15.5, 15.0), br t, 2H; 2.518−2.456 (4.0), two br q, 2H; 2.173−2.107, br m, overlapping solvent; 2.089−2.039, m, 2H.

***threo*-2,3-Bis(5-thianthreniumyl)butane Diperchlorate (18) and *erythro*-2,3-(5,10-Thianthreniumdiyl)butane Diperchlorate (19).** A stream of *cis*-2-butene was bubbled into a suspension of 480 mg (1.52 mmol) of $Th^{\bullet+}ClO_4^-$ in 8 mL of MeCN cooled in an ice bath until the color of $Th^{\bullet+}$ had faded to light pink, about 30 min. A white precipitate had formed. After addition of 60 mL of dry ether the precipitate was recovered, giving 420 mg of a mixture of **18** and **19** in the ratio (NMR) 95/5. This ratio corresponds with 0.59 mmol (78% of $Th^{\bullet+}$ units) of **18** and 0.031 mmol (2.0% of $Th^{\bullet+}$ units) of **19**. GC assay of the filtrate gave 0.357 mmol of Th, an amount which is larger than equatable to the yield of **19** and most of which is attributable to the GC decomposition of **18** and **19** remaining in solution. Pure **18** was obtained by successive precipitations from MeCN with ether and crystallization from MeCN/ether, mp 169.5−170 °C dec. Growth of a single crystal for X-ray crystallography was successful (Figure F5). Separation of pure **19** was not successful. Adduct **18** changed slowly into **19** in MeCN solution.

An NMR spectrum of the mixture of **18** and **19** had clearly separated spectra of the two adducts although the alkyl signals from **19** were not strong enough to be integratable. ^{1}H NMR, CD_3CN, 500 MHz (**18**): 8.102 (8.0, 0.5), dd, 2H; 8.042 (8.0, 1.0), dd, 2H; 7.921 (7.8 ave, 1.5), td, 2H; 7.870, m of overlapping dd and td, 4H; 7.765 (7.75, 1.3 ave), td, 2H; 7.738 (8.0, 2.0), dd, 2H; 7.725 (8.0, 2.0), dd, 2H; 4.349 (6.8 ave), q, 2H; 1.396 (7.0), d, 6H. ^{13}C NMR (**18**): 136.987, 136.675, 136.632, 136.442, 136.324, 135.984, 131.901, 131.616, 131.518, 131.146, 115.361, 115.728, 47.399, 11.509. ^{1}H NMR, CD_3CN, 500 MHz (**19**): 8.612 (5.5, 3.5), dd; 8.525 (6.0, 3.5), dd; 8.194 (6.0, 3.5), dd; 8.126 (5.75, 2.75), dd; 4.734, m; 1.453 (7.0), d. ^{13}C NMR (**19**): 137.975, 137.844, 137.165, 136.490, 126.474, 123.347, 53.983, 14.267.

***erythro*-3,4-Bis(5-thianthreniumyl)hexane Diperchlorate (20) and *threo*-3,4-(5,10-Thianthreniumdiyl)hexane Diperchlorate (21). (A)** To a suspension of 740 mg (2.34 mmol) of $Th^{\bullet+}ClO_4^-$ in 8 mL of MeCN was added 2.0 mL (12 mmol) of *trans*-3-hexene. The color of the solution was purple after 1 h, but after 6 h of stirring the now colorless solution had deposited a white precipitate. More precipitation occurred on adding 50 mL of ether. Workup gave 360 mg (0.72 mmol, 31% of $Th^{\bullet+}$ units) of **21**. A bisadduct (**20**) was not detectable with NMR spectroscopy. Single-crystal growth for X-ray crystallography was successful (Figure F6), mp 153−154 °C (expl).

(B) A similar experiment was carried out with 311 mg (0.984 mmol) of $Th^{\bullet+}ClO_4^-$ and had faded to light pink and a white precipitate had formed. Workup after addition of 30 mL of ether gave 168 mg of a mixture of **20** and **21** in the ratio averaging 7/93 from integrations of aromatic and alkane protons. This represents stoichiometric conversions of $Th^{\bullet+}ClO_4^-$ into 5% of **20** and 67% of **21**. Assay of the filtrate gave 0.60 mmol of Th, an excessive amount arising from decomposition in the GC of adducts remaining in solution. Decomposition to give Th on injection into the GC inlet was confirmed independently. Successive precipitations of the mixture of adducts gave 133 mg (0.266 mmol) of **21**, mp 160−160.5 °C (expl) and 14.4 mg of a mixture containing 0.011 mmol of **20** and 0.013 mmol of **21**. We were unable to prepare a pure sample of **20**, which changed slowly into **21** in solution.

