

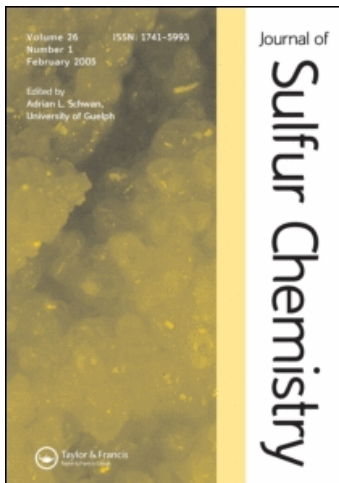
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An overview of some reactions of thianthrene cation radical. Products and mechanisms of their formation

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REVIEW ARTICLE

**An overview of some reactions of thianthrene cation radical.
Products and mechanisms of their formation**

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A comprehensive review of recent chemistry of thianthrene cation radical is presented. Particularly, products and mechanisms of their formation from reactions with azo compounds, hydrazones, oximes, sulfonamides, alcohols, phenols, alkenes, alkynes and organometallics are discussed. Also, reactions of 5-(substituted)thianthrenium salts are reviewed.

Keywords: Thianthrene cation radical; Organometallics; Alcohols; Alkenes; Alkynes

1. Introduction

A number of articles and reviews of chemistry of the thianthrene cation radical have appeared since it was characterized with esr spectroscopy in 1962 [1–4]. Among those reviews are a personal account of entering the realm of thianthrene cation radical chemistry [5, 6] and a progression of reports of the cation radical's chemistry as the chemistry unfolded with the passage of time [5–15]. In the present review, we have written about reactions of thianthrene cation radical that have been reported in the more recent years. To place the work of the recent years in perspective we have also gone back in time in some cases so that our review includes reactions that have been reported in earlier reviews. Rather than just report, however, we have also tried to assess the work that has been published.

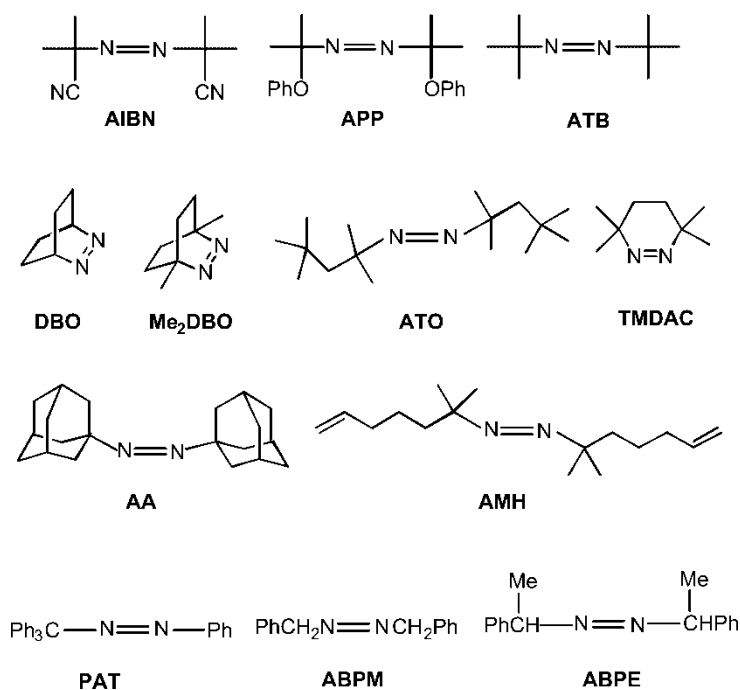
Throughout the review we use the symbol Th for thianthrene, ThO for thianthrene 5-oxide and Th^{•+} for the thianthrene cation radical. Joule [14] has noted how many different symbols for thianthrene cation radical are to be found in the literature. Throughout our drawings for reactions and schemes we use, where convenient, \curvearrowright S to denote Th, \curvearrowright S=O to denote ThO, \curvearrowright S^{•+} to denote Th^{•+} and \curvearrowright S⁺ to denote the 5-thianthrenium group. In most of our drawings, the anion (ClO₄⁻ or BF₄⁻) that accompanies a thianthrenium group has been omitted.

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In the discussions that follow on mechanisms of reaction a recurring uncertainty is noted, as to whether or not a reaction is preceded by electron-transfer and formation of free radicals. In some cases the question is clearly answerable, but in many others the question, as noted by Glass [15], remains. We have frequently included in this review the unexpected side reactions that have occurred. The last part of the review is devoted, in fact, to some reactions of 5-(substituted)thianthrenium salts, reactions that were encountered as side reactions in primary studies.

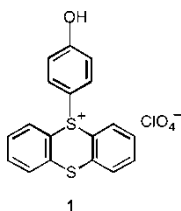
2. Reactions with azo compounds

Reactions with the following azo compounds, listed with their acronyms, are reviewed. In the earliest investigation of reactions between Th^{+} and azo compounds, Kim chose the well-known free-radical initiator bis-azoisobutyronitrile (**AIBN**) [16]. However, no reaction occurred between **AIBN** and Th^{+} in acetonitrile (MeCN) at room temperature over a period of two days. Therefore, reaction in boiling MeCN was studied, with the objective of thermally producing 2-cyanopropyl radicals in the presence of Th^{+} . The only thianthrene-derived products of reaction, however, were a (5-thianthreniumyl)thianthrene dimer and thianthrene oxides, whose formations were not attributable to participation by **AIBN**. Thus, a reaction between **AIBN** and Th^{+} could not be validated.



In a related study, but at room temperature, with azo-bis-2-phenoxy-2-propane (**APP**), the major products of reaction were phenol and 5-(4-hydroxyphenyl)thianthrenium perchlorate (**1**) [17]. The phenol originated, however, from the protonolysis of **APP**, and having been

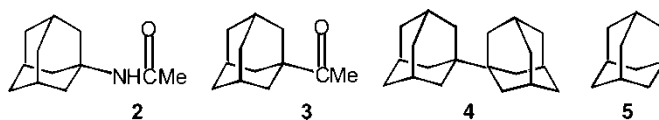
formed, the phenol reacted as expected with $\text{Th}^{+\cdot}$ to give **1**.



A small amount of an unusual product, 2-(5-thianthreniumyl)propene, was obtained, but its origin was indefinable. Thus, the direct reaction of $\text{Th}^{+\cdot}$ with an azo compound could, again, not be demonstrated.

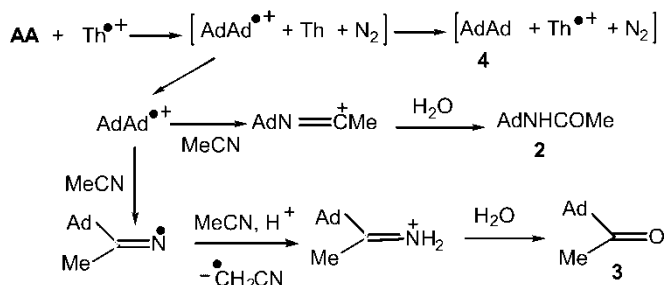
The direct reaction of $\text{Th}^{+\cdot}$ with azoalkanes was encountered with the serendipitous discovery that $\text{Th}^{+\cdot}\text{ClO}_4^-$ reacted rapidly with azoisobutane (**ATB**) in MeCN at room temperature, resulting in the quantitative formation of N_2 and an almost 80% yield of *N*-(*tert*-butyl)acetamide [13]. Difficulty with the quantitative assay of gaseous hydrocarbon products from **ATB** led to further work with azo compounds having larger molecular weights, namely, azoadamantane (**AA**) [18], 2,3-diazabicyclo[2.2.2]oct-2-ene (**DBO**) [19], azo-*tert*-octane (azobis-2,4,4-trimethylpentane, **ATO**) [20], 3,3,6,6-tetramethyl-1,2-diazacyclohexene (**TMDAC**) [20], 1,4-dimethyl-2,3-diaza[2.2.2]oct-2-ene (**Me₂DBO**) [20], azobis-2-methyl-6-heptene (**AMH**) [21], azobisphenylmethane (**ABPM**) [13], and phenylazotriphenylmethane (**PAT**) [13]. All of these azo compounds, except **DBO**, underwent quantitative oxidation by $\text{Th}^{+\cdot}$. The extent of oxidation was measured with N_2 evolved and/or the products that were formed. Details of product formation will follow, but the salient feature is that the products were derived mainly from hydrocarbon cations rather than radicals. Products of free-radical origin were, in fact, found in small quantities or not at all.

Reaction of **AA** with $\text{Th}^{+\cdot}\text{ClO}_4^-$ in MeCN led to a 91% yield of *N*-adamantylacetamide (**2**). Small amounts of adamantyl methyl ketone (**3**, 5.5%), 1,1'-biadamantyl (AdAd, **4**, 2.5%) and adamantane (AdH, **5**, 0.2%) were obtained, too, thus accounting for 99% of the adamantyl groups in the **AA**.



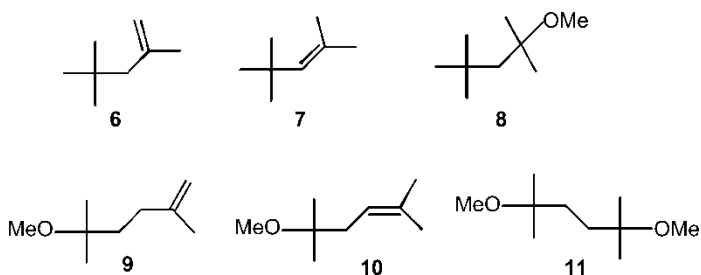
Products **3** and **5** were shown to be derived from adamantyl radicals because their formation was prevented by the inclusion of a trapping agent, BrCCl_3 . Formation of **4**, seemingly attributable to the dimerization of adamantyl radicals, was not prevented in that way. Exploration of the fate of adamantyl radicals was pursued with the photolysis of **AA** in MeCN [22]. The dominant products of photolysis were, in fact, **5** and products attributable to the solvent-derived radical $\cdot\text{CH}_2\text{CN}$. It was concluded, therefore, that in the oxidation of **AA** by $\text{Th}^{+\cdot}$, free adamantyl radicals (Ad^\cdot) were not formed, or if formed did not survive oxidation to Ad^+ by $\text{Th}^{+\cdot}$. It was proposed, therefore, that products seemingly attributable to reactions of free Ad^\cdot were more likely to have been derived from the biadamantyl cation radical ($\text{AdAd}^{+\cdot}$), which, itself, was formed in a solvent cage (scheme 1).

The difficulty of certifying products of free radical (Ad^\cdot) reactions in work with **AA** was encountered also later in work with **ATO**, **TMDAC** and other azo compounds. **ATO** and **TMDAC** gave N_2 quantitatively in reaction with $\text{Th}^{+\cdot}$ in CH_2Cl_2 containing methanol. But, with the exception of 2-3% of 2,2,4-trimethylpentane from **ATO**, the hydrocarbon products

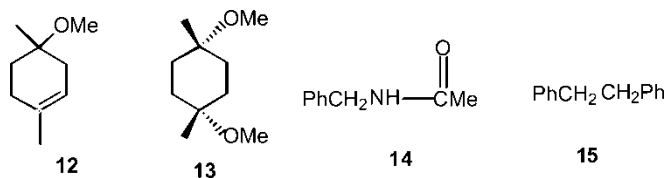


Scheme 1

from **ATO** and **TMDAC** were mixtures of alkenes and alkyl methyl ethers, attributable only to reactions of cations. That is, from **ATO** were obtained **6** (66%), **7** (13%) and **8** (6%), while **TMDAC** gave **9** (13%), **10** (13%) and **11** (70%).

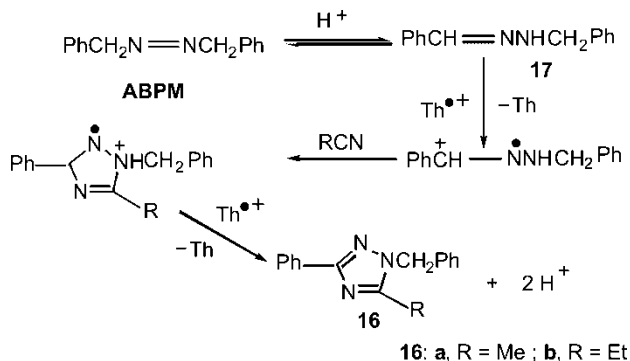


It is notable that the bicyclic **Me₂DBO** was also oxidized completely (N₂ evolution) by Th^{•+} in contrast with **DBO** which was inert to oxidative decomposition [19]. We shall discuss this difference later. Products from oxidation of **Me₂DBO** by Th^{•+} were not sought, but analogous oxidation by tris(*p*-bromophenyl)aminium cation radical gave a mixture of seven products, prominent among which were the methyl ethers **12** (41%) and **13** (cis- and trans-, 35%), of obvious cationic origin. It is likely that these products would have been obtained with the use of Th^{•+}. The summary of the findings with **ATO**, **TMDAC** and **Me₂DBO** is that oxidation of each was complete and gave primarily cation-derived rather than free-radical derived products.



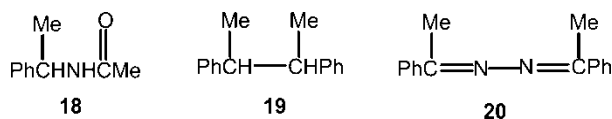
Reaction of **ABPM** with Th^{•+}ClO₄⁻ in MeCN gave a large amount (54%) of *N*-benzylacetamide (**14**) whose source was undoubtedly the benzyl cation. A significant amount (19%) of bibenzyl (**15**) was also obtained, whose origin may well have been a solvent-cage redox reaction between the dimer cation radical and Th^{•+} analogous to that proposed for AdAd formation (scheme 1). A third and unexpected product (26%) from the reaction with **ABPM** was the triazole **16a**. The source of **16a** was benzaldehyde benzylohydrazone (**17**), the tautomer of **ABPM**, formed by catalysis from the protons released in the reaction medium (scheme 2) [13, 23]. Reaction in propionitrile (EtCN) gave similar results and the triazole **16b** (60%) [23].

In a similar investigation, *meso*-azobis-1-phenylethane (**ABPE**) was oxidized quantitatively by Th^{•+}ClO₄⁻ in MeCN [24]. The products, in addition to thianthrene, were

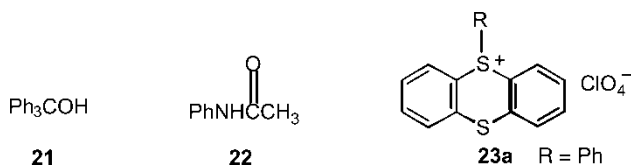


Scheme 2

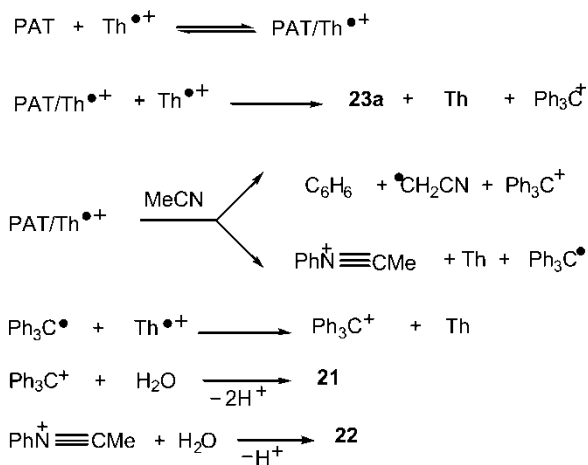
N-(1-phenylethyl)acetamide (**18**, 39%), 2,3-diphenylbutane (**19**, 24%), acetophenone azine (**20**, 9%) and acetophenone (19%), accounting for 91% of the ABPE. The origin of **18** was reaction of 1-phenylethyl cation with MeCN. Formation of **19**, diagnostic of 1-phenylethyl radicals, was not prevented, however, by added BrCCl_3 , so that the origin of **19** was assigned to solvent-cage formation of $\mathbf{19}^{\bullet+}$ and its reduction by Th in the cage, analogous to the earlier proposal for formation of AdAd (scheme 1) [18]. Acetophenone formation was traced to the hydrolysis of its 1-phenylethyldiazone, the tautomer of ABPE, while the azine **20** is the product of the two-electron oxidation of ABPE. Tautomerization of ABPE, with only single α -H atoms, could not lead to cycloaddition of solvent and triazole formation, as was observed with ABPM with its requisite α -methylene group [13, 23]. Consequently, the tautomeric hydrazone remained, to suffer hydrolysis to acetophenone.



Reaction of $\text{Th}^{\bullet+}\text{ClO}_4^-$ with phenylazotriphenylmethane (**PAT**) gave 92% of N_2 and 74% of triphenylmethanol (**21**), again indicative of triphenylmethyl cation formation. The phenyl group was found in acetanilide (**22**, 14%), 5-phenylthianthrenium perchlorate (**23a**, R = Ph; 50%) and benzene (7%). The formation of **22** suggests that the phenyl cation was trapped by MeCN, while the formation of **23a** and benzene suggests that the phenyl radical was trapped by $\text{Th}^{\bullet+}$ (to give **23a**) and solvent (to give benzene). It is unlikely that the free phenyl cation could be formed, however, or that the free phenyl radical could survive reaction with the solvent to be trapped as **23a** by $\text{Th}^{\bullet+}$. The formation of all products may, instead, have arisen from reaction of the complex **PAT**/ $\text{Th}^{\bullet+}$ with the solvent and with more $\text{Th}^{\bullet+}$ (scheme 3) [13].



Seeking further insight into the formation of radicals in the oxidation of azo compounds, the reaction with AMH was studied. Evidence was sought for the formation of the radical clock (**24**) and the corresponding cation (**25**). The reactions were carried out in CH_2Cl_2 with and without added di-*tert*-butylmethylpyridine, whose function was to deprotonate **25** and its

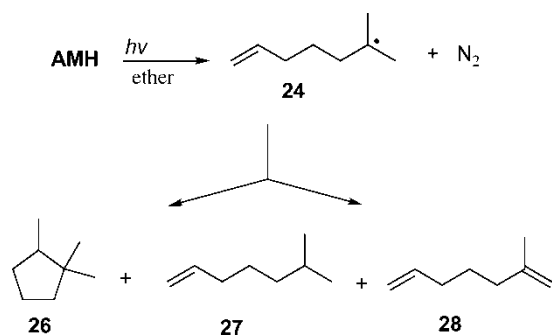


Scheme 3

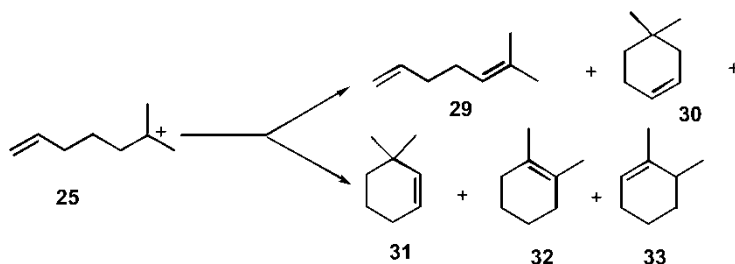
cyclization products. Photolysis of **AMH** (in ether solution) gave the expected products of cyclization (**26**) and disproportionation (**27** and **28**) of **24** (scheme 4).