(C) This experiment was carried out in an NMR tube shielded from light with foil except for brief periods when in the probe. The *trans*-3-hexene was added to a suspension of $Th^{\bullet+}ClO_4^-$ in CD_3CN. It was necessary to wait for 35 min before an NMR spectrum could be obtained. At that time the color of the solution was pink and the NMR signals of Th were broadened. The relative amounts of **20** and **21** were obtained by integrating the methyl-group triplets and was 10/90. After 95 min the solution was colorless, the signals from Th were in their proper field, signals from ThO were observable, and the dominant signals were from **21**. Integration of methyl-group triplets gave a ratio **20**:**21** of 10/90. After 3 h, the NMR spectrum was essentially the same and integration of the methyl-group triplets gave a ratio 5/95. After the lapse of 1 day, the signals from **20** were no longer visible.

^{1}H NMR, CD_3CN, 500 MHz (**21**): Despite the apparent symmetry of **21** the NMR spectrum was complex and indicative of long-range, virtual couplings.[6] 8.629−8.599, m, 4H; 8.181−8.153, m, 4H; 4.114, m with 11 lines visible suggestive of dtd (7.5, 5.25, 3.5), 2H; 2.0−1.96, m overlapping solvent, 2H; 1.62−1.53, m with 12 lines visible suggestive of ddq (16.0, 7.0, 7.0), 2H; 1.200 (7.25), t, 6H. ^{13}C NMR (**21**): 137.598, 137.547, 137.531, 137.243, 125.735, 122.457, 62.488, 26.747, 11.476.

It was not possible to obtain a complete NMR spectrum of **20**.

***threo*-2,3-Bis(5-thianthreniumyl)-4-methylpentane Diperchlorate (22) and *erythro*-2,3-(5,10-Thianthreniumdiyl)-4-methylpentane Diperchlorate (23).** To a stirred suspension of 500 mg (1.58 mmol) of $Th^{\bullet+}ClO_4^-$ in 8 mL of MeCN was added dropwise 1.5 mL (12 mmol) of 4-methyl-*cis*-2-pentene. The solution was pale yellow after 30 min and had no precipitated solid. Addition of 60 mL of ether caused precipitation of white solid which was recovered to give 410 mg of a mixture of **22** and **23** in the ratio 80/20. This represents 0.488 mmol (62% of initial $Th^{\bullet+}$ units) of **22** and 0.122 mmol (7.7% of $Th^{\bullet+}$ units) of **23**. GC analysis of the filtrate gave 0.39 mmol (25% of $Th^{\bullet+}$ units) of Th. The data account for 95% of $Th^{\bullet+}ClO_4^-$. Separation of the adducts by precipitations and crystallization gave 340 mg (0.476 mmol) of **22**, mp 118−119 °C dec, and 44 mg (0.088 mmol) of **23**, mp 95−97 °C dec. An Ortep diagram of **22** (Figure F7) was obtained. ^{1}H NMR, CD_3CN, 500 MHz (**22**): 8.205 (8.5), d, 1H; 8.105 (7.75), d, 1H; 8.057−7.964, m, 4H; 7.865−7.776, m, 8H; 7.750−7.716, m, 2H; 4.489 (1.75 ave), t, 1H; 4.262 (7.1 ave, 1.75 ave), qd, 1H; 2.696 (7.0), hept, 1H; 1.465 (7.0), d, 3H; 1.441 (7.0), d, 3H; 0.642 (7.0), d, 3H. ^{13}C NMR (**22**): 28 of possible 30 peaks were obtained: 138.065, 137.315, 137.090, 136.865, 136.770, 136.742, 136.703, 136.612, 136.300, 136.241, 136.142, 132.402, 132.300, 132.264, 132.161, 132.051, 131.672, 131.648, 131.206, 116.068, 115.563, 115.346, 55.191, 48.730, 28.783, 21.962, 19.636, 12.618. The larger intensities of peaks at 136.612 and 115.346 ppm suggested that each represented two C atoms with the same chemical shift.

Kingsbury and Best[5] have reported that the coupling (3.5-3.7 Hz) between protons on carbon atoms C_2 and C_3 in *threo* isomers of 2,3-dibromo- and 2,3-dichloro-4-methylpentane is smaller than that (10.6 Hz) in the *erythro* isomers. In analogy, the small coupling (1.75 Hz) of the corresponding atoms in **22** is suited to a *threo* isomer. ^{1}H NMR, CD_3CN, 500 MHz (**23**): 8.679−8.660, m, 1H; 8.612−8.594, m, 1H; 8.577−8.543, m, 2H; 8.188−8.169, m, 2H; 8.131−8.109, m 2H; 5.058 (7.4 ave), quint, 1H; 4.302 (8.0), t, 1H; 2.28−2.21, m overlapping solvent; 1.415 (7.5), d, 3H; 1.303 (6.5), d, 3H; 1.185 (6.5), d, 3H. The quintet at 5.058 ppm and the triplet at 4.302 ppm are attributable to the protons on C_2 and C_3, and their large coupling constants are suited to *cis*-related, *erythro* protons.[5,7,8]

Monoadduct **23** was sufficiently unstable in MeCN as to interfere with long-time acquisition of ^{13}C NMR data.