These products were, indeed, obtained from oxidation of **AMH** by $\text{Th}^{\bullet+}$, but they represented only about 10% of the **AMH**. The major products of reaction were the diene (**29**) and the cyclohexenes (**30–33**, scheme 5), whose origins were attributed to **25**. Here, then the participation of radicals in the reaction was found, but, again only to a small extent.

In contrast with the several azo compounds whose oxidations by $\text{Th}^{\bullet+}$ are described above, **DBO** was resistant to oxidative decomposition by $\text{Th}^{\bullet+}$. Instead, **DBO** behaved as a nucleophile, with which $\text{Th}^{\bullet+}$ underwent substitution at a ring position (**34**, equation (1)).

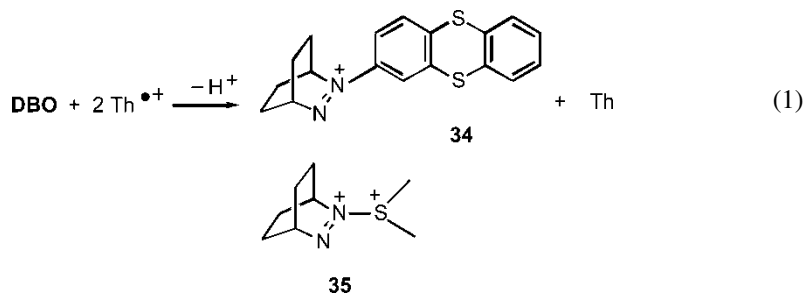


Scheme 4

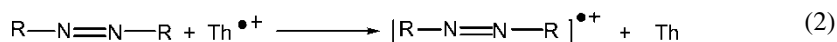


Scheme 5

Substitution at a ring position rather than at sulfonium sulfur is uncommon in the chemistry of $\text{Th}^{\bullet+}$. It has been observed with pyridine [25]. It occurs in preference to reaction at sulfonium sulfur because the consequence of that would be formation of two adjacent onium groups (**35**).

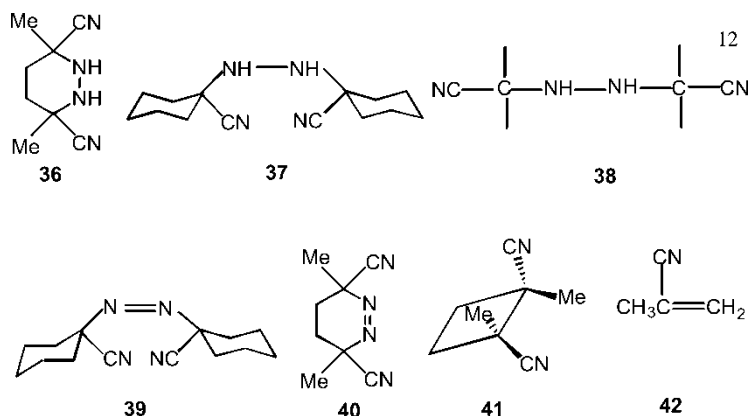


The difference in behavior of **DBO** and **Me₂DBO** is not one of oxidation potentials. Rather, it is probable that although oxidation of an azo compound can be represented in a simplistic way (equation (2)), a complex between reactants is formed, which can lead to oxidative decomposition only if the alkyl group attached to the azo linkage can form stabilized cation and radical fragments, possible with the tertiary C atoms of **Me₂DBO** but not with the secondary C atoms of **DBO**. Consequently, the complex **DBO/Th^{•+}** enters the substitution route [20].



It is apparent, furthermore, that in all of the oxidative reactions of azoalkanes, the tertiary- or benzylic-carbon based radicals that are formed are also readily susceptible to oxidation into tertiary and benzylic cations. That is, the feature which promotes oxidative decomposition also promotes the dominant cationic chemistry that ensues.

In an interesting corollary to the reactions of azo compounds, the hydrazo compounds **36–38** were oxidized by $\text{Th}^{\bullet+}$ in MeCN. Oxidation of **37** and **38** gave the corresponding azo compounds **39** and **AIBN**. It has already been noted that **AIBN** is resistant to further oxidation. Apparently, **39** was also resistant. The cyclic azo compound **40** was obtained from **36** but did not survive its well known thermal (even at low temperature) instability, decomposing instead into **41** (49%) and **42** (26%) [26a]. The stereochemical configurations of **36** and **40**, as had been reported in an earlier publication [26b], were not resolved, whereas the configuration of **41**, obtained earlier [26b] by oxidation of **40** with KMnO_4 , was the pure trans isomer.

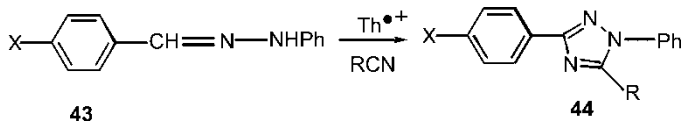
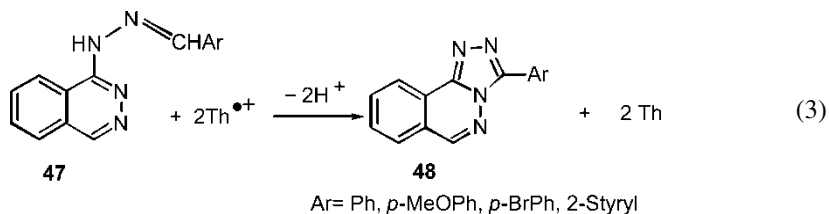


3. Reactions with hydrazones

We have recorded earlier in the reactions of azo compounds that the benzylhydrazone (17) of benzaldehyde, the tautomer of **ABPM**, was found to undergo oxidative cycloaddition to nitrile solvents, forming triazoles (16). That discovery was followed with the use of some aryl aldehyde phenylhydrazones (43), which gave high yields of triazoles (44), scheme 6 [23].

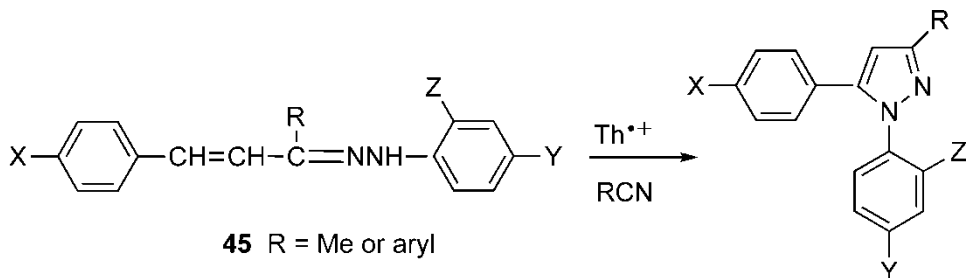
In extending these reactions to arylhydrazones of α , β -unsaturated ketones, Kovelesky and Shine found that, instead of addition to solvent MeCN, intramolecular cyclization occurred [27]. A series of derivatives of benzalacetones (45, R = Me) and chalcones (45, R = aryl) was used and high yields of pyrazoles (46) were obtained in both MeCN and dichloromethane solutions, scheme 7. Formation of 46 was represented as the intramolecular cyclization of 45^{*+} , scheme 8. Apparently, intramolecular cyclization was more facile than intermolecular reaction with solvent. The possibility that pyrazolines were formed first, by acid-catalyzed cyclization of 45, and that the pyrazolines were next oxidized to the final products, was invalidated with control experiments.

Intramolecular cyclization was found to occur exclusively also with the phthalazinyldiazones (47) of some aryl aldehydes (equation (3)). Yields of *s*-triazolo[3,4-*a*]phthalazines (48) greater than 94% were obtained [28]. It is notable here that cyclization occurred by reaction at a heterocyclic nitrogen atom, akin to reactions at the nitrogen atom of solvent nitriles.

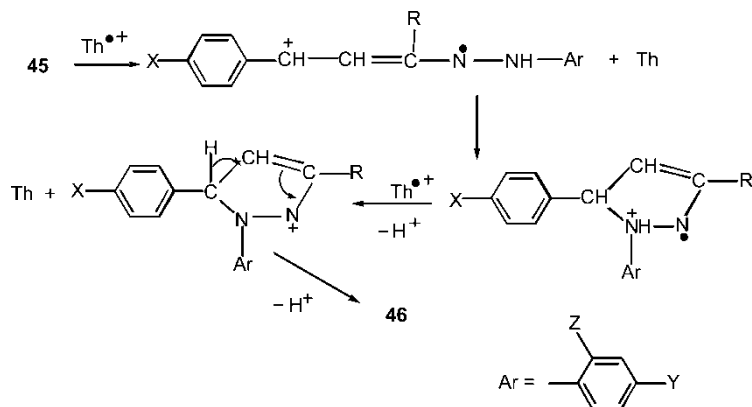


R	X, %44		
	H	Mc	McO
Me	81	71	93
Et	96	-	62

Scheme 6



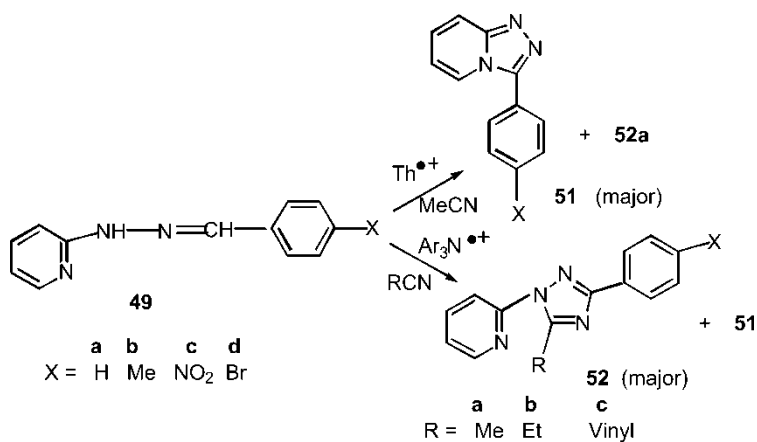
Scheme 7



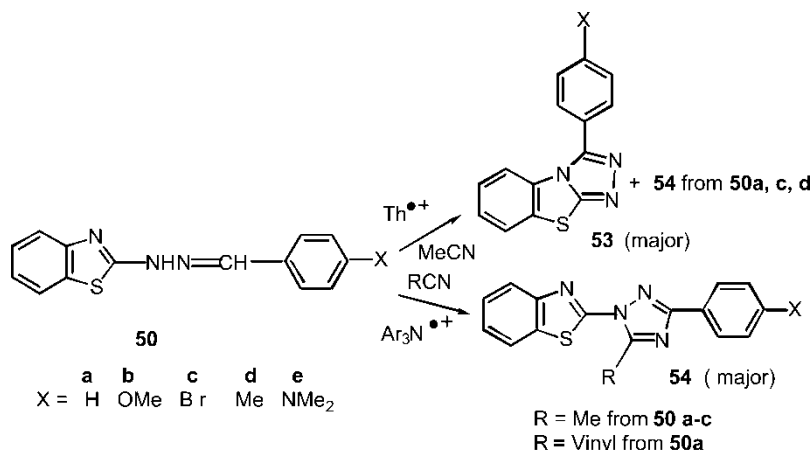
Scheme 8

In related work with pyridylhydrazones (**49**) [29] and benzothiazolylhydrazones (**50**) [30] of aryl aldehydes, Park and coworkers found that both intramolecular cyclization and addition to nitrile solvent occurred. The outcome of reactions of **49** and **50** was made more complex with the use of not only $\text{Th}^{\bullet+}$ as oxidant, but also of the tris(2,4-dibromophenyl)amine cation radical ($\text{Ar}_3\text{N}^{\bullet+}$). Thus, oxidation of **49** by $\text{Th}^{\bullet+}$ led mainly to intramolecular cyclization (**51**) and smaller amounts of addition (**52**) to MeCN. In contrast, oxidation of **49** by $\text{Ar}_3\text{N}^{\bullet+}$ led mainly to **52** and smaller amounts of **51**, scheme 9.

Similar results were obtained with oxidations of **50**, scheme 10. Explaining the divergence in these oxidations presents a challenge. Park has attributed the difference to the difference in oxidation potentials of Th (1.3 V) and Ar_3N (1.5 V) vs SCE. That is, with the poorer oxidant, $\text{Th}^{\bullet+}$, **49** and **50** enter intramolecular cyclization via their cation radicals, $\text{49}^{\bullet+}$ and $\text{50}^{\bullet+}$. On the other hand, the better oxidant, $\text{Ar}_3\text{N}^{\bullet+}$, is said to take **49** and **50** to their dicationic states, e.g., 50^{2+} , and it is the dication that reacts preferentially with solvent RCN. In support of this proposal, is the finding that oxidation of **49a** by tris(4-bromophenyl)aminium ion (oxidation

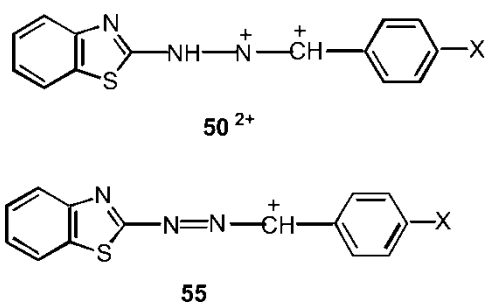


Scheme 9



Scheme 10

potential of $\text{Ar}_3\text{N}^{1.05\text{ V}}$) gave only **51a** and none of **52a**. One may wonder, though, why $\mathbf{50}^{2+}$ would survive in a nitrile solvent rather than shed a proton to diminish the concentration of charge. Loss of a proton from $\mathbf{50}^{2+}$ would leave the nitrilium ion **55** and it is not clear why **55** should not cyclize like $\mathbf{50}^{+}$ and produce **53**.

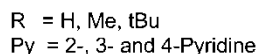
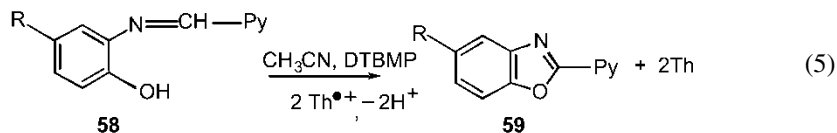
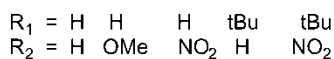
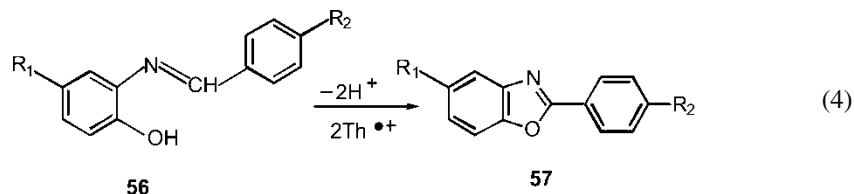


Another possibility may be considered for the difference in pathways initiated by the oxidants $\text{Th}^{\bullet+}$ and $\text{Ar}_3\text{N}^{\bullet+}$. That is, in an initial complex between hydrazone and oxidant, cyclization is inhibited by the structure of the tris(2,4-dibromophenyl)ammonium ion, causing the complex to lead instead to reaction with the solvent.

4. Reactions with phenolic Schiff bases

High yields of benzoxazoles (**57**, equation (4)) [31] and **59** (equation (5)) [32] were obtained in reactions of phenolic Schiff bases (**56** and **58**) with $\text{Th}^{\bullet+}\text{ClO}_4^-$ in MeCN

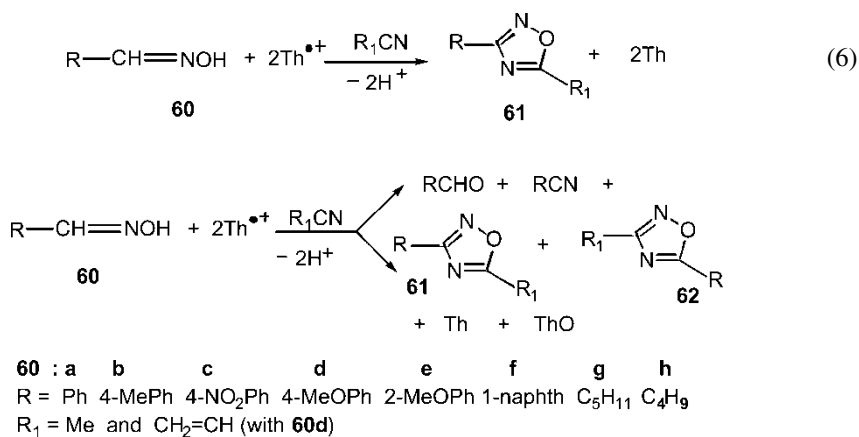
containing DTBMP.



Oxidation of the N = C bond occurred rather than electrophilic attack of $\text{Th}^{\bullet+}$ on the electron rich phenolic ring, a substitution reaction that has been observed in reactions of phenols with $\text{Th}^{\bullet+}$ [33]. Furthermore, intramolecular cyclization within the oxidized Schiff base occurred, rather than reaction with solvent MeCN.

5. Reactions with oximes

At first sight one might expect oximes (**60**) to undergo oxidative addition to nitrile solvents as is the pattern for hydrazones. The products would be oxadiazoles (**61**, equation (6)). But, this is by no means the rule with oximes. In a series of oximes (**60**, scheme 11) the major product was the nitrile RCN [34]. Only with **60d** was a substantial amount of **61d** obtained. With two of the oximes (**60a** and **60c**), significant amounts of an isomeric oxadiazole (**62a** and **62c**) were obtained. Rather than small amounts of ThO, as is often the case with reactions of $\text{Th}^{\bullet+}$ in which hydrolysis of $\text{Th}^{\bullet+}$ is the source of the ThO, the amounts of ThO obtained in the oxime reactions were large and equal to the sum of the amounts of RCHO and RCN.