Conversions of Bis- (9 and 18) into Monoadducts (10 and 19). Experiments were carried out mostly with **9a** and **9c**. The conversions into **10a** and **10b** were monitored daily for 8 to 10 days with NMR spectroscopy. On each day of measurement, the complete NMR spectrum was recorded. The relative amounts of **9** and **10** were measured in two ways. The pair of aromatic dd in the spectrum of **10** that was furthest downfield (8.55−8.60 ppm) and was always separated cleanly from any other NMR signals was used as a standard representing 4H. In the region 8.1−8.2 ppm the second pair of 4H

dd of **10** partly overlapped the furthest downfield aromatic 4H multiplet of **9**. Integration of this overlapped region allowed for the calculation of that part of the overlap due to **9** and, by difference, that due to **10**. The data thus allowed for the calculation of the relative amounts of **9** and **10**. The signals from the two CH protons in **9** and **10** were integrated as an overlapping multiplet. The part of the multiplet attributable to **10** was assessed as 2H (relative to the 4H standard of **10**), so that the balance of the integrated multiplet could be attributed to **9** and thus provide a second measure of the relative amounts of **9** and **10**. These data were translated into first-order rates of conversion from calculations of the concentration of **9** given by the ratios at the timed intervals.

Three separate runs (two with **9a** and one with **9c**) were made in NMR tubes that were shielded from light except for the brief time in the NMR probe. One run was made with **9c** in an unshielded NMR tube, one run was made with a solution of **9c** that contained added Th, and three (two with **9a** and one with **9c**) runs were made in the dark with solutions containing added $Th^{\bullet+}ClO_4^-$. The replicated runs had the same character so that details are given only for single examples.

(A) With 9c in the Dark. The NMR tube, shielded with metal foil contained a solution of 9.0 mg (0.009 mmol) of **9c** in 1.5 mL of CD_3CN. Within a few hours, the peaks of **10c** and Th were discernible. After 2 d, with the standard for **10c** set as 4H, the two separate and clear multiplets of Th at 7.55 and 7.30 ppm integrated as 4.1H each. This character was repeated in NMR spectra recorded for 8 d. As the concentration of Th increased, the definition of its pairs of dd became more pronounced. On each day of measurement, the integral for Th was the same as that for **10c**. On days 3−8, the spectra of Th and **10c** were very well resolved. The solution remained colorless throughout the run. The ratios **9c**:**10c** were calculated after 10 h, 1, 2, 3, 6, and 8 d, and were, respectively, 93/6, 73/27, 62/38, 48/52, 28/72, and 14/86; $k = 9.6 \pm 0.5 \times 10^{-3}$ h^{-1}, $r = 0.9936$.

(B) With 9c in the Light. The solution contained 8.0 mg (0.008 mmol) of **9c** in 1.5 mL of CD_3CN. The NMR tube was unshielded and was illuminated with laboratory natural and fluorescent light. A light pink color appeared soon after exposure to light and remained during the 11 d of the experiment. The intensity of the color diminished during overnight darkness and re-appeared in daylight. Optical density measurements were not made on this solution, but were recorded in separate experiments.

Within a few hours, the appearance of **10c** was evident, but peaks of the Th spectrum were not seen. After 1 d, the signals from **10c** were pronounced and well resolved, but in the region of 7.3 ppm for Th only a broadening of the baseline could be seen. The ratio **9c**:**10c** was then 72/28. This behavior continued during 8 d of measurement. Thus, after 5 d the signals from Th appeared as abroad hump spanning 7.1−7.6 ppm, whereas those from **10c** were cleanly defined sets of dd. After the eighth day, well-defined peaks of ThO were found, overlapping in part the broad hump for Th spanning 7.3−7.6 ppm. On the 11th day, the spectrum of ThO was clearly defined, whereas that for Th was again a broad band. The spectrum of **9c** was no longer discernible**.** The ratio **9c**:**10c** after 10 h, 1, 2, 3, 5, 6, and 8 d was 94/6, 72/28, 57/43, 43/57, 24/76, 19/81 and 7/93; $k = 11.5 \pm 0.18 \times 10^{-3}$ h^{-1}, $r = 0.9995$.

(C) With 9c and Added Th in the Dark. The solution contained 8.4 mg (0.0084 mmol) of **9c** and 4.0 mg (0.0019 mmol) of Th in 1.5 mL of CD_3CN. Two well-defined dd of Th were evident at 7.52 and 7.30 ppm throughout the whole of this run. That is, no broadening of the Th peaks was observed at any time. In all integrations those of the two Th dd were equal and, obviously, greater than that of the **10c** standard. For example, after 3 d, the two Th dd represented 21.7 and 22.5 H as compared with the 4H standard. Absolute yields of **10c** and newly formed Th were not calculated. Ratios **9c**:**10c** after 10 h, 1, 3, 5, 6, and 8 d were, respectively, 95/5, 73/27, 47/53, 33/67, 27/73, and 15/85; $k = 9.3 \pm 0.4 \times 10^{-3}$ h^{-1}, $r = 0.9963$.

(D) With 9a in the Dark. A solution of 8.2 mg (0.011 mmol) of **9a** in 1.0 mL of CD_3CN was used. The NMR spectra recorded daily were much like those obtained with **9c**. That is, integrations of **10a** equated to those of Th. The signals from Th were well defined and none from ThO were seen. The ratios **9a**:**10a** after 1, 2, 3, 4, 6, 8, and 10 d were 83/17, 67/33, 58/42, 45/55, 32/68, 22/78, and 18/82; rate $k = 8.0 \pm 0.3 \times 10^{-3}$ h^{-1}, $r = 0.9978$.

(E) With 9a and Added $Th^{\bullet+}ClO_4^-$ in the Dark. To a solution of 7.7 mg (0.0106 mmol) of **9a** in 1.0 mL of CD_3CN was added 2.7 mg (0.0085 mmol) of $Th^{\bullet+}ClO_4^-$. After 1 d, signals from **10a** were pronounced, but none of Th could be seen. This pattern continued until the third day when a shallow band for Th appeared at 7.1−7.4 ppm. After 4 d, the broad band for Th was intensified and signals from ThO were evident among those from **9a**. The signals from ThO and the intensity of the band spanning 7.3−7.5 ppm increased with time, until after 6 d they dominated the upfield aromatic region. At all times, the spectrum of **10a** was well defined. Assays of the ratio **9a**:**10a** were made with the overlapped CH multiplets and after 1, 2, 3, 4, 6, and 8 d were 80/20, 68/32, 62/38, 54/46, 34/66, and 20/80: $k = 8.2 \pm 0.67 \times 10^{-3}$ h^{-1}, $r = 0.9867$.

(F) The Effect of Added Th on the Addition of $Th^{\bullet+}ClO_4^-$ to Cycloheptene. Three suspensions (A, B, and C) were made, each of 300 mg (0.95 mmol) of $Th^{\bullet+}ClO_4^-$ in 8 mL of MeCN. In B and C the solvent contained 0.25 and 0.125 mmol, respectively, of dissolved Th. To each stirred suspension was added 1.5 mL of cycloheptene. The suspensions became colorless within a few min. After a further 5 min, 40 mL of ether was added. The precipitates were collected and weighed, respectively, 190, 210, and 190 mg. The NMR ratios **9a**:**10a** were 65/35, 67/33, and 68/32, respectively.

(G) The Absence of Reaction between 10a and Th. A solution of 7.9 mg (0.015 mmol) of **10a** and 7.7 mg (0.035 mmol) of Th in 1.0 mL of CD_3CN was kept in an NMR tube shielded from light. The NMR spectrum was recorded periodically for 6 d during which time signals from **9a** were not observed.

(H) The Effect of Light on Solutions of 9a. A. A solution of 17.3 mg (0.0238 mmol) of **9a** in 3 mL of MeCN in a cuvette was exposed periodically to fluorescent light and daylight during several days. The absorbance at 540 nm, characteristic of $Th^{\bullet+}$, was recorded daily, increasing when lights were on and decreasing when they were off. The maximum concentration of $Th^{\bullet+}$ that was reached was calculated with the use of the extinction coefficient for $Th^{\bullet+}$ in concentrated sulfuric acid,[12] and amounted to 3.4% of the initial amount of **9a**. **B**. A similar solution was exposed to daylight for 14 h. The absorption spectrum had maxima at 539, 915, and 1032 nm, characteristic of $Th^{\bullet+}$. Using extinction coefficients for these wavelengths,[12] the concentration of $Th^{\bullet+}$ was found to be 7.9×10^{-5} M, namely 1% of the initial amount of **9a**.