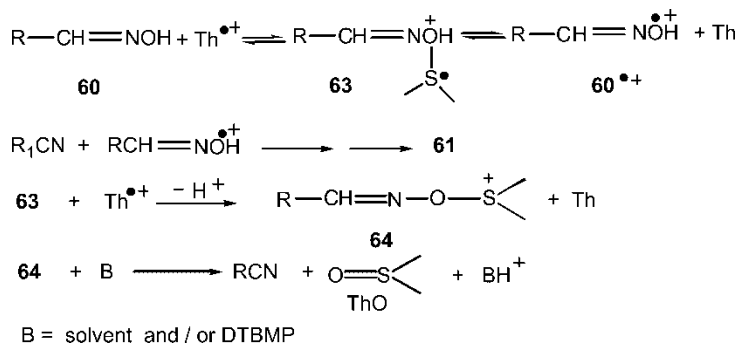


Scheme 11

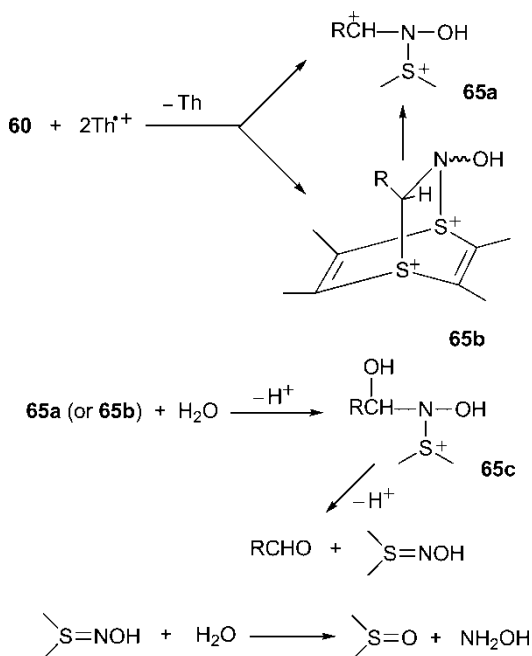
The use of ^{18}O -labeled **60b** and **60d** showed that the oxygen atom in the ThO was derived from the oxime. On the other hand, work up with H_2^{18}O showed that the oxygen atom in RCHO was derived from the H_2O . Another significant observation was that reaction in the presence of DTBMP increased the formation of RCN at the expense, particularly, of forming **61** and **62**. Even in the reactions of **60d**, the yield of **61d** was diminished by adding DTBMP.

To account for the competing formations of **61** and RCN accompanied by ThO, scheme 12 was proposed. In this scheme formation of $\text{60}^{\bullet+}$ is enhanced by electron donating aryl groups as in **60d** and impeded by groups such as in **60a, g, h**.

Formation of RCHO accompanied by ThO was explained with reaction of Th^+ at the nitrogen atom of **60** (scheme 13) giving **65a**, a reaction analogous to those with ammonia and amines [8, 35]. At the time the oxime reactions were studied, however, the cyclic intermediates that govern the reactions of Th^+ with alkenes (section 10.1) had not been discovered. It is possible now to conjecture that the route to **65a** may begin with cycloaddition to the unsaturated



Scheme 12



Scheme 13

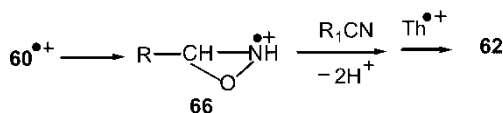
linkage $-\text{CH}=\text{NOH}$, with formation of a cyclic intermediate (**65b**). That is, formation of **65c** may be more complex than depicted originally. The relative importance of the reactions shown in schemes 12 and 13 can be assessed by the amounts of RCN and RCHO that are formed in the reactions of **60**. In all cases, the amount of RCN was many times greater than that of RCHO, establishing scheme 12 as the dominant pathway of these oxime reactions.

Finally, to account for the occasional formation of an isomeric oxadiazole (**62a, c**) the formation of an oxaziridine cation radical (**66**) was invoked, and attack of solvent (R_1CN) on the ring's oxygen atom led eventually to **62** (scheme 14).

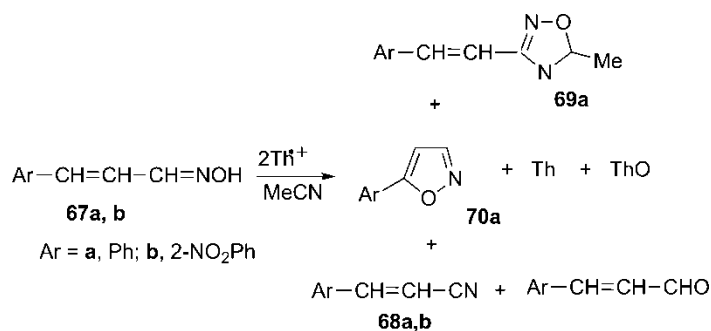
Reaction of $\text{Th}^{\bullet+}$ with cinnamyl aldoxime (**67a**) gave mainly cinnamyl nitrile (**68a**) along with small amounts of an oxadiazole (**69a**) from reaction with the solvent and an isoxazole (**70a**) from intramolecular cyclization (scheme 15) [36]. Neither **69b** nor **70b** were obtained with the use of 2-nitrocinnamaldoxime. Inclusion of DTBMP drove these reactions rapidly toward almost entirely (85%) nitrile formation (**68a, b**).

Reactions of the oximes of unsaturated ketones (**71**) did not go to completion but gave, nevertheless, substantially only isoxazoles (**72**) from intramolecular cyclization. In the presence of DTBMP the reactions went to completion with yields of **72** reaching 88%, scheme 16.

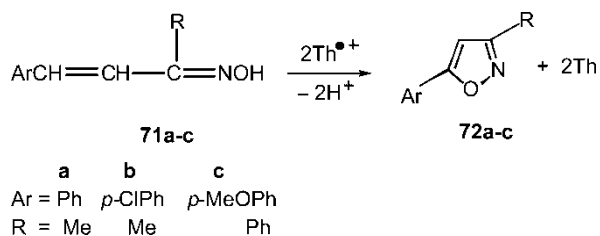
There is yet another facet of the complex reactions of oximes with $\text{Th}^{\bullet+}$. All of the reactions we have described were carried out in an argon atmosphere. In the presence of oxygen an oxime and $\text{Th}^{\bullet+}$ catalyzed the conversion of Th into ThO [34]. Catalysis has been represented as going through the oxime cation radical and has been studied in detail with **60d**,



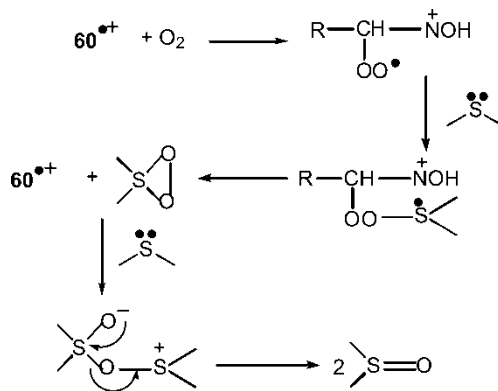
Scheme 14



Scheme 15



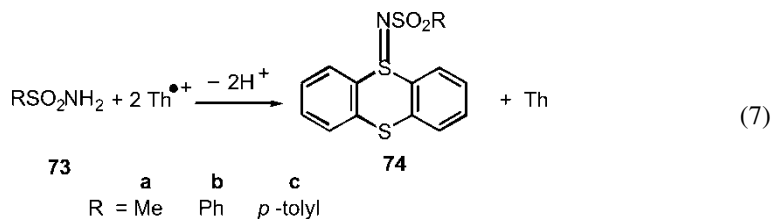
Scheme 16



scheme 17 [37]. The combination of **60d** and Th^{+} served also to catalyze the conversion of other sulfides (R_2S) into sulfoxides (R_2SO) and phosphines (R_3P) into phosphine oxides (R_3PO) [37].

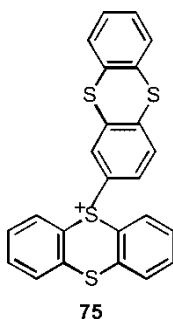
6. Reactions with sulfonamides

Reactions of $\text{Th}^{+}\text{ClO}_4^-$ with methane-(**73a**), benzene-(**73b**) and *p*-toluenesulfonamides (**73c**) and their *N*-aryl derivatives have been carried out. For the most part the reactions have given small or low yields of anticipated thianthrenium products, mixed with varieties of other products attributable to oxidation of the sulfonamide. Sulfonamides **73a–c** themselves reacted with $\text{Th}^{+}\text{ClO}_4^-$ to form sulfilamines (**74a–c**, equation (7)) in yields of 10, 26 and 21%, respectively [38].



The reactions took inordinately long times to go to apparent completion, namely 80, 90, and 40 days respectively. As a consequence, the major product of each reaction was the thianthrenium dimer (**75**). The *N*-propyl and *N*-benzyl derivatives of **73c** were essentially unreactive with $\text{Th}^{+}\text{ClO}_4^-$, from which over very long periods of reaction (90–180 days) the dimer **75** was obtained. In the earliest work with sulfonamide reactions [39], *N*-aryl derivatives of **73b** and **73c** were used. These were the *N*-phenyl (**76a**) and *N*-*o*-tolyl (**76b**) derivatives of **73b**, and the *N*-phenyl (**78a**) and *N*, *N*-diphenyl (**78b**) derivatives of **73c**. Their reactions

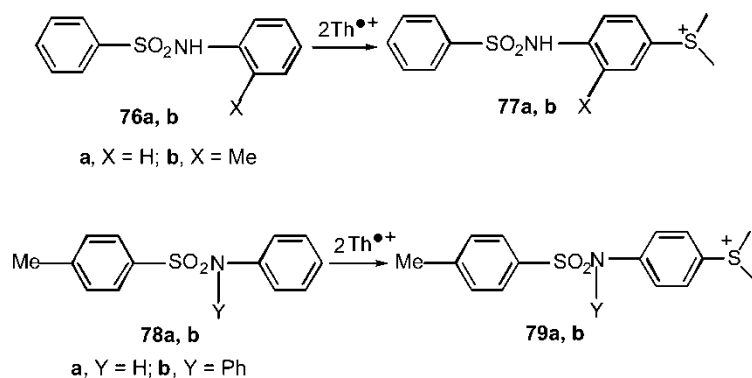
with $\text{Th}^{+\bullet}\text{ClO}_4^-$ resulted in substitution at the *p*-position of the aryl groups (**77** and **79**) as shown in scheme 18.



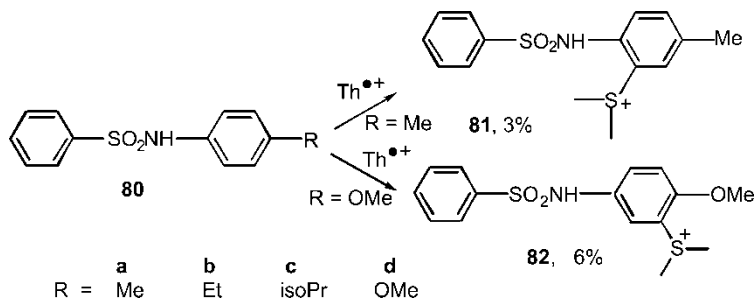
Curiously, the yields of products **77** and **79** were very high, too high, in fact, to suit the customary substitution stoichiometry of $\text{Th}^{+\bullet}$ reactions. The reason for the overly high yields remains unknown.

The effect of having *p*-substituents in the *N*-phenyl group of **76a** has also been explored, with **80a–c** [40] and **80d** [41]. Only **80a** and **80d** gave products containing the 5-thianthrenium group (**81** and **82**), but in very poor yield (scheme 19). The difference in the position of that group in the aryl ring (**81** and **82**) is notable.

Other products were obtained in these reactions whose structures suggest that they originated in oxidations of the sulfonamides. For example, compounds **83** and **84** were obtained from **80a**, and compounds **85–87** from **80b**. Comparable and even more extensive oxidations appeared to have occurred with **80d**. The use of *N*-(*p*-anisyl)methanesulfonamide (**88**) gave

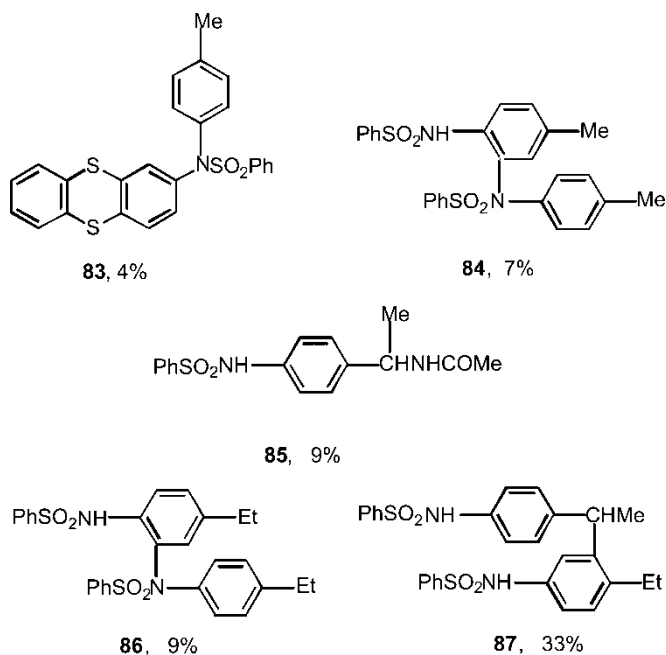


Scheme 18



Scheme 19

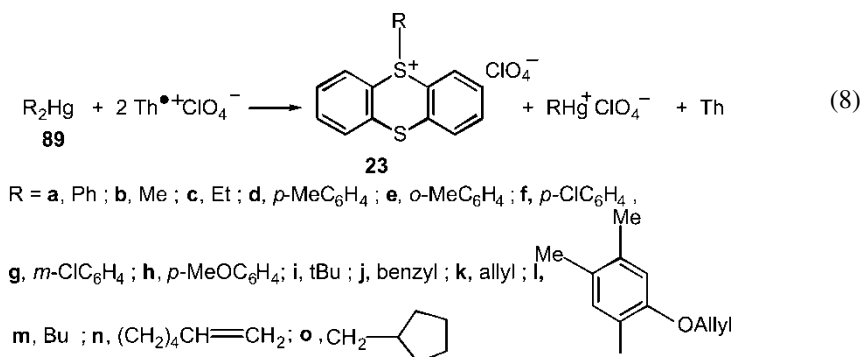
a product analogous to **82** in 5% yield. Most striking was the apparent rapidity of reactions of $\text{Th}^+\text{ClO}_4^-$ with **80d** and **88** and the extensive oxidations that followed, resulting in recovery of 90% of Th.



7. Reactions with organometallics

7.1 Organomercurials

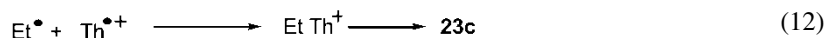
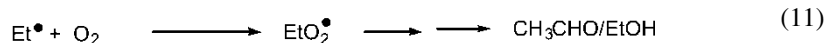
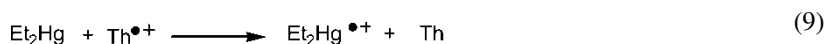
Reactions of Th^+ with organomercurials can be surprisingly complex. We shall see that reactions according to two stoichiometries ($\text{Th}^+:\text{R}_2\text{Hg}$) of 2:1 and 4:1 can be encountered. Furthermore, the question of whether electron-transfer and radical formation were involved is constant. In the first exploration of this chemistry it was found that dialkyl- and diarylmercurials (**89a-h**) reacted cleanly with $\text{Th}^+\text{ClO}_4^-$ as shown in equation (8) [42].



The products were thianthrene (Th), a 5-(substituted)thianthrenium perchlorate (**23**) and an alkyl- or arylmercuric perchlorate which, however, was isolated more conveniently as the

chloride (RHgCl). Each product except for **23c** was isolated in high yield. The simplicity of the reactions was fortuitous, however, as will be seen later, because the stoichiometric amounts of reactants were chosen as 2:1. The mechanism of reaction was not explored. The possibility of initial steps of electron-transfer and R• formation was acknowledged, but it was felt then that the high yield of **23b** and the apparent absence of products from trapping of radicals by oxygen in the air did not lead themselves to an electron-transfer and an alkyl radical sequence. The trapping of radicals by O₂ had been documented by Kochi in oxidations of R₂Hg by the hexachloroiridate ion [43].

Mechanistic exploration of the reactions with Th⁺ClO₄⁻ was begun by Sugiyama and Shine with Et₂Hg and Ph₂Hg. High yields of **23c**, Th and EtHg⁺ (isolated as EtHgCl) were obtained in reactions carried out under both argon and oxygen atmosphere. Small amounts of CH₃CHO and EtOH were obtained from reactions under O₂ and were labeled in ¹⁸O when ¹⁸O₂ was used. It was concluded, therefore, that reaction began with electron-transfer and produced ethyl radicals allowing for trapping of Et• by both Th⁺ and O₂, the Th⁺ being, however, the far better trap (equations (9)–(12)) [44].



There is a problem with the proposed formation and trapping of ethyl radicals, however, in that no corresponding evidence for formation and trapping of phenyl radicals could be found in reactions of Ph₂Hg with Th⁺ClO₄⁻. Neither phenol nor biphenyl were found in reactions carried out in air, although Ph• reacts rapidly with O₂ to form PhOO• from which phenol and or biphenyl might be derived.

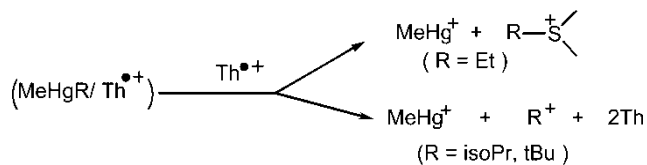
Thus, it appeared that Et₂Hg reacted by one mechanism, electron-transfer and radical formation, while Ph₂Hg reacted by another, either ipso attack displacement at the Ph-Hg bond or collapse of a complex between reactants without phenyl radical formation.

To distinguish between electron-transfer radical formation and direct displacement, the reactions of the series MeHgR (R = Et, isoPr, tBu) were studied [45]. The basis of the study was that if MeHgR^{•+} was formed it should decompose to give the more stabilized R• and MeHg⁺ rather than Me• and RHg⁺. On the other hand, if displacement of a group from MeHgR was to occur, the Me group should be displaced, leaving RHg⁺. In the event, 91–96% of MeHg⁺, isolated as MeHgCl, was obtained, indicative of electron-transfer. Of the groups R in MeHgR, only the Et group found its way to form a 5-alkylthianthrenium salt (**23c** in this case). The fate of the assumed isoPr and tBu radicals was further oxidation by Th⁺ to the cations, and they were found on work up as RNHCOCH₃, ROH, alkene and RCl.

All of these reactions were carried out under argon, avoiding the possibility (and question) of trapping radicals by O₂. Thus, with the MeHgR reactions the case appears to have been made for an electron-transfer reaction and decomposition of MeHgR^{•+}. Whether or not the same results would be obtained from a reaction involving a complex (scheme 20) is not known.

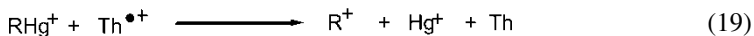
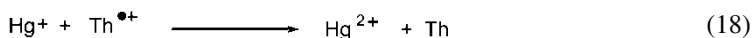
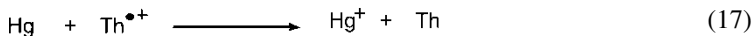
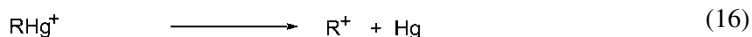
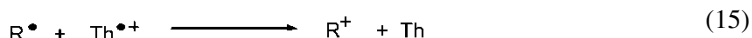
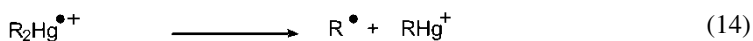
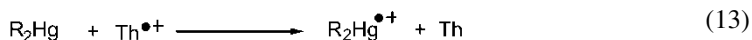
Apart from the usual type products described above, reactions of MeHgR with Th⁺ also gave small amounts of 1-RTh and 2-RTh (R = Et, isoPr). The products were attributed to reactions of R• at a ring position of Th⁺. Similarly, small amounts of such products were obtained in reactions of Et₂Hg and Bu₂Hg with Th⁺ClO₄⁻ [45].