(I) ESR Experiments with 9a. A 300 MHz spectrometer was used. Because of dielectric loss by the polar solvent, a sample was placed in a 1 mm capillary tube within a 4 mm esr tube. A control spectrum was recorded with a solution of $Th^{\bullet+}PF_6^-$ in CD_3CN. The test solutions were of **9a** in CD_3CN, each approximately 8 mM. A solution of **9a** that had been sealed for 5 d in an ampule protected from light was colorless when opened for esr scanning. An esr signal could not be found. The capillary was exposed to laboratory fluorescent light, and its solution became pink within 1 h. After 3 h, the esr spectrum was like that of the control. A second ampule containing a 1-day-old, colorless solution that had been protected from light was exposed to laboratory light. The solution became pink within 1 h, and the color intensified on standing. The ampule was opened after 3 h, and its solution gave an esr signal identical with that of the control. All esr signals were single lines of approximately 3 G width. The *g*-values, calculated from the microwave frequency and field strength, were 2.0066 for the control and 2.0065 for the light-exposed ampule. The magnetic field was not calibrated with use of another radical standard. The esr spectrum of $Th^{\bullet+}$ in concd sulfuric acid has five lines of 1.3 G width, spans 5 G, and has $g = 2.0081$.[10,12]

(12) Shine, H. J.; Piette, L. *J. Am. Chem. Soc.* **1962**, *84*, 4798−4806.

The signals recorded in CD_3CN solution appear to exhibit spin-exchange narrowing and loss of hyperfine splitting.[13]

(J) With 18 in the Dark. As in part A with **9c**, the solution contained 8.3 mg (0.012 mmol) of **18**. Two days elapsed before enough of **19** for integration had formed. Th had formed, and its signals were not broadened. Integrations of the relative amounts of **18** and **19** were made in three NMR regions, namely, the aromatic multiplets spanning 8.63−8.51 and 8.21−8.03 ppm, the methine multiplets centered at 4.73 and 4.32 ppm, and the methyl doublets at 1.45 and 1.39 ppm. The three ratio measurements were averaged. The methyl 6 H doublet for **18** at 1.39 ppm was used as the integration standard. The ratio **18**:**19** after 2, 4, 6, 8, 10, and 12 d was 89/11, 82/18, 73/27, 65/35, 60/40, and 52/58; $k = 2.6 \pm 0.14 \times 10^{-3}$ h^{-1}, $r = 0.9945$.

(K) With 18 in the Light. The procedure was like that with **9c**. The solution (8.0 mg, 0.0116 mmol, in 1.0 mL) became pink within a few hours. The NMR signals from **18** and **19** were distinct, but none was seen from Th. Integrations were again made at 2, 4, and 6 d intervals. During this time the spectrum of **19** was unaccompanied by any other monoadduct signals. After 6 d, small peaks of ThO were found as well as of a new multiplet at 5.45 ppm and doublet at 1.57 ppm. These changes were not followed further. The ratio **18**:**19** after 2, 4, 6, 8, 10, and 12 d was 87/13, 77/23, 67/33, 60/40, 55/45, and 45/55; $k = 2.6 \pm 0.14 \times 10^{-3}$ h^{-1}.

(L) Attempted Conversion of 6a into 7a in CD_3CN. A solution of **6a** in CD_3CN was monitored daily with NMR spectroscopy for 6 d during which time **7a** could not be detected.

Formation of 1-(Thianthreniumyl)cycloalkenes. Conversion of 10a into 11a. (A) In CD_3CN. To a solution of a small amount of **10a** in 1.0 mL of CD_3CN was added 0.2 mL of D_2O. The NMR spectrum was monitored to follow the conversion of **10a** (two C*H*-S$^+$ protons) into **11a** (one alkenyl proton). The conversion was complete after 7 d, after which signals from **10a** were no longer seen. Some Th had been formed, too, and the integrated ratio **11a**:Th was 95/5.

(B) In MeCN. Isolation of 11a. To a solution of 130 mg (0.255 mmol) of **10a** in 6 mL of MeCN was added 0.5 mL of water. The solution was stirred for 7 d, after which ether was added to precipitate 73 mg (70%) of white solid, mp 157−163 °C dec. Crystallization from MeCN/ether gave **11a**, mp 171−172 °C dec. ^{1}H NMR, CD_3CN, 500 MHz (**11a**): 8.402 (7.75, 1.0, 1.5), dd, 2H; 7.823 (7.9, 1.0,1.25, 0.5), ddd, 2H; 7.777 (7.5, 7.75, 1.5, 1.5, 1.0), td, 2H; 7.721 (8.0, 7.5, 1.5, 1.5, 1.5), td, 2H; 5.904 (7.0, 6.5), t, 1H; 2.337 (2.2, 2.2), t, 2H; 2.271 (2.6, 2.0, 2.6), q, 2H; 1.672, m, 2H; 1.494, m, 2H; 1.359, m, 2H. Anal. Calcd for $C_{19}H_{19}S_2ClO_4$ (**11a**): C, 55.5; H, 4.66; S, 15.6; Cl, 8.63. Found: C, 55.5; H, 4.43; S, 15.5; Cl, 9.02.

Conversion of a Mixture of 9b and 10b into 11b in MeCN. Isolation of 11b. A solution of 200 mg of a mixture of **9b** and **10b**, ratio 10/90, was dissolved in 5 mL of MeCN. After 14 d, ether was added to precipitate 8.8 mg of solid, mp 169.5−171 °C dec, deduced to be **11b** from the NMR spectrum. ^{1}H NMR, CD_3CN, 500 MHz (**11b**): 8.136 (8.0, 1.5, 0.5), ddd, 2H; 7.939 (8.0, 1.0, 0.5), ddd, 2H; 8.845 (7.5, 8.0, 1.5, 1.5, 8.0, 1.5, 1.5), overlapping ddd, 2H; 7.741 (7.25, 8.0, 1.5, 1.5, 7.5, 1.5, 1.0), overlapping ddd, 2H; 5.953 (7.0, 6.5), t, 1H; 2.298−2.229, m, 4H; 1.687−1.639, m, 2H; 1.476−1.430, m, 2H; 1.292−1.246, m, 2H.

Conversion of 9c into 10c and 11c in CD_3CN. Effect of Water. (A) In Dry CD_3CN. A solution of **9c** in CD_3CN was monitored with NMR spectroscopy. Conversion into **10c** was detected during the first day and after 6 d the ratio of **9c**:**10c** was 20/80. Soon, **11c** began to appear, and after 16 d, when **9c** was not detected, the ratio **10c**:**11c** was 80/20.

(B) In Wet CD_3CN. A separate solution of **10c** in CD_3CN was monitored for 3 d. No **11c** but a small amount of Th was detected. Two drops of D_2O was added to the NMR tube. After a further 3 d, the ratio **10c**:**11c**:Th was 60/35/5. At that time, 0.1 mL of D_2O was added, and after a further 3 d the ratio of components was 10/80/10. After 8 d, only **11c** and Th were found, in the ratio 90/10.

Conversion of 7a into 8a. Effect of Water. (A) In Dry CD_3CN. A solution of a small amount of **7a** in 1.0 mL of CD_3CN was monitored with NMR spectroscopy. The relative amounts of **7a**, **8a**, and Th were assayed through integration of unoverlapping parts of their aromatic signals. That is, for **7a** we used the multiplet (4H) in the region 8.643−8.512 ppm, for **8a** the multiplet (6H) in the region 7.948−7.687 ppm, and for Th the multiplet (4H) in the region 7.359−7.294 ppm. After 13 d signals from **7a** could not be seen, while **8a** and Th had been formed in the ratio 35/65. GC analysis of the solution showed the presence of 1,3-cyclohexadiene, but quantitative assay was not made.

(B) In Wet CD_3CN. Isolation of 8a. To a solution of 6.7 mg (1.35 mmol) of **7a** in 1.0 mL of CD_3CN was added 0.2 mL of D_2O. After 18 h, **7a** could no longer be detected, while **8a** and Th had been formed in the ratio 85/15. The CD_3CN was evaporated with an air jet and the residue was washed three times with ether to remove Th. The remaining solid was dissolved in CD_3CN and was found with NMR spectroscopy to be free of Th. A small amount of ether was added to cause crystallization of **8a**, mp 227−228 °C dec. A single crystal was grown successfully for X-ray crystallography (Figure F8). ^{1}H NMR, CD_3CN, 500 MHz (**8a**): 8.109 (8.0, 1.5, 1.5), dd, 2H; 7.919 (8.0, 1.5, 0.5, 0.5, 1.5, 0.5, 0.5), ddd, 2H; 7.830 (7.5, 8.0, 1.5, 1.5, 8.0, 1.5, 1.5), overlapping ddd, 2H; 7.722 (8.0, 7.5, 1.0, 1.0, 7.5, 1.0, 1.0), overlapping ddd, 2H; 6.021 (4.0, 1.5), tt, 1H; 2.170−2.127, m, 2H; 1.909−1.886, m, 2H; 1.662−1.614, m, 2H; 1.528−1.481, m, 2H.

Conversion of 4a into 5a. Isolation of 5a. A solution of a small amount of **4a** in 1.0 mL of CD_3CN containing 0.2 mL of D_2O was monitored periodically with NMR spectroscopy for assay of **4a**, **5a**, and Th. After 2 d, for example, the ratio of these compounds was, respectively, 90/8/3, and after 31 d 20/43/38. Finally, after 64 d, the amount of **4a** was too small to measure, while the ratio **5a**:Th was 55/45. The solution was treated as described earlier to give **5a**, mp 241−242 °C dec. ^{1}H NMR, 200 MHz, $CDCl_3$ (**5a**): 8.135 (7.82, 1.50, 1.52), dd, 2H; 7.925 (7.80, 1.51, 1.41), dd, 2H; 7.827 (7.40, 7.82, 1.52, 1.53, 1.56), td, 2H; 7.715 (7.62, 7.47, 1.81, 1.60, 1.55), td, 2H; 6.183, m, 1H; 2.454, m, 2H; 2.279, m, 2H; 2.046−1.976, m (overlapping solvent).