We turn now to a surprising finding that some dialkyl and diarylmercurials can react with Th⁺ beyond the 2:1 level of reactant ratio, the reactions consuming four moles of Th⁺ per



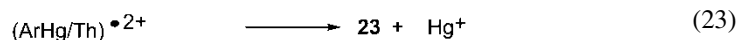
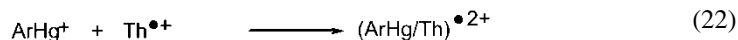
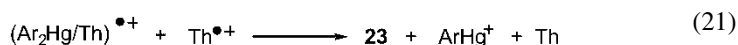
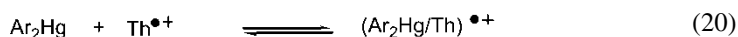
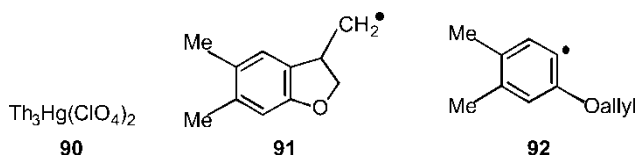
Scheme 20

mole of mercurial. This was first found in reactions of three R_2Hg : $\text{R} = \text{tBu}$ (**89i**), benzyl (**89j**), allyl (**89k**) [45]. The products of reactions containing group R were, after work up, mainly RNHCOCH_3 , ROH , and RCl . Only the allyl group appeared as a 5-alkylthianthrenium perchlorate, in 40% yield. The mercury content of these R_2Hg appeared as metallic Hg, and/or the ions Hg^+ and Hg^{2+} , isolated as Hg_2Cl_2 and HgO in the work up. Small amounts of isobutene and even smaller amounts of isobutane were obtained from reactions of tBu_2Hg . Thus, these three mercurials were divested of their Hg atoms in oxidation, a circumstance that can be represented with equations (13)–(19).



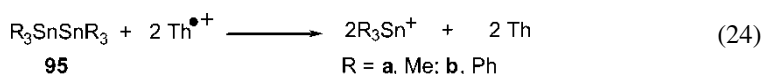
Equations (13)–(16) represent the complete decomposition of R_2Hg into R^+ and Hg at the $\text{Th}^{\bullet+}/\text{R}_2\text{Hg}$ ratio 2:1. This, in fact, describes the reactions of $\text{Th}^{\bullet+}\text{ClO}_4^-$ with tBu_2Hg in the 2:1 ratio, from which metallic Hg was obtained in 88–92% yield. With a reactant ratio of 4:1 of $\text{Th}^{\bullet+}\text{ClO}_4^-$ and tBu_2Hg , the mercury content was obtained as Hg_2Cl_2 and HgO . Depending on the method of work up used in the reactions of these R_2Hg , an entirely new type of product, $\text{Th}_3\text{Hg}(\text{ClO}_4)_2$ (**90**), could be isolated. In this product the Hg^{+2} ion, as $\text{Hg}(\text{ClO}_4)_2$, is shown to be complexed with Th, awaiting conversion into Th and HgO in an alternate work up procedure. The complete oxidation of these R_2Hg at 4:1 reactant ratio stems from the instability and/or reactivity of the corresponding ions RHg^+ . In the case of tBu_2Hg the instability of free tBuHg^+ (equation (14)) appears to have been experienced in the reaction at the 2:1 ratio. Covalent PhCH_2HgCl and tBuHgCl were found separately to be oxidizable by $\text{Th}^{\bullet+}\text{ClO}_4^-$, while even metallic Hg was found to be oxidizable by $\text{Th}^{\bullet+}\text{ClO}_4^-$ to Hg^+ and Hg^{2+} , depending on the relative amounts $\text{Th}^{\bullet+}$ and Hg [45]. The complete oxidation of di-*tert*-butyl-, dibenzyl- and diallylmercury may be thought to be relatable to the stability of the corresponding cations (R^+). That, however, is not a controlling factor because complete oxidation of a number of diaryl mercurials was also, surprisingly, found to occur [46]. The reactive Ar_2Hg were **89d**, **89e**, **89h**, and di(2-allyloxy-4,5-dimethylphenyl)mercury, **89i**. Diphenyl mercury (**89a**) did not react beyond the 2:1 reactant ratio. The difference between R_2Hg and Ar_2Hg in the 4:1 reactions was that all of the aryl groups in Ar_2Hg ended as 5-arylthianthrenium perchlorate **23** ($\text{R} = \text{aryl}$) meaning that ArHg^+ , as well as Ar_2Hg , reacted with $\text{Th}^{\bullet+}$. The Hg atoms in Ar_2Hg ended in the complex **90** or, as a consequence of work up, as HgO and small amounts

of Hg_2Cl_2 . No evidence for aryl radical involvement was found. In fact, **89i** gave only **23i** in which the allyloxy group remained intact. No evidence for cyclization (**91**) of the 2-allyloxy-4,5-dimethylphenylradical (**92**) was found. The reactions of the Ar_2Hg can be described with equations (20)–(23) and (18).

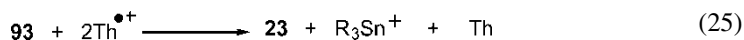


7.2 Organotin

Reactions of three classes of organotin with $\text{Th}^+\text{ClO}_4^-$, carried out under argon, have been reported [47]. Of these, reactions of R_4Sn (**93**) and R_3SnMe_3 (**94**) parallel those of R_2Hg and RHgMe to a considerable extent. Reactions of R_3SnSnR_3 (**95**) resulted in oxidative cleavage of the Sn-Sn bond (equation (24)) and will not be considered further.

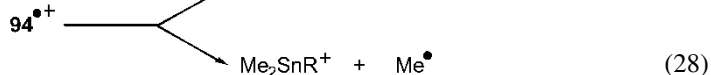
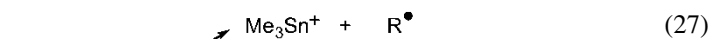
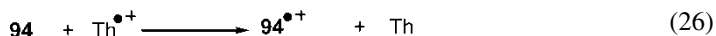


The studies of reactions of **93** (R = **a**, Me; **b**, Et; **c**, Bu; **d**, Ph; **e**, vinyl, and **94** (R = **a**, Et; **b**, isoPr; **c**, tBu; **d**, allyl; **e**, vinyl; **f**, Ph) were designed, as with those of the R_2Hg and RHgMe series, to seek evidence for an electron-transfer mechanism, a mechanism which had earlier been uncovered with similar stannanes by Kochi and coworkers [48]. Reactions of all of **93a–e** gave good yields of **23a–c**, **m**, **p** (R = vinyl) and R_3Sn^+ (isolated as R_3SnCl), equation (25).



Small amounts of 1-RTh, 2-RTh and R_2Th were obtained with **93a–c**. About 7% of the Ph groups in **93d** ended as benzene and, similarly, about 7% of the vinyl groups in **93e** as ethene. These results were accepted as complying with a mechanism of electron-transfer/radical formation. As had been found in reactions of dialkylmercurials (e.g., **89i**, **k**), among **94b–d** only the allyl radical (from **94d**) was trapped as a 5-alkylthianthrenium salt. Most of the isoPr (**94b**) and tBu (**94c**) radicals were oxidized to their cations. Small amounts of 1-isoPrTh and 2-isoPrTh were obtained, indicative of trapping isoPr radicals at ring position of $\text{Th}^{\bullet+}$. In the reactions of **94** only those of **94b–d** resulted in complete cleavage of the R-Sn bond

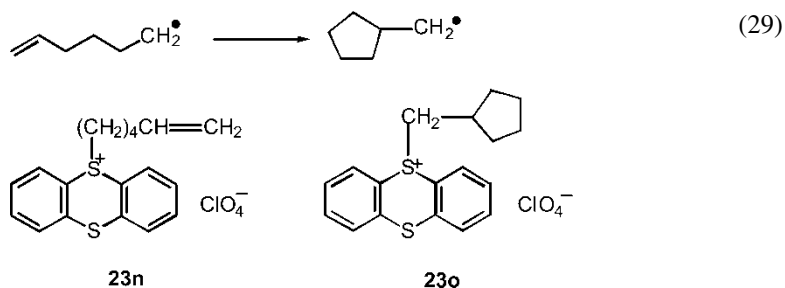
and formation of Me_3Sn^+ (equations (26) and (27)).



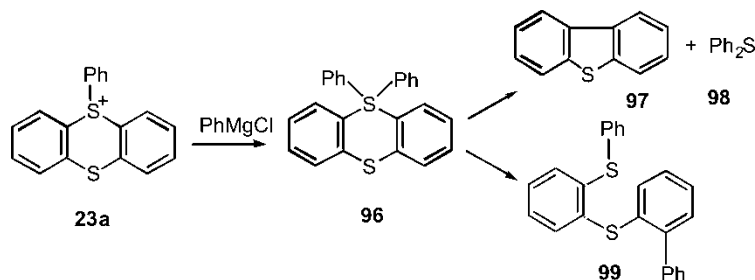
Cleavage of the R-Sn and Me-Sn bonds occurred competitively in reactions of **94a**, **e**, **f** (equations (27) and (28)), causing the formation of two 5-R-thianthrenium perchlorates; that is, one with R = Et, Ph or vinyl and the other one with R = Me. The ratios of cleavage of groups was found to be Et/Me (24), Ph/Me (14), vinyl/Me (12). Extraordinary amounts of hydrocarbon (RH) were obtained from **94d-f**; that is, propene from **94d** (17% of allyl groups), benzene from **94f** (38% of phenyl groups) and ethene from **94e** (23% of vinyl groups).

7.3 Reactions with Grignard reagents

Reactions of $\text{Th}^+\text{ClO}_4^-$ with Grignard reagents differed in several respects from reactions with organomercurials and organostannanes. First, the reactions with Grignards could not be carried out in MeCN. The solvents were ether and tetrahydrofuran (THF) in which $\text{Th}^+\text{ClO}_4^-$ is not soluble and had to be used in suspension. Reactions involving these two solvents gave unquestionable evidence of radical formation. In addition, results of reactions in ether differed in some respects from those in THF. From reactions with RMgCl , R = butyl (Bu), 2-butyl (sBu) and *tert*-butyl (tBu), in ether substantial amounts of RH and significant amounts of alkene, R(-H), were obtained, attesting to abstraction of H^{\bullet} from the solvent and to disproportionation of R^{\bullet} . With only BuMgCl was R. trapped by Th^+ to form **23m** (R = Bu) [49]. Reactions of $\text{Th}^+\text{ClO}_4^-$ with 5-hexenylMgCl gave evidence of the formation of the 5-hexenyl radical and its cyclization (equation (29)) to the cyclopentylmethyl radical. The RH formed in the reaction was a mixture of 1-hexene and cyclopentylmethane (CPM) in which the amount of CPM (14%) was greater than obtained (9%) from the Grignard alone. Moreover, a mixture of two 5-thianthrenium perchlorates, (**23n**, **o**) was obtained, containing 36% of **23o**. These results leave no doubt that electron-transfer from RMgCl to Th^+ had occurred [49].



Strong evidence for electron-transfer was given also in the reaction of $\text{Th}^+\text{ClO}_4^-$ with PhMgCl in ether [50]. Large amounts (44–57%) of benzene were formed, greater, in fact, than of **23a**. Small amounts of $\text{CH}_3\text{CH}(\text{Ph})\text{OEt}$, biphenyl, 1-PhTh, and 2-PhTh were also obtained, indicative of Ph^{\bullet} involvement. Evidence was obtained showing that PhMgCl also attacked the primary product (**23a**), scheme 21. Small amounts of dibenzothiophene (**97**, 2%), diphenyl sulfide (**98**, 2%) and 2-phenyl-2'-(phenylthio)diphenylsulfide (**99**, 15%) were formed. The origin of (**97–99**) was ligand coupling in the sulfurane **96**.



Scheme 21

Reactions of RMgCl with $\text{Th}^{+\cdot}\text{ClO}_4^-$ in THF led to large amounts of RH, attesting again to the involvement of R^\bullet in hydrogen-atom abstraction from the solvent. Formation of 5-R-thianthreniumyl perchlorates (**23a**, **m**) was found with R = Ph [50] and Bu [49]. Polymerization of THF occurred in the reactions of all of the RMgCl.

7.4 Phenyllithium

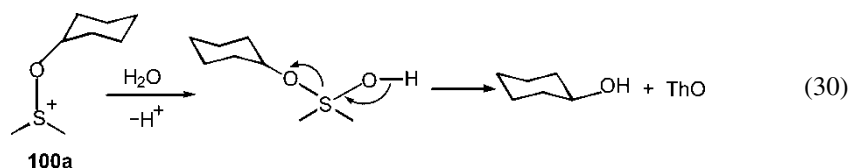
Phenyllithium (PhLi) reacted quickly with a suspension of $\text{Th}^{+\cdot}\text{ClO}_4^-$ in ether. The greater part of the phenyl group in PhLi was converted into benzene. Small amounts of $\text{CH}_3\text{CH}(\text{Ph})\text{OEt}$ and biphenyl were formed too. None of **23a** was isolable but evidence for its having been formed was provided by identification of small amounts of **97** and **98** [50].

8. Reactions with alcohols, pinacols and phenols

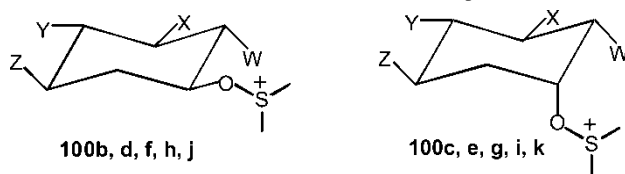
8.1 Reactions with alcohols

Reactions of $\text{Th}^{+\cdot}\text{ClO}_4^-$ with alcohols were first reported by Shine and Yueh in the early 1990s [51–53]. It was recognized at that time that 5-alkoxythianthrenium salts had been formed; but the salts were thought, erroneously, to be unstable in MeCN solution, decomposing into alkenes and ThO soon after formation. It remained for Zhao and Shine to show later that 5-alkoxythianthrenium perchlorates were formed and isolable in good yields from reactions in dichloromethane, and that the chemistry attributed earlier to decompositions in solution was occurring in the inlets of GC columns [54–56].

The first salt to be isolated was 5-cyclohexyloxythianthrenium perchlorate (**100a**) [54]. Thermal decomposition into cyclohexene and ThO was shown to occur in MeCN solution, slowly at 50 °C and rapidly at 100 °C. Cleavage of **100a** in MeCN by aqueous K_2CO_3 into cyclohexanol and ThO occurred quantitatively, and use of H_2^{18}O showed that H_2O was the source of the oxygen atom in the ThO (equation (30)).



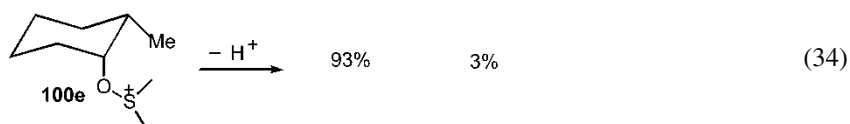
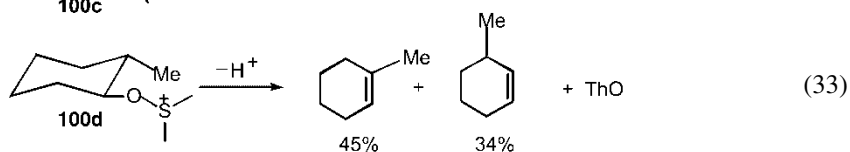
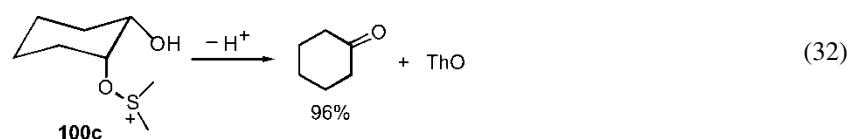
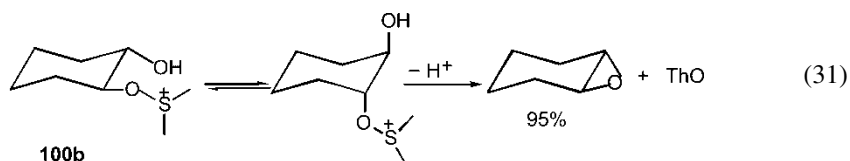
Thereafter, analogs of **100a** were prepared from five sets of *cis*- and *trans*-substituted cyclohexanols. The 5-thianthrenium perchlorates (**100b–k**, table 1) were shown with NMR

Table 1. *Cis*- and *trans* 5-(substituted)thianthrenium perchlorates (**100b–k**)

100	W	X	Y	Z	100
b	OH	H	H	H	c
d	Me	H	H	H	e
f	H	H	H	Me	g
h	H	H	Me	H	i
j	H	Me	H	Me	k

spectroscopy and, in some cases, X-ray crystallography, to have retained the configuration of the parent cyclohexanols [55].

Each of these salts underwent decomposition in MeCN at 100 °C to give products consistent with its structure. Some examples are given in equations (31)–(34).

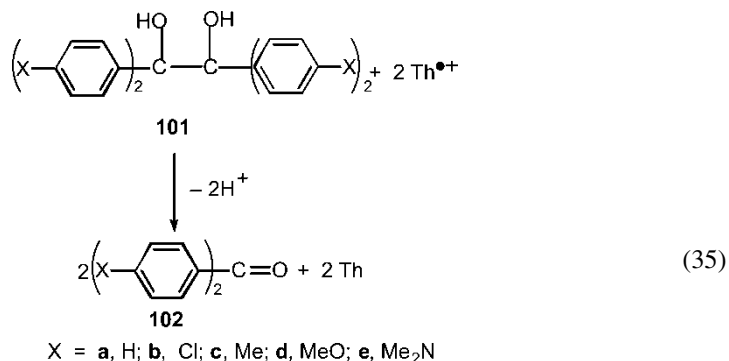


Successful isolation and characterization of 5-alkoxythianthrenium perchlorates was also achieved with a series of 23 acyclic primary and secondary alcohols [56]. Several of these were again subjected to thermal decomposition in dichloromethane and MeCN solutions and were found to give ThO and alkenes consistent with their structures.

These thermal decompositions and those of the cyclohexyloxy derivatives [55] confirmed the character of the earlier findings of Shine and Yueh in which decomposition occurred in the GC inlet [51–53]. The later results [54–56] are definitive of the reactions of alcohols with Th⁺. Reactions of a series of 5-alkoxythianthrenium perchlorates with I⁻ and Br⁻ were studied [56] and results are reported later in this review.

8.2 Reactions with arylpinacols

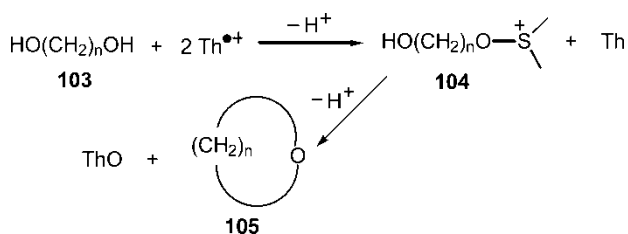
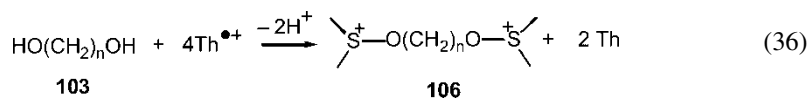
Quantitative oxidations of a number of tetraarylpinacols (**101a–e**) into diaryl ketones (**102a–e**) occurred in reactions with $\text{Th}^+\text{ClO}_4^-$ and Th^+BF_4^- (equation (35)) provided that a sufficient amount of DTBMP was present to prevent acid catalyzed pinacol rearrangement [57]. Similar oxidations of 2,3-diphenyl-2,3-butanediol (to acetophenone) and of 1,1-dimethyl-2,2-diphenylethanediol (to acetophenone and acetone) occurred cleanly. Oxidation of pinacol itself appeared not to occur; instead small amounts of pinacolone and tetramethyloxirane were obtained.



8.3 Reactions with α , ω -diols

In an early report on the reactions of alcohols with $\text{Th}^+\text{ClO}_4^-$, it was noted that reaction of 1,5-pentanediol gave 98% of tetrahydropyran [52]. The formation of a cyclic ether from reactions of 1,4-butanediol and 1,6-hexanediol was also been recorded [58]. It was recognized at that time that each cyclic ether was probably formed from an intermediate α -(5-thianthreniumoxy)- ω -alkanol **104**, scheme 22.

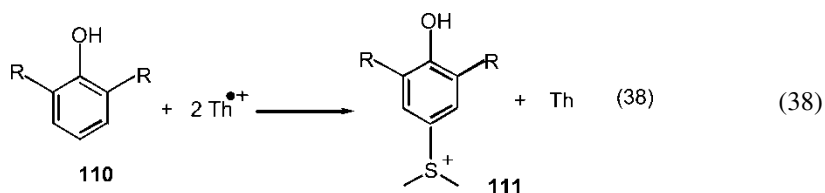
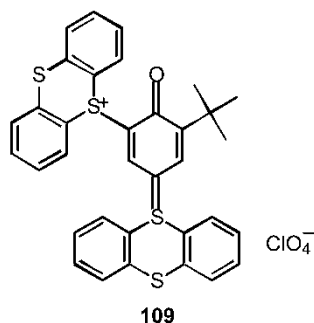
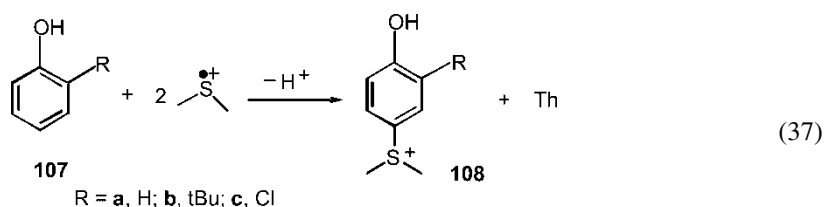
Later work has validated this conception with the isolation of a series of **104** tetrafluoroborates, $n = 4-10, 12$. Isolation of **104** was accomplished from reactions of Th^+BF_4^- with an excess of α , ω -diol **103** (ratio Th^+ : diol 1/4). Conversion of **104** into cyclic ethers (**105**) was achieved only with $n = 4-6$. With the use of an excess of Th^+BF_4^- (Th^+ : diol 2/1 and 4/1) α , ω -bis(5-thianthreniumoxy)alkanes **106** were obtained in good yield, equation 36 [59].



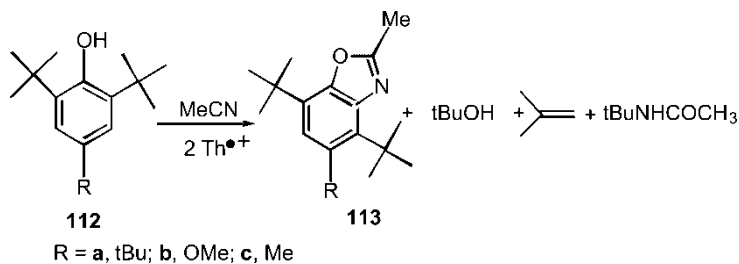
Scheme 22

9. Reactions with phenols

It was shown a long time ago that phenols (**107**) do not react with Th^+ at their oxygen atom. Instead, Th^+ behaves as an electrophile and aromatic electrophilic substitution occurs (equation (37)) [60,61]. Later, it was shown by Shin that when an excessive amount of $\text{Th}^+\text{ClO}_4^-$ was used in reaction with **107b**, both **108b** and **109** were formed in a 2:1 ratio [33]. 2,6-Disubstituted phenols (**110a-f**) underwent substitution in the 4-position, (equation (38)) [33]. Good yields of **111a-c** were obtained, whereas reactions of **110d-f** gave only 50–60% yields of **111** in reactions that appeared not to go completion. Some other phenols bearing *tert*-butyl groups underwent interesting oxidation and substitution reactions. Benzoxazoles (**113a-c**), for example, were obtained from the 2,6-di-*tert*-butylphenols **112a-c** (scheme 23). Benzoxazoles analogous to **113a** were obtained from reactions of **112a** in solvents EtCN and $\text{CH}_2=\text{CHCN}$.

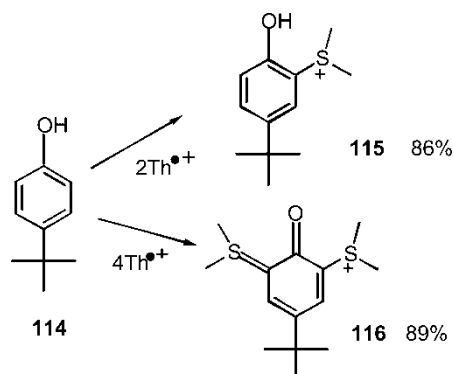


R = a, Me; b, iPr; c, tBu; d, Cl; e, Br; f, F



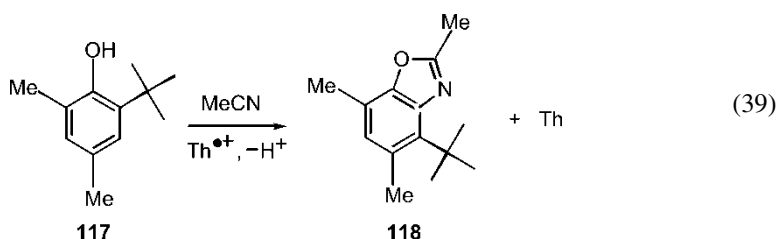
Scheme 23

4-*tert*-Butylphenol (**114**) underwent substitution at the 2- and the 2,6-positions, depending on the relative amount of $\text{Th}^{\bullet+}$ that was used (scheme 24). Formation of **116** occurred by deprotonation of its di-(5-thianthrenium) precursor. Deliberate deprotonation of all (5-thianthrenium)-phenols (**108** and **111**) by treatment with base was also reported.

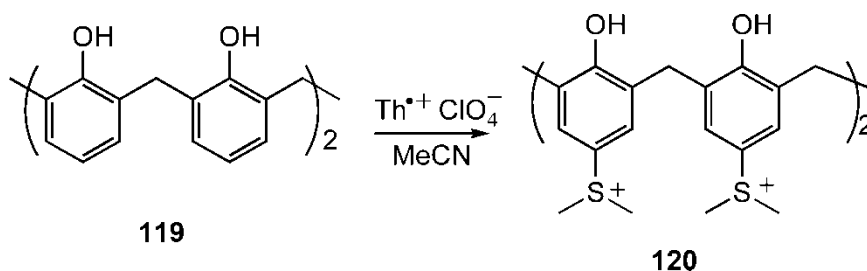


Scheme 24

Formation of a benzoxazole (**118**) from 2,4-dimethyl-6-*tert*-butylphenol (**117**) was accompanied with rearrangement (equation (39)).



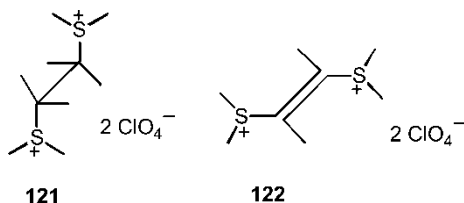
The ease of reaction of $\text{Th}^{\bullet+}$ with phenols has been applied to a calix[4]arene, shown as **119**, in which the four arene units were phenol [62]. This is shown in abbreviated form in scheme 25. Similar results were obtained with a calix[4]arene containing OMe groups in place of OH groups.



Scheme 25

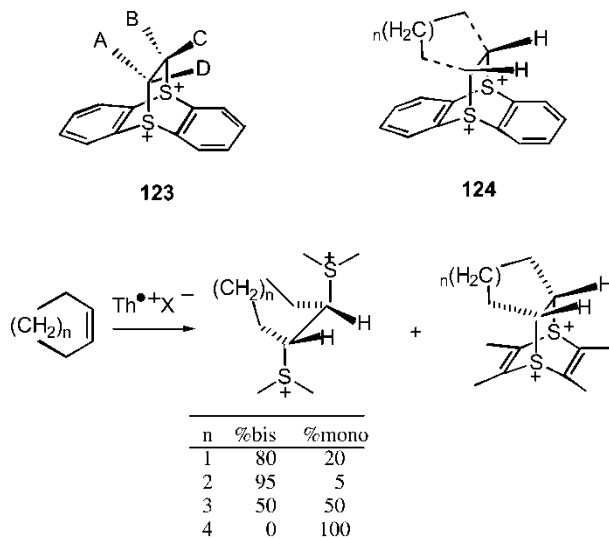
10. Reactions with alkenes, cycloalkenes and alkynes

Additions of $\text{Th}^+\text{ClO}_4^-$ to alkenes, cycloalkenes and alkynes have been known for 25 or more years. At that earlier time the adducts were known to contain two thianthrenium units, that is, as in **121** from addition to double bonds and as in **122** from addition to triple bonds [63]. The trans relationship of the two thianthrenium units in **121** was deduced chemically in the early work [64] and proven later with X-ray crystallography of the adduct of cyclohexene [65]. The trans relationship in **122** was demonstrated also in later years, when the fuller picture of additions to C-C unsaturated bonds was brought out, as presented below.



10.1 Additions to alkenes and cycloalkenes

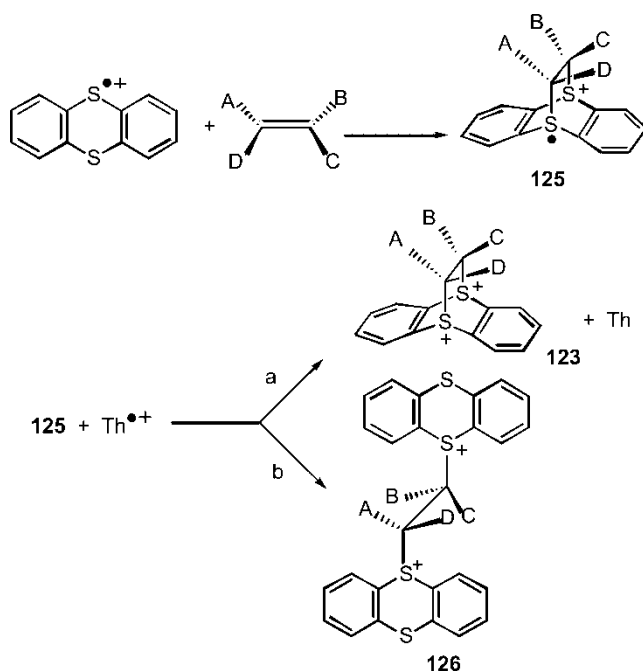
Recent work [66–68] has shown that two types of adduct can be formed when Th^+ reacts with a C-C double bond. They are bisadducts, the type **121** that was first discovered [63–65], and monoadducts, shown as **123** for acyclic alkenes and as **124** for cycloalkenes. Each class of adduct (**121–124**) is dicationic; the counter ions may be ClO_4^- (as in the earliest work) or BF_4^- , PF_6^- and SbF_6^- as preferred in the later work [66–69]. Additions to cycloalkenes have been confined to cyclopentene, cyclohexene, cycloheptene, cyclooctene and 4-methylcyclohexene. From each of these cycloalkenes except cyclooctene, both bis- and monoadducts have been obtained in relative amounts varying with the ring, scheme 26. From cyclooctene, only a monoadduct has been obtained [66, 67]. It can be seen in scheme 26 that the two 5-thianthrenium units in the bisadducts are *trans*-related; the bondings of the 5,10-thianthreniumdiyl portion of monoadducts are *cis*-related.



Scheme 26

Addition of $\text{Th}^{\bullet+}\text{X}^-$ to alkenes gave, similarly, mixtures of bis- and monoadducts, the relative amounts again varying with the alkenes' structures. In general, among the 13 alkenes that were used, cis alkenes gave more bis- than monoadduct, while the opposite was found with trans alkenes [67, 68].

Most striking of these additions was their stereospecificity. That is, the configuration of an alkene was retained in both the bis- and monoadduct derived from the alkene. This was shown with X-ray crystallography of a number of adducts and confirmed with NMR spectroscopy of all adducts. Retention of configuration in both types of adduct led to an understanding of how the additions occur (scheme 27) [67, 68]. The configurations of the adducts becomes established in the first step of reaction, a stereospecific cycloaddition that forms a dionic cation radical (**125**). Thereafter, **125** reacts with a second $\text{Th}^{\bullet+}$ either by electron-transfer (path a) to give a monoadduct (**123**) and Th, or by displacement to give a bisadduct (**126**). In that way, the configurational relationship of groups A–D in the alkene is retained; cis alkenes thus gave erythro monoadducts and threo bisadducts, whereas trans alkenes gave threo monoadducts and erythro bisadducts [68]. The mixture of groups A–D in an alkene (scheme 27) was initially defined as A = B = D = alkyl or H, C = H, when it was believed that tetraalkyl ethenes did not form adducts. Later, it was found that 2,3-dimethyl-2-butene (A = B = C = D = Me) does indeed form a monoadduct; it is unstable in MeCN at room temperature and was detectable with NMR spectroscopy only at low temperatures. The decomposition is discussed further in this review.



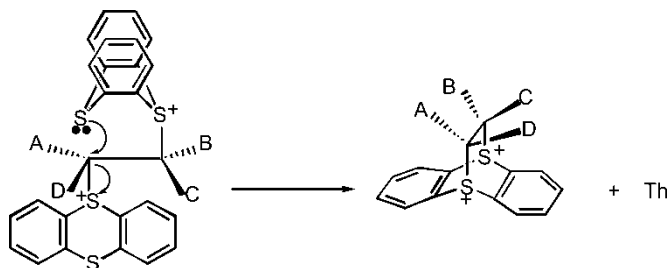
Scheme 27

Several reactions of adducts were encountered during the studies of their formation: the slow intramolecular conversion of bis- into monoadducts; the conversion of both bis- and monoadducts into (5-thianthreniumyl)alkenes; and the decomposition of monoadducts of highly branched alkenes in MeCN to form 2-oxazolines. These reactions are reported in this review.

10.2 Conversion of bis- into monoadducts

Conversion of bis- into monoadducts was encountered frequently in attempts to isolate pure bisadducts by fractional crystallization of mixtures of adducts. It is a slow reaction, too slow to account for the initial formation of both bis- and monoadduct in the additions of Th^{+} to an alkene; those additions occur competitively, in parallel.

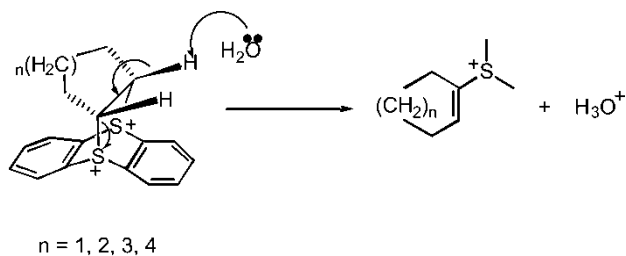
Conversion of a bis- into a monoadduct occurs by intramolecular displacement of Th from the bisadduct (scheme 28) [67]. The conversion was confirmed with the use of isolated bisadducts of cycloheptene and *cis*-2-butene [67].



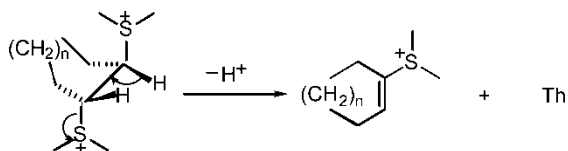
Scheme 28

10.3 Formation of (5-thianthreniumyl)alkenes

Formation of (5-thianthreniumyl)alkenes was first observed as a slow, spontaneous reaction when monoadducts of cycloalkenes were kept in MeCN solution. The rate of ring-opening deprotonation was increased by the addition of small amounts of water to the solution, scheme 29 [67]. Subsequently, it was found that both mono- and bisadducts of cycloalkenes and alkenes could be converted rapidly into (5-thianthreniumyl)alkenes by stirring solutions in MeCN with basic alumina for short times [68]. The conversion of a bisadduct requires not only deprotonation but also loss of Th, shown for cycloalkene adducts in scheme 30.

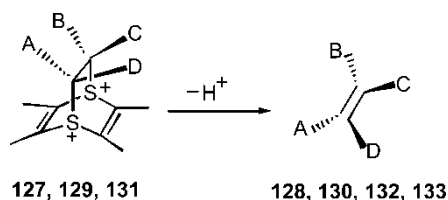


Scheme 29



Scheme 30

Among adducts of acyclic alkenes eliminations were more complex. A monoadduct of a symmetrical alkene gave a single (5-thianthreniumyl)alkene, whose configuration (*E*- or *Z*-) depended on the configuration of the original alkene. For example, the adduct (**127**) of *trans*-2-butene gave (*Z*)-2-(5-thianthreniumyl)-2-butene (**128**), whereas the adduct (**129**) of *cis*-5-decene gave (*E*)-5-(5-thianthreniumyl)-5-decene (**130**), scheme 31.