Conversion of 13a into 14a. Isolation of 14a. The preparation of **13a** has been reported earlier.[1] A control NMR experiment showed that **13a** in 1.0 mL of CD_3CN containing 0.2 mL of D_2O was converted into **14a** and Th in the ratio 80/20 completely after 1 d. Therefore, a solution of 61.8 mg (0.118 mmol) of **13a** in 4 mL of MeCN and 0.5 mL of water was stirred for 1 d, after which ether was added to precipitate 33.8 mg (0.0796 mmol, 67.5%) of product, mp 173.5−175 °C after crystallization from MeCN/ether. ^{1}H NMR, CD_3CN, 500 MHz (**14a**): 8.158 (8.0, 1.0,1.0), dd, 2H; 7.932 (8.0, 0.5, 0.5), dd, 2H; 7.851 (8.25, 8.0, 1.5, 1.5, 7.5, 1.5, 1.5), overlapping ddd, 2H; 7.737 (7.5, 8.0, 1.5, 1.5, 8.0, 1.5, 1.5), overlapping ddd, 2H; 5.759 (8.5, 8.5), t, 1H; 2.475, m, 2H; 2.249−2.207, m, 2H; 1.545−1.497, m, 2H; 1.391−1.307, m, 4H; 0.982−0.935, m, 2H. Anal. Calcd for $C_{20}H_{21}S_2ClO_4$ (**14a**): C, 56.5; H, 4.98; S, 15.1; Cl, 8.34. Found: C, 56.8; H, 5.20; S, 15.0; Cl, 8.35.

Reactions of Adducts with Sodium Thiophenoxide in MeCN. The general procedure was to stir overnight a solution of the reactants in MeCN containing a GC standard in a septum-capped or sealed vessel. The mmolar amount of PhSNa always exceeded that of the adduct. Naphthalene was used as GC standard with column A for reactions of **6a**, **9a**, **10a**, and **17a**. Both naphthalene (col A) and 2-butanone (col B) were used for reaction of **3a**. The number of assays was 3−5, and averaged results are reported. A detailed example is given with **9a**.

A solution of 56.7 mg (0.0779 mmol) of **9a** and 37.7 mg (0.285 mmol) of PhSNa was stirred overnight. GC analysis gave 0.0779 mmol (100%) of cycloheptene, 0.00423 mmol (5.4%) of 1-(phenylthio)cycloheptene, 0.155 mmol (99%) of Th, and 0.115

(13) Bersohn, M.; Baird, J. C. *An Introduction to Paramagnetic Resonance*; Benjamin: New York, 1996; p 54.

mmol (148%) of diphenyl disulfide (DPDS), based on the amount of **9a**.

Reaction of **10a** gave 93% of cycloheptene, 4.3% of 1-(phenylthio)cycloheptene, 94% of Th, and 103% of DPDS. Reaction of **6a** gave 99% of cyclohexene, 2.4% of 1-(phenylthio)cyclohexene, 93% of Th, and 109% of DPDS. Reaction of **3a** gave 6.0% of cyclopentene, 25% of 1-(phenylthio)cyclopentene, 69% of 1,2-*trans*- di(phenylthio)cyclopentane, 101% of Th, and 42% of DPDS.

Reaction of **17a** with PhSNa was carried out in the usual way. GC assay gave 95% of 1,5-cyclooctadiene, 97% of Th, and 99% of DPDS. Following GC assay, the solution (10 mL) was poured into 15 mL of NaOH solution, and this was extracted three times with 10 mL of ether. The residue from workup of the ether solution was assayed in MeCN with GC and gave 95% of Th and 89% of DPDS.

Preparation of 1-(Phenylthio)cycloheptene. To a stirred solution of 2.3 g (20 mmol) of cycloheptanone and 2.2 g of thiophenol (20 mmol) in 20 mL of dichloromethane (CH_2Cl_2) was added 5.7 g (40 mmol) of P_2O_5. The mixture was stirred for 18 h, the supernatant solution was decanted and the residue washed with CH_2Cl_2. The combined CH_2Cl_2 solution was washed with 10% NaOH solution. After drying (K_2CO_3) and evaporation of the CH_2Cl_2, the residue was distilled to give 2.36 g (11.6 mmol, 58%) of product, bp 188−193 °C/140 mmHg; lit. bp 105−110 °C/0.005 mmHg.[14] GC on col A showed the presence of a minor impurity, which was removed with chromatography on a column of silica gel, petroleum ether elution. ^{1}H NMR, $CDCl_3$, 200 MHz: 7.340−7.171, m, 5H; 6.154 (6.62, 6.58), t, 1H; 2.348 (5.53, 5.37), t, 2H; 2.198, m, 2H; 1.734, m, 2H; 1.538, m, 4H.