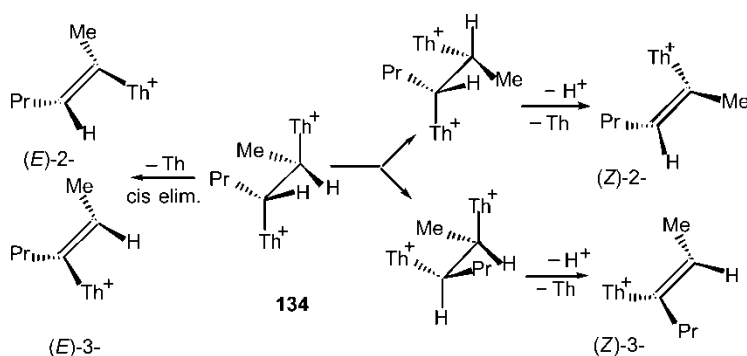


	A	B	C	D
127	Me	H	Me	H
128	Me	Th ⁺	Me	H
129	Bu	Bu	H	H
130	Bu	Bu	Th ⁺	H
131	Me	H	Et	H
132	Me	Th ⁺	Et	H
133	Me	H	Et	Th ⁺

Scheme 31

A monoadduct of an unsymmetrical alkene gave two (5-thianthreniumyl)alkenes; for example, **132** and **133** from the adduct (**131**) of *trans*-2-pentene (scheme 31).

Even more complex were eliminations from bisadducts, because rotation about the central bond allowed for elimination of H⁺ and Th from more than one conformer. Thus, the bisadduct (**134**) of *cis*-2-hexene gave a mixture of four products (*E*)-2-, (*E*)-3-, (*Z*)-2- and (*Z*)-3-(5-thianthreniumyl)-2-hexene, scheme 32 [68].

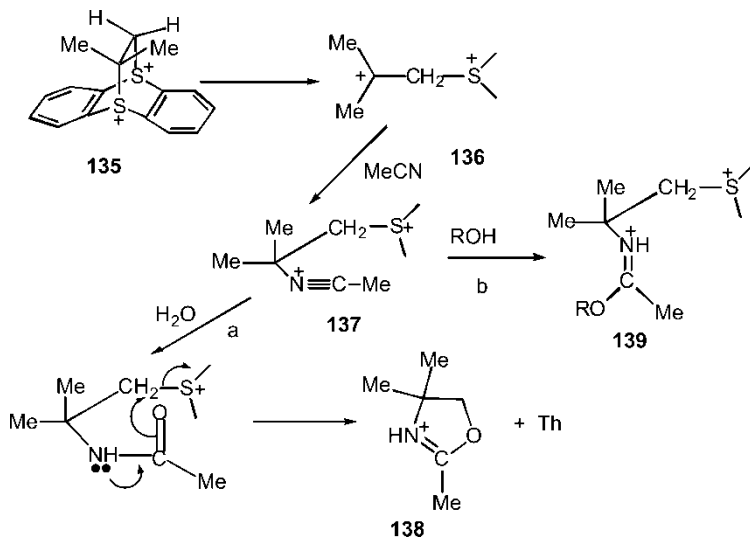


Scheme 32

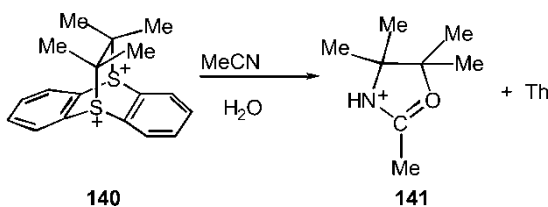
10.4 Formation of 2-oxazolines

Formation of 2-oxazolines occurred when monoadducts of some branched alkenes were allowed to stand in MeCN solution [69]. The chain's branching in the adduct had to be such as to allow for the slow spontaneous cleavage of a C—S⁺ bond with formation of a

carbonium ion. Adducts that had this property were those of isobutene, 2-methylbutene, 2-methyl-2-butene, and 2-methylpentene. The sequence of the reactions that ensued is shown in scheme 33 with the adduct of isobutene (**135**). Spontaneous opening of the adduct gave the dication (**136**), which by Ritter reaction with the solvent gave **137**. The intermediate **137** next reacted with water in the solvent, and the amide thus formed cyclized with loss of Th to give protonated 2,4,4-trimethyl-2-oxazoline (**138**). It was found that by including small amounts of an alcohol (ROH) in the solvent, formation of **138** could be diverted into formation of a 5-[(1-alkoxyalkylidene)ammonio]alkylthianthrenium salt (**139**) [69].



We have referred above to the monoadduct of 2,3-dimethyl-2-butene (DMB). That adduct (**140**) could not be detected when DMB reacted with Th⁺ in MeCN at room temperature. Reaction led instead only to Th [68]. Subsequently, it was found that an adduct is formed and is isolable if prepared at -15°C ; its formation at -15°C was characterized with ¹H NMR spectroscopy [70]. The adduct has short life in MeCN at room temperature, too short to be detectable in the time scale of NMR spectroscopy. At room temperature, protonated 2,4,4,5,5-pentamethyl-2-oxazoline (**141**) was formed, as in scheme 34. With more rapid scanning voltammetry the formation of **140** was detectable at 25°C [70]. It appears that addition to DMB is made rapid by its electron-rich nature, but the adduct is also readily opened for carbonium ion formation at either of its junctions, resulting in the formation of **141** and Th, scheme 34.

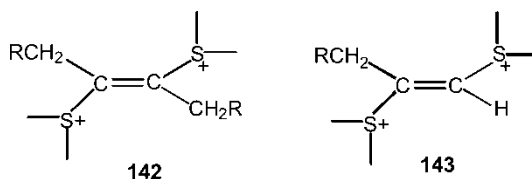


10.5 Addition to vinylpyridines

Bisadducts of $\text{Th}^+\text{ClO}_4^-$ to 2- and 4-Vinylpyridines have been reported by Woo *et al.* [71].

10.6 Addition to alkynes

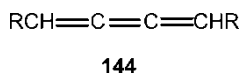
When additions of $\text{Th}^+\text{ClO}_4^-$ to alkynes were first reported, no information about the configuration of the adducts was available [63]. New work with two series of alkynes, symmetrical [72] and terminal [73], has settled the point of configurations with X-ray crystallography and NMR spectroscopy; adducts are *trans*-di-(5-thianthreniumyl)alkenes **142** and **143**.



142, R = H, Me, Et, Pr

143, R = Et, Pr, Bu, pentyl, hexyl, heptyl

These adducts were found to undergo some remarkable reactions when stirred in MeCN solutions with basic alumina. The adducts **142** were converted into cumulenes (**144**) and the cumulenes themselves were converted by further reactions with solvent MeCN and water in the solvent (or on the alumina) into α -hydroxyalkynes (**145**) and α -acetamidoalkynes (**146**), scheme 35; and into α , β -diketones (**147**) and hydrogen, scheme 36. The alkyne itself was also regenerated from part of the **142**, along with ThO and Th (scheme 37).

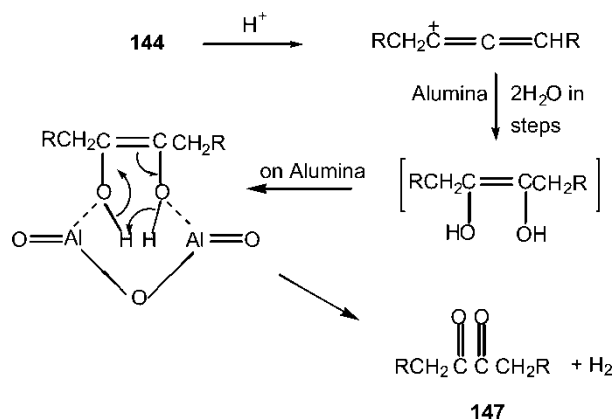
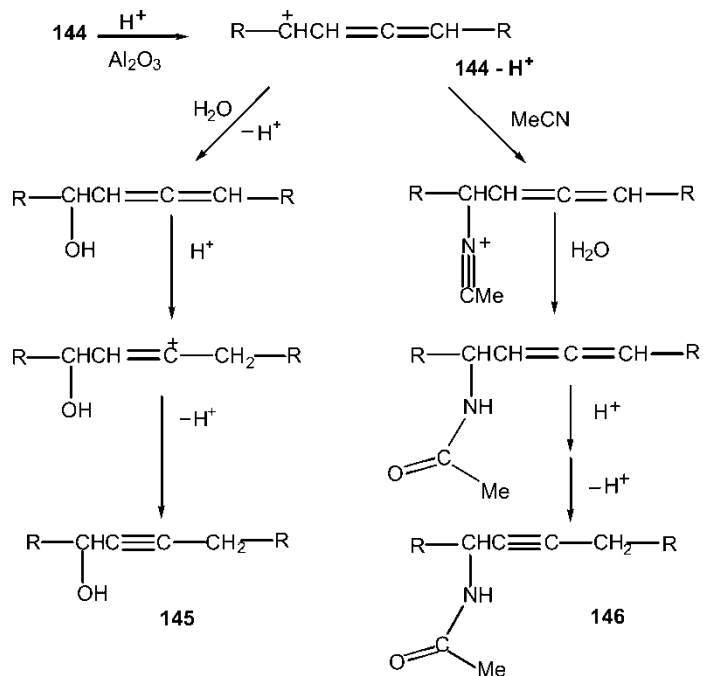


Treatment of adducts **143** with basic alumina caused elimination of only one 5-thianthrenium group and formation of 1-(5-thianthreniumyl)alkynes (**148**, scheme 38). After isolation, further reaction of **148** on alumina led to hydration and isolation of a mixture of syn and anti ylides (**149** and **150**, scheme 39). If left in contact with alumina, the ylides were hydrolyzed into α -ketols (**151**) and Th (scheme 39).

In the additions of Th^+ to alkynes, no evidence was found for formation of cyclic monoadducts (**152**) analogous to those (**123**) obtained in additions to alkenes. Interestingly, then, the 3-phenyl-1,2-dithiete cation radical (**153**), which is formed from phenylacetylene and $\text{Cl}_2\text{CS}_2/\text{AlCl}_3$, is shown as adding to phenylacetylene to form the 2,5-diphenyl-1,4-dithiin cation radical (**154**), scheme 40 [74]. Benzothiete cation radicals have been implicated in forming Th^+ itself from a variety of sulfur containing compounds [75, 76].

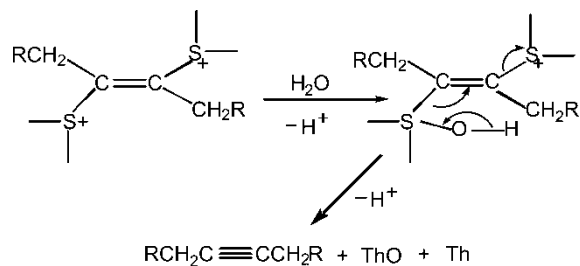
10.7 Additions to non-conjugated dienes

Additions of Th^+BF_4^- and Th^+PF_6^- to a series of non-conjugated dienes have been reported [77, 78]. It was found with acyclic terminal dienes that, depending on the relative amounts of diene and Th^+ that were used, additions to either only one double bond or to both double bonds would occur. Thus, if the molar ratio of diene/ Th^+ was 4:1 or even 2:1, addition to only one of the double bonds of 1,5-hexa-, 1,7-octa-, 1,8-nona- and 1,9-decadiene occurred [77]. Addition gave, however, a mixture of bis- (**155**) and monoadducts (**156**), scheme 41. In most of the additions the ratio of bis:mono was approx. 3/2. By fractional crystallization

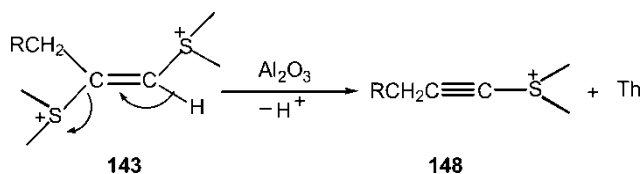


each monoadduct (**156a-d**) was isolated, containing only a small amount of the bisadduct, and allowing for NMR characterization of the separated monoadducts and, thereafter, of bisadducts, too, in mixtures. When an excess of Th^{4+} was used, namely in the molar ratio of diene: Th^{4+} 1/4, addition to these dienes gave a mixtures of four products: **155**, **156**, di(bis)- (**157**) and di(mono)adduct (**158**) (scheme 41).

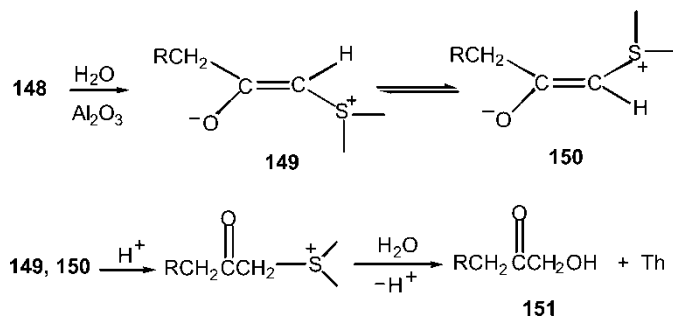
The composition of each mixture of tetrafluoroborate salts, (**155** + **156**)/(**157** + **158**), was measured with NMR spectroscopy and was for $n = 2, 4, 5, 6$ respectively, 3/1, 7/3, 2/3, 2/3. Fractional crystallization allowed for the separation of only the di(mono)adducts **158b-d** which were characterized with NMR spectroscopy.



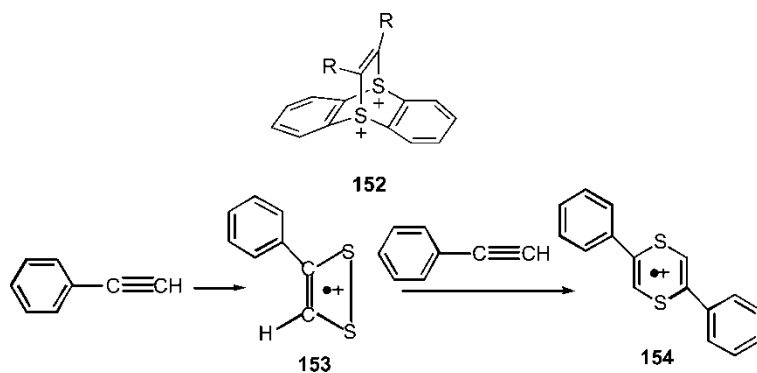
Scheme 37



Scheme 38

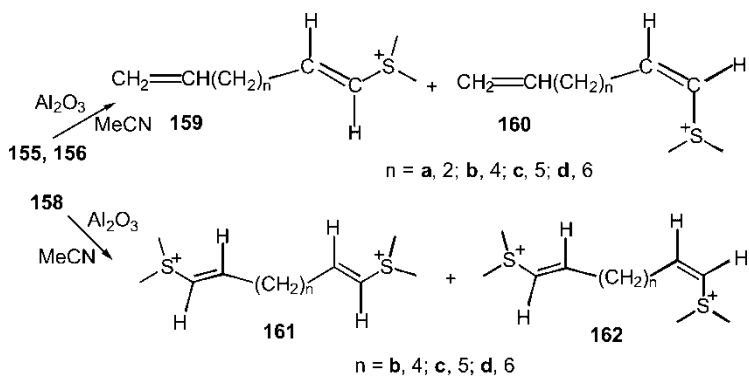
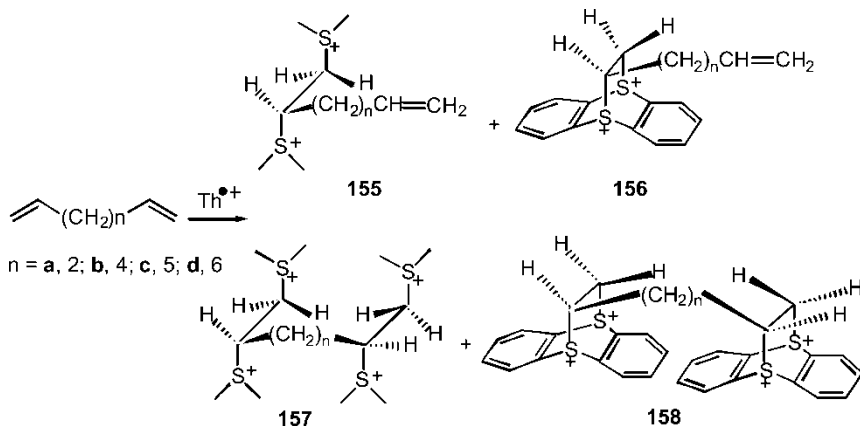


Scheme 39



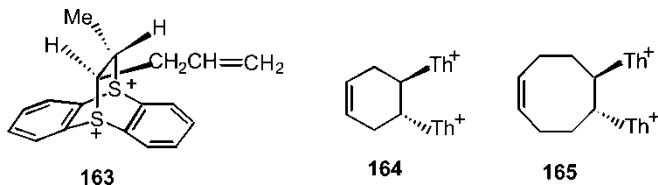
Scheme 40

Reaction of an MeCN solution of the tetrafluoroborate of each of **155a–d** with basic alumina allowed for the preparation and NMR characterization of each of the (*E*)-isomers of the 1-(5-thianthrenium)diene **159a–d**. Reactions, thereafter, of a mixtures of bis- and monoadducts (**155 + 156**) gave a mixture of **159** and the (*Z*)-isomer (**160**), allowing for the NMR characterization of the corresponding (*Z*)-isomers (**160a–d**), scheme 42.



Similar treatment of each of the tetrafluoroborates of the di(mono)adducts **158b–d** gave mixtures of (*E,E*)- and (*E,Z*)-di-(5-thianthreniumyl)dienes (**161** and **162**), scheme 42. The (*E,E*)-isomer was dominant in each mixture, allowing for its NMR characterization.

Reaction of $\text{Th}^{+\text{+}}\text{BF}_4^-$ with 1,4-hexadiene, 1,4-cyclohexadiene and 1,5-cyclooctadiene resulted in addition to only one of the double bonds [78]. In the case of 1,4-hexadiene, addition occurred at the 4,5-bond rather than 1,2-bond. The adducts **163–165** were isolated from these three dienes and were characterized with X-ray crystallography.

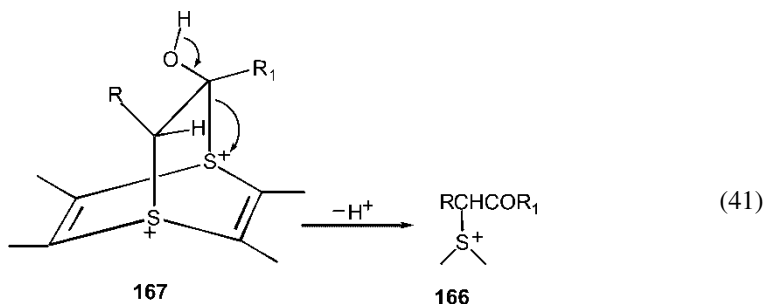
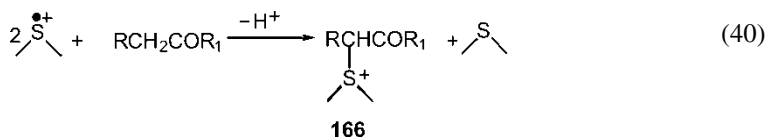


11. Reactions with ketones, aldehydes and stable enols

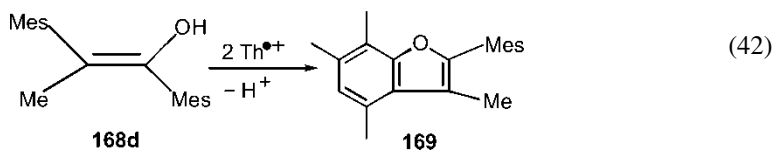
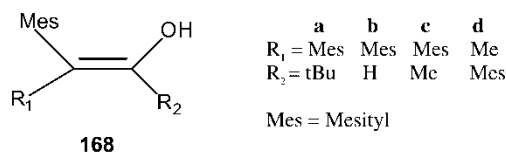
11.1 With ketones and enols

The reactions of ketones and aldehydes with $\text{Th}^{+\text{+}}$ are subset of additions to alkenes. Reactions with ketones produce an α -ketosulfonium salt **166** (equation (40)), and for that to occur the

ketone must be capable of enolizing; that is, it must have a hydrogen atom on an α -carbon atom. When first discovered the reaction was described as involving the ketone's enolic form [10], and that has been confirmed by Wayner, who compared addition to an enol with addition to an alkene [65]. The detailed mechanism of addition to enols is not known, however. That is, addition to alkenes is now known to begin with stereospecific cycloaddition (scheme 27), but whether this occurs with enols is not at all known. If reaction with ketones did, in fact, follow the path of alkene additions, an intermediate such as **167** would have to be invoked. Such an intermediate would readily decompose to give **166** (equation (41)). That possibility has never been investigated.



The reactions of some well-known cation radicals with a series of stable, isolable enols (**168**) have been reported by Schmittl and Röck [79]. Oxidation of the enols occurred and led to either benzofurans by intramolecular cyclization of a cationic intermediate, or to oxazoles by cyclization after reaction of the intermediate with solvent nitrile. Among the cation radicals was $\text{Th}^{\bullet+}\text{ClO}_4^-$, which in reaction with **168d** gave the benzofuran **169** (equation (42)). One may conjecture here, too, the possibility that formation of **169** begins with an addition as in **167** rather than oxidation, analogous to the formation of 2-oxazolines in some reactions with alkenes [69].

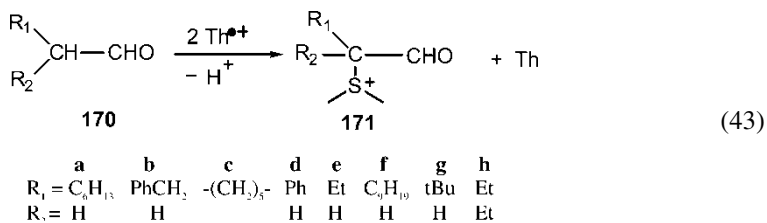


11.2 With aldehydes

Twenty years were to elapse after the reaction of $\text{Th}^{\bullet+}$ with ketones was reported [10], before the same reaction with aldehydes was described [80a]. Reaction of $\text{Th}^{\bullet+}\text{BF}_4^-$ with **170a-h**

gave **171a–h** (equation (43)). Only **171a–c**, however, were isolable as stable, crystalline products. The remaining products, **171d–h**, although identifiable with ^1H NMR spectroscopy, decomposed on storage.

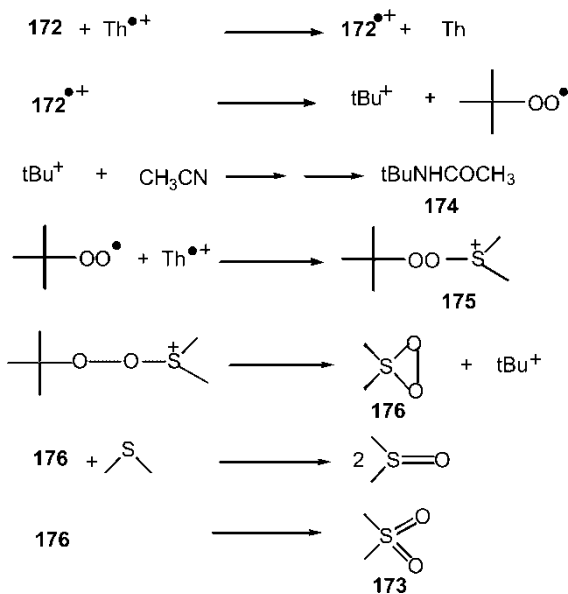
The formation of products **171** must surely require addition of $\text{Th}^{\bullet+}$ to the enolic form of **170**. The enolic content of simple aldehydes, such as acetaldehyde and isobutyraldehyde, is greater than that of acetone (in aqueous solution) [80b], foretelling the facile reaction of $\text{Th}^{\bullet+}$ with aldehydes via their enols. In that case, the possible involvement of a cyclic intermediate, such as suggested for ketones (**167**), may also be conjectured for aldehydes.



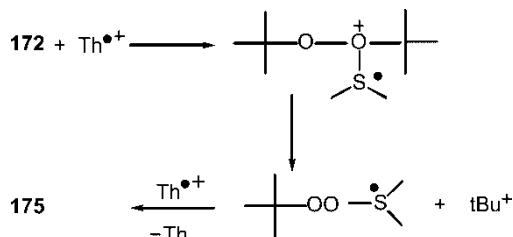
12. Reactions of peroxides and disulfides

12.1 Di-tert-butylperoxide

There are two reports of the reaction of the $\text{Th}^{\bullet+}$ with di-*tert*-butylperoxide (**172**) [81, 82], the more definitive of which [82] is reviewed here. The products of reaction were Th , ThO , thianthrene 5,5-dioxide (**173**) and *tert*-butylacetamide (**174**). It was assumed, reasonably, that the oxygen atoms in the ThO and **173** were derived from **172** as shown in the scheme 43 [82]. In this scheme the *tert*-butylperoxy radical is formed and is trapped by $\text{Th}^{\bullet+}$ to generate the 5-(*tert*-butylperoxy)thianthrenium ion (**175**). The fate of the *tert*-butyl cation is the formation of **174**. Scheme 43 calls for the formation of and oxygen transfer reactions of the thianthrene



Scheme 43

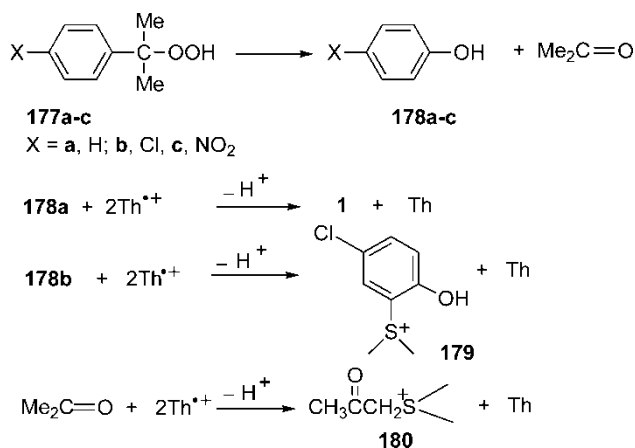


Scheme 44

dioxirane (**176**), reactions that have been entertained also in oxime chemistry (scheme 17). A second route to **175** can be proposed that avoids formation of the *tert*-butylperoxy radical, scheme 44.

12.2 Cumylhydroperoxides

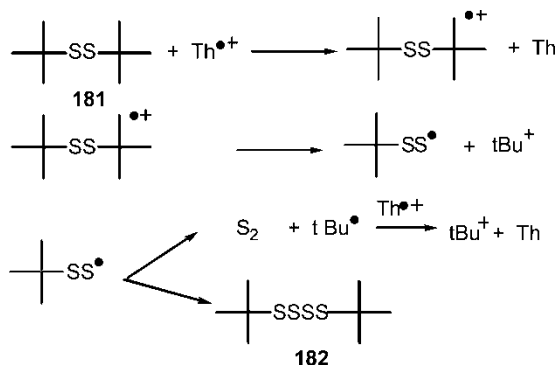
Three cumylhydroperoxides (**177a–c**) were found to react rapidly in MeCN solution containing $\text{Th}^{\bullet+}\text{ClO}_4^-$ [83]. The products of reactions were mixture of a phenol (**178a–c**), acetone and the thianthrenium salts (**1**, **179**, **180**) derived from reaction of $\text{Th}^{\bullet+}$ with the phenol and with acetone (scheme 45). Products **1**, **179** and **180**, therefore, were not the primary products of reactions of $\text{Th}^{\bullet+}$ with **177**, but with the phenols and acetone derived from **177**. It appears that, initially, the well-known [84] acid catalyzed rearrangement and scission of **177** occurred, the acid arising, presumably, from hydrolysis of some of the $\text{Th}^{\bullet+}$. Of the three phenols only **178a**, **b** reacted with $\text{Th}^{\bullet+}$, while **178c** was unreactive and was recovered in high yield.



Scheme 45

12.3 Di-*tert*-butylsulfide

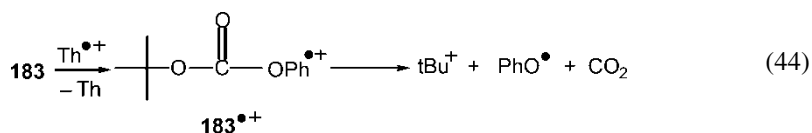
This sulfur analog (**181**) of **172** underwent oxidative decomposition in reaction with $\text{Th}^{\bullet+}$. In contrast with **172**, however whose oxygen atoms were transferred to thianthrene nuclei, the sulfur atoms of **181** were for the most part eliminated as S_2 . A small amount of the tetrasulfide **182** was obtained along with the principal product tBuNHCOMe (**174**). The products and stoichiometry of their formation are accommodated with scheme 46 [85].



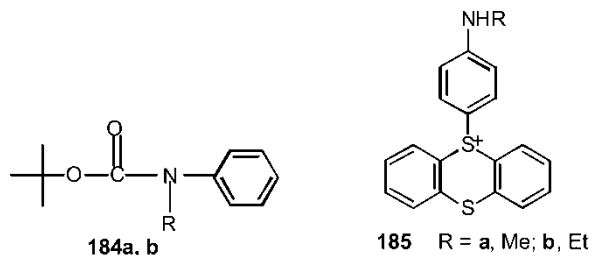
Scheme 46

13. Reactions with carbonates and carbamates; oxidative decarboxylation

The reaction of $\text{Th}^{\bullet+}\text{ClO}_4^-$ with *tert*-butyl phenylcarbonate (**183**) in MeCN gave almost quantitative yields of Th, **1** and **174**. The data point to the oxidative decomposition of **183** (equation 44) followed by the trapping of the phenoxy radical by $\text{Th}^{\bullet+}$ and the *tert*-butyl cation by solvent [86].



Analogous reactions with *tert*-butyl N-methylphenyl- (**184a**) and *tert*-butyl N-ethylphenyl carbamates (**184b**) gave **174** and the 4-(5-thianthreniumyl)arylamine perchlorates (**185a, b**) [87].



14. Formation and reactions of $\text{Th}^{\bullet+}$ on zeolites

14.1 Reaction with isooctane and with water

When Th is adsorbed by zeolites, either by thermal evaporation or from solution, $\text{Th}^{\bullet+}$ is formed [88–90]. The mechanism of oxidation and the nature of the electron acceptor are not known, but the zeolite must have acidic sites for reaction to occur. The adsorbed $\text{Th}^{\bullet+}$ is stable in the zeolite pores for very long periods of time. Two interesting reactions of the adsorbed $\text{Th}^{\bullet+}$ were observed. When isooctane was used as solvent, *tert*-butylthianthrene was formed in high yield. It is apparent that the solvent underwent rupture, but the mechanism of reaction remains unsolved. Adsorbed $\text{Th}^{\bullet+}$ disappeared rapidly when subjected to a stream of nitrogen

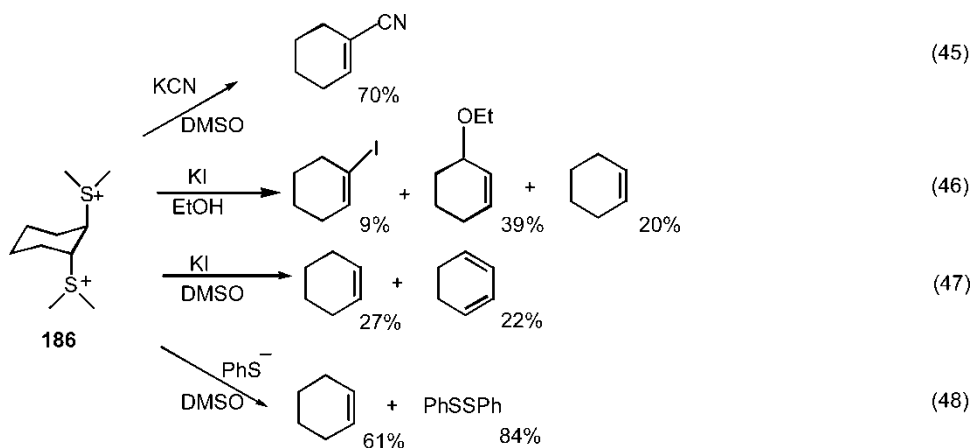
saturated with water, but was reformed quantitatively when the water was stripped from the zeolite with warm dry nitrogen. The temporary disappearance of the $\text{Th}^{+\cdot}$ was attributed to the reversible complexing of water with $\text{Th}^{+\cdot}$, and not to the well-known irreversible reaction that forms equal amounts of Th and ThO. The reaction of $\text{Th}^{+\cdot}$ with water to give equal amounts of Th and ThO was the first reaction of the cation radical to be studied and has had a long and controversial history [15]. The prevailing view is that the reaction begins with the reversible formation of a complex between $\text{Th}^{+\cdot}$ and water [11, 12], a view that has received more recent support with studies of $\text{Th}^{+\cdot}$ generated by photochemically-initiated electron transfer reactions [91, 92]. The work of Garcia and coworkers is an interesting addition to this historical reaction. If the interpretation is correct, it is evidence for the isolated, pore-trapped complex of $\text{Th}^{+\cdot}/\text{H}_2\text{O}$ whose formation has been invoked hitherto only from kinetic evidence.

15. Reactions of 5-(substituted)thianthrenium salts

In a number of the reactions of $\text{Th}^{+\cdot}$ that we have reviewed, a 5-(substituted)thianthrenium salt was formed and subsequently underwent further reaction with a nucleophile in the medium. These occurrences led eventually to extensive studies of the chemistry of 5-(substituted)thianthrenium salts themselves and, therefore, those studies are included in this review. The reactions of 5-(substituted)thianthrenium salts with nucleophiles embrace three types: simple nucleophilic displacement of the substituent, opening of the thianthrenium ring, and the formation and reaction of aryne intermediates.

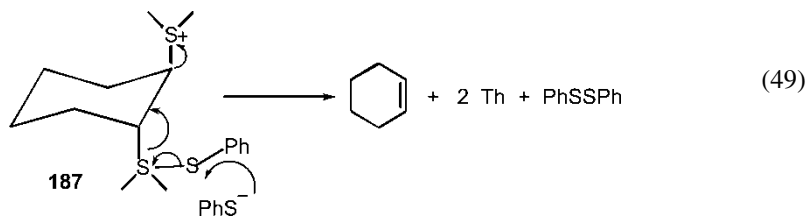
15.1 Nucleophilic displacements

Reactions of this kind were first taken up not so much as a direct enquiry but rather to establish the configuration (trans as it turned out) of the adduct of $\text{Th}^{+\cdot}\text{ClO}_4^-$ with cyclohexene [64]. Thus, reactions of 1,2-di(5-thianthrenium)cyclohexane diperchlorate (**186**) with CN^- , I^- , Br^- and PhS^- were carried out. The reactions disclosed the complexities that were to be more fully explored in later years. Reactions of **186** are summarized in equations (45)–(48).

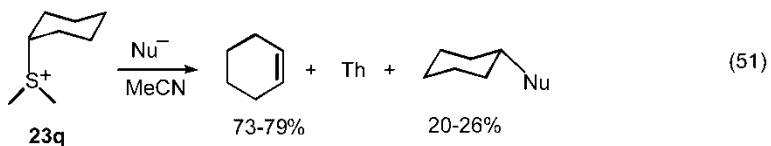
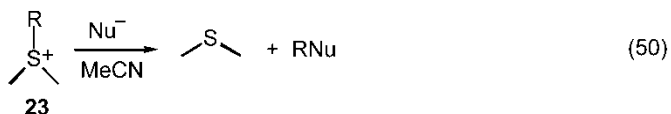


Thianthrene was formed quantitatively in each reaction. The cyclohexyl ring underwent mixtures of substitution followed by elimination (equations (45) and (46)) or elimination entirely (equations (47) and (48)). The reactions were harbingers of E2C elimination and sulfurane reactions that were elucidated in later studies. The formation of so much PhSSPh from

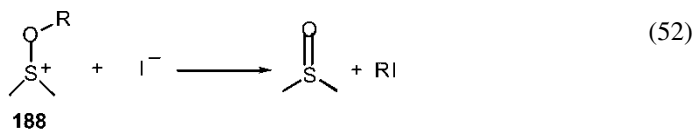
reaction with PhS^- was suggestive, particularly, of involvement of a sulfurane intermediate (**187**, equation (49)).



A systematic investigation of reactions of 5-alkyl- and 5-cycloalkylthianthrenium salts (triflates) with I^- , Br^- and PhS^- was reported by Liu and Shine 20 years later [93]. Nucleophilic displacement ($\text{S}_{\text{N}}2$) prevailed in all cases (**23**, equation (50)) in which $\text{R} = \text{Me}$, Et, isoPr, Bu, neopentyl, benzyl, cyclopentyl and cycloheptyl. A small amount of alkene was obtained with $\text{R} = \text{Bu}$, cyclopentyl and cycloheptyl. The dominant reaction with $\text{R} = \text{cyclohexyl}$ (**23q**), however, was $\text{E}2\text{C}$ elimination (equation (51)), a reaction long known to be associated with reactions of cyclohexyl derivatives with weak nucleophiles.