1-(Phenylthio)cyclohexene was prepared similarly in 75% yield, bp 170−176 °C/55 mmHg; lit. bp 115 °C/0.1 mmHg.[15]^{1}H NMR, $CDCl_3$, 200 MHz: 7.335−7.180, m, 5H; 6.067, m, 1H; 2.178−2.102, m, 4H; 1.708−1.566, m, 4H overlapped with solvent water.

1-(Phenylthio)cyclopentene was prepared analogously in 67% yield. The product (5.9 g) was distilled three times, bp 176−179 °C/115 mmHg; lit. bp 110 °C/0.1 mmHg,[15] 85 °C/0.2 mmHg.[14] GC showed the presence (4%) of an impurity, which was removed with chromatography on silica gel. ^{1}H NMR, $CDCl_3$, 200 MHz: 7.413−7.251, m, 5H; 5.736−5.709, br m, 1H; 2.440−2.352, m, 4H; 2.033−1.923, m, 2H.

Preparation and Separation of 1-, and 3-(Phenylthio)-cyclopentene and *trans*-1,2-(Diphenylthio)cyclopentane. In a pressure tube were placed 1.13 g (8.13 mmol) of *trans*-1,2-dichlorocyclopentane, 4.40 g (33.3 mmol) of PhSNa, and 10 mL of ethylene glycol. The tube was heated and periodically cooled and opened for GC assay on column A. On this column, 1- and 3-(phenylthio)cyclopentene could not be distinguished and were assayed together. After 19 h at 110 °C followed by 4 d at 140 °C, the solution contained 4% of dichlorocyclopentane, 29% of (phenylthio)cyclopentenes, and 67% of *trans*-1,2-di-(phenylthio)cyclopentane. The solution was poured into 60 mL of aqueous NaOH solution and extracted with ether. Drying ($MgSO_4$) and workup of the ether solution gave a residue which was separated with chromatography on a column of silica gel and elution with petroleum ether. The eluates were monitored with thin-layer-chromatography on commercial silica gel indicator plates. Workup of appropriate eluate fractions gave, finally: (a) 140 mg (0.739 mmol, 9.8%) of 1-(phenylthio)-cyclopentene as an oil whose NMR spectrum complemented that of authentic 1-(phenylthio)cyclopentene, (b) 130 mg (0.795 mmol, 9.1%) of 3-(phenylthio)cyclopentene as an oil, ^{1}H NMR, $CDCl_3$, 200 MHz: 7.421−7.197, m, 5H; 5.913−5.867, m (7 peaks), 1H; 5.818−5.761, m (7 peaks), 1H; 4.330−4.271, m, 1H; 2.424−2.278, m, 3H; 2.087−1.945, m, 1H. Literature bp 190 °C/15 mmHg,[16] and (c) 870 mg (2.94 mmol, 36%) of *trans*-1,2-di(phenylthio)cyclopentane, mp 39−40 °C. ^{1}H NMR, $CDCl_3$, 200 MHz: 7.304−7.059, m, 10H; 3.593−3.548, two m, 2H; 2.412−2.272, m, 2H; 1.944−1.661, m, 4H. Mass spectrum, Calcd for $C_{17}H_{18}S_2$: 286.084996. Found: 286.084748. Mass, % abundance: 286 (M^+), 16; 177 ($M - C_6H_5S$), 100; 131 ($M - 2C_6H_5$), 20; 109 (C_6H_5S), 16; 67 ($M - 2C_6H_5 - H$), 42.

X-ray Crystallography. A crystal was encapsulated in a thin shell of epoxy cement and mounted on the tip of a glass fiber. Data were collected with a Bruker AXS automated CCD diffractometer using the Bruker AXS package and using Mo Kα radiation ($\lambda = 0.71069$ Å). The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were calculated in ideal positions (riding model). Refinement of F^2 against all reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors-(gt) etc., and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on all data will be even larger. All software used is contained in the SHELXTL 5.10[17] program library.

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Supporting Information Available: Figures F1−F8 (Ortep diagrams) and tables giving X-ray crystallographic data for **9a**, **4b**, **15a**, **17a**, **18**, **21**, **22**, and **8a**. This information is available free of charge via the Internet at http://pubs.acs.org.

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