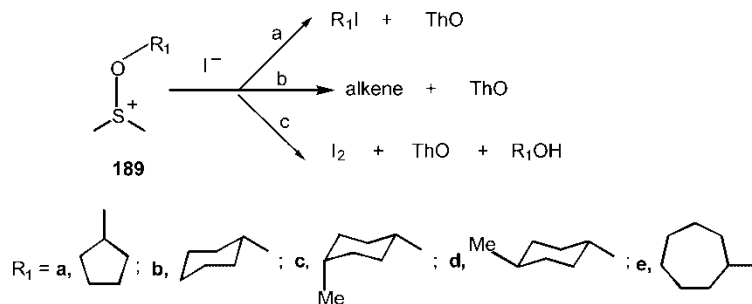


Nucleophilic displacement of the alkyl group was found to be the dominant reaction of I^- , and Br^- with a series of 5-alkoxythianthrenium perchlorates (**188**, equation (52)). Second order kinetics of reaction with I^- were diagnostic of $\text{S}_{\text{N}}2$ displacement [56]. Accompanying the $\text{S}_{\text{N}}2$ reaction, however, was the formation of small amounts of iodine and ROH, indicative of displacement at sulfonium sulfur, a reaction that became more pronounced in later work with 5-(cycloalkoxy)thianthrenium salts (**189**, scheme 47) [94]. Three types of reaction were significant in the reaction of I^- with cycloalkoxy derivatives. $\text{S}_{\text{N}}2$ displacement (path a) was dominant in reactions of **189a, e**; $\text{E}2\text{C}$ elimination (path b) and reaction at sulfur (path c) were dominant in reactions of **189b, c**; all paths (a, b, c) were substantial in reactions of **189d**.

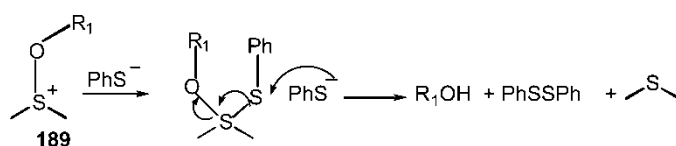


$\text{R} = \text{Me}$, Et, Pr, isoPr, Bu, pentyl, hexyl

The reactions of PhS^- with **189b-e** were strikingly different from the reactions of I^- . The reactions were entirely thiophilic, ending in the quantitative formation of Th, ROH, and PhSSPh (scheme 48). The thiophilicity of PhS^- was seen earlier in reaction with **186** [64]. It will be encountered again in ring-opening reactions of thianthrenium salts.



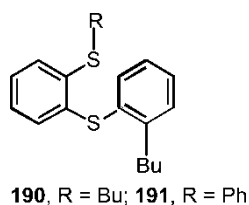
Scheme 47



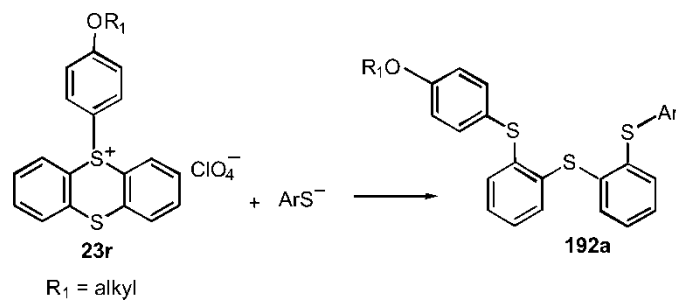
Scheme 48

15.2 Ring-opening reactions

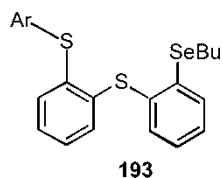
Opening of the thianthrene ring in 5-thianthrenium salts was encountered serendipitously in the reactions with Grignard reagents. For example, the substituted diphenyl sulfide (**190**) was formed from reaction of BuMgCl with 5-butylthianthrenium perchlorate [49] and **191** was formed from BuMgCl and 5-phenylthianthrenium perchlorate [50].



(52)

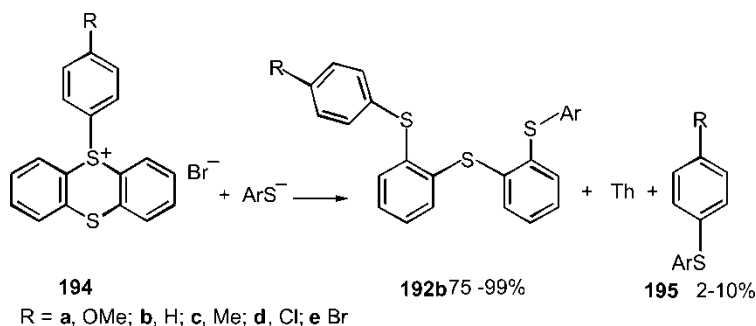


Scheme 49



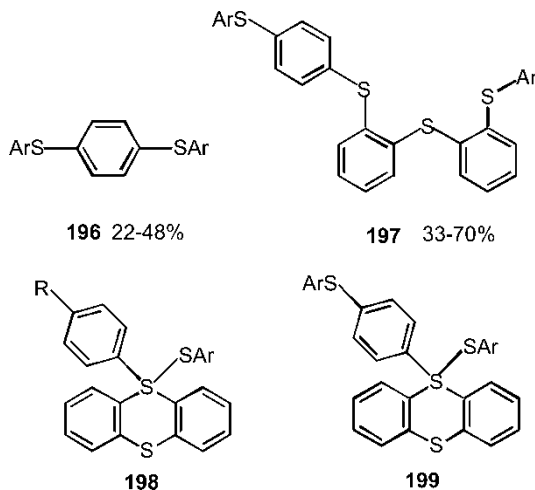
The first exploration of ring-opening as the major reaction was provided by Kim and Rim in the reactions of a series of 5-(*p*-alkoxyaryl)thianthrenium perchlorates (**23r**) with aryl thiolates in THF at ambient temperatures (scheme 49) [95]. The products (**192a**) were obtained in high yields; the possibility of a sulfurane intermediate was noted. The formation of a series of butylselenium products (**193**) was also reported from reactions of BuSeLi with 5-aryltthianthrenium perchlorates [96].

Analogous reactions of aryl thiolates (ArS^- , Ar = phenyl, *p*-tolyl, *p*-chlorophenyl) with 5-aryltthianthrenium bromides (**194a-c**) in MeCN resulted in the formation of **192b** and diaryl sulfides (**195**) as major products (scheme 50) [97].

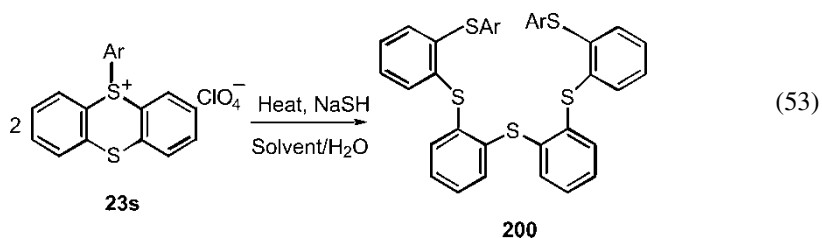


Scheme 50

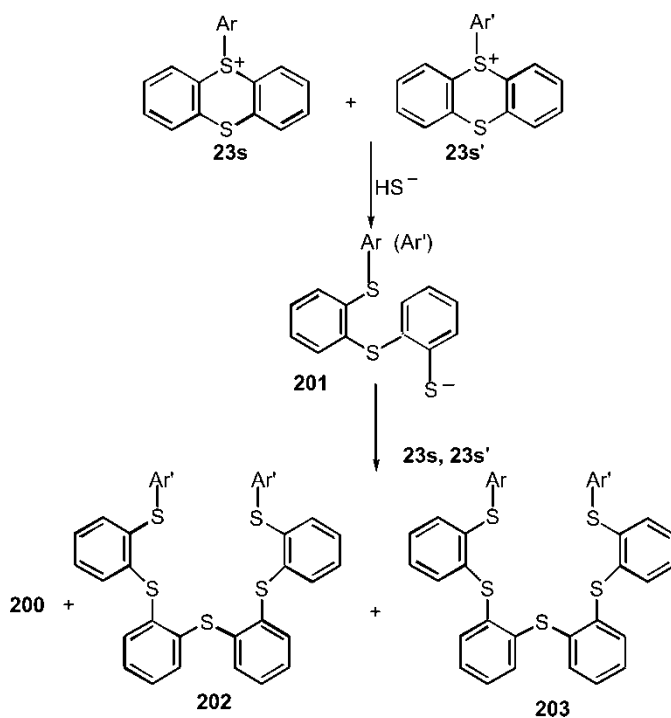
With reactions of **194d, e** not only were **192b** and **195** formed but also products containing two arylthio groups, namely **196** and **197**. These reactions of **194** with ArS^- were depicted as involving a sulfurane intermediate from which products were formed by ligand coupling. The precursor of **192b** and **195** was the sulfurane **198**, while that of **196** and **197** was **199**.



The additional arylthio group in **199** occurred in displacement of halogen (Cl, Br) from **194d, e** prior to sulfurane formation. An entirely analogous course of reaction occurred between **194a–e** and sodium aryl oxides (ArONa, Ar = Ph, *p*-tolyl, *p*-chlorophenyl) [98].

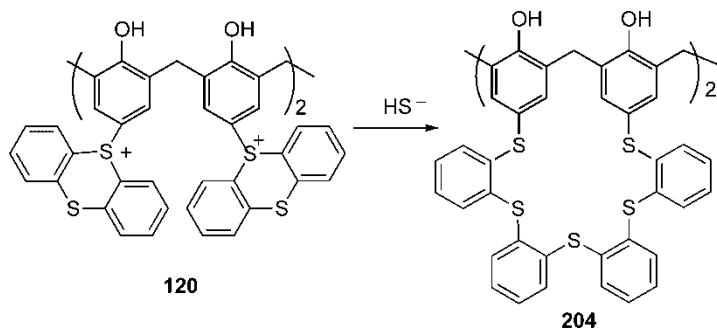


The use of HS⁻ as a nucleophile in reaction with a series of 5-aryltianthrenium perchlorates **23s** initiated very interesting ring-opening reactions involving two molecules of **23s** (equation (53)) [99]. When a mixture of two different **23s** was used three pentasulfides were formed, namely, **200**, **202** and **203** in approximately equal amounts (scheme 51).



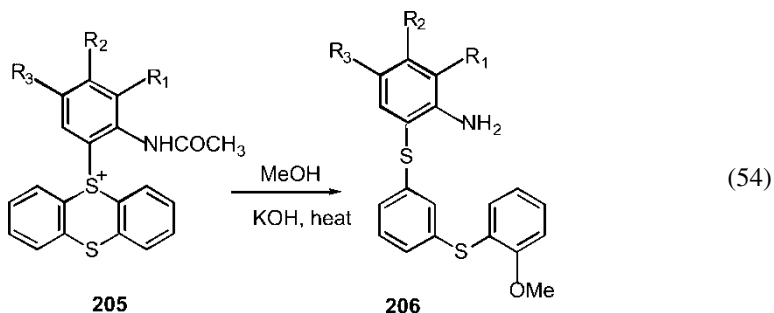
Evidently, initial reaction of **23s** with HS⁻ generated a ring-opened thiolate (e.g., **201**) which then reacted randomly with both compounds **23s** and **23s'** to form **200–203** (scheme 51). Similar reactions using NaSeH and **23s** leading to selenium analogs of **200** have been reported, too [96].

Kim has used the reaction of HS⁻ with the 5-(*p*-hydroxyphenyl)thianthrenium ion incorporated in a calix[4]arene, shown in part as **120**. Bonding of adjacent thianthrenium ions occurred within **120** (scheme 52) [62].

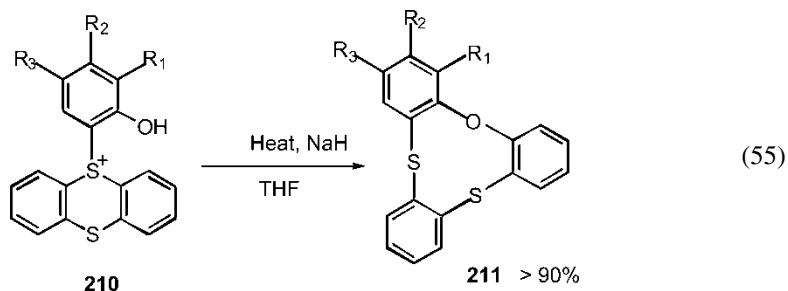


Scheme 52

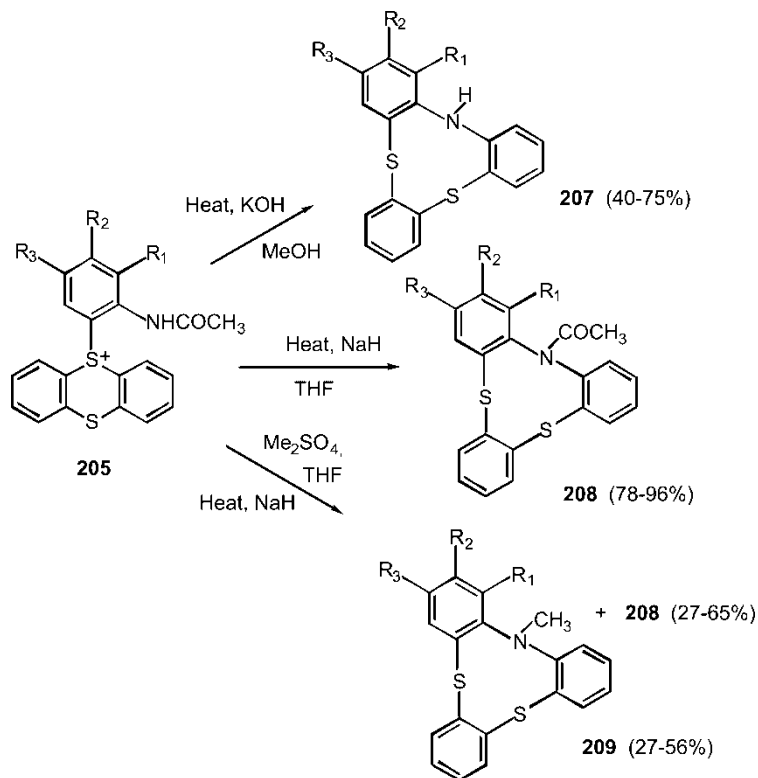
Ring-opening also with methoxide ion was encountered when a number of 5-[polysubstituted-2-(acetamido)aryl]thianthrenium perchlorates (**205**) were heated in a solution of methanol containing KOH (equation (54)) [100].



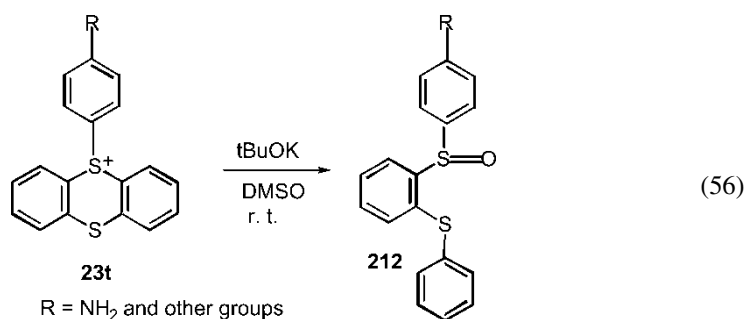
It is evident that the acetamido group in **205** suffered hydrolysis, too. The acetamido group in **205** was involved not only in forming **206** but also in more complex ways, resulting in novel nine-membered heterocycles (**207–209**), scheme 53. Products (**211**) analogous to **207** were obtained when 5-(2-hydroxyaryl)thianthrenium perchlorates (**210**) were used (equation (55)) [100].



Although heating compounds **205** with KOH in MeOH caused ring-opening and formation of various diaryl sulfides (equation (54)), treatment of a variety of 5-(*p*-substituted-aryl)thianthrenium perchlorates (**23t**) with tBuOK in dimethylsulfoxide (DMSO) at room temperature caused ring-opening and diarylsulfide (**212**) formation (equation (56)) [101].

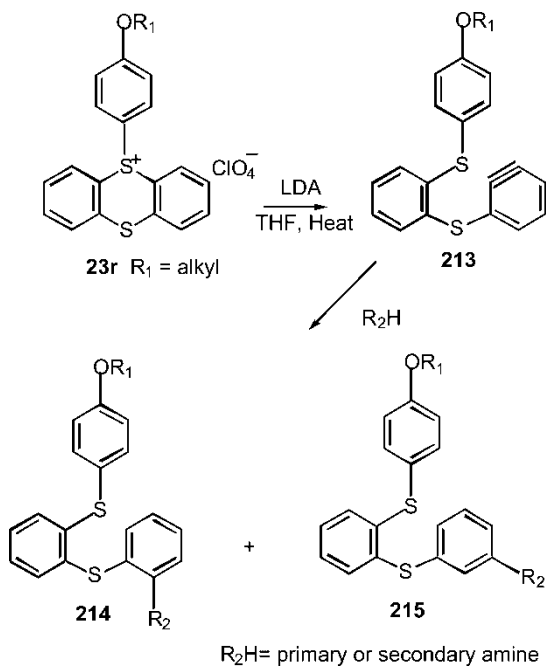


Formation of the sulfinyl group in **212** was attributed to reactions of DMSO at the sulfonium sulfur atom of **23t**.



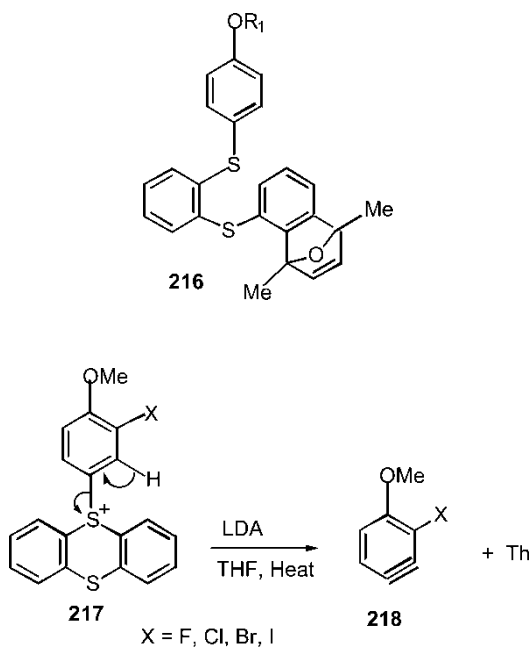
15.3 Reactions involving arynes

Two types of aryne intermediates have been encountered in reactions of particular 5-arylthianthrenium perchlorates with strong bases. The aryne was formed in the thianthrene ring or in the attached aryl ring. Formation of the thianthrene aryne occurred in reaction of 5-(*p*-alkoxyphenyl)thianthrenium perchlorates with heated solutions of lithium diisopropylamide (LDA) in THF [101, 102]. The aryne was trapped in situ by primary or secondary amines (scheme 54).



Scheme 54

The formation of the aryne (**213**) was deduced from the structures of two products (**214** and **215**), obtained in relative amounts that varied with the amine. Direct evidence for the aryne was obtained by trapping (**216**) with 2,5-dimethylfuran.



Scheme 55

Elimination of thianthrene from 5-[(3-halogen-4-alkoxy)aryl]thianthrenium perchlorates (**217**) and formation of an aryne (**218**) from the substituent occurred as shown in scheme 55 [103]. The aryne was trapped with 2,5-dimethylfuran and also with a variety of substituted 2-aminobenzophenones. The presence of the halogen atom in **217** led to elimination of Th rather than to deprotonation (**23r**) of the thianthrenium ring seen earlier.

Acknowledgements

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