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REACTION OF THIANTHRENE CATION RADICAL WITH GRIGNARD REAGENTS

EVIDENCE FOR ELECTRON TRANSFER AND TRAPPING OF ALKYL RADICALS BY THE THIANTHRENE CATION RADICAL

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Abstract—Reactions are reported between RMgCl and thianthrene cation radical perchlorate ($\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$) suspended in ether and tetrahydrofuran (THF). In ether solution reactions R = Bu, s-Bu, t-Bu, 5-hexenyl, and cyclopentylmethyl. Major products were the alkane, the alkene R(−H) in some cases, and, in the cases of R = Bu, 5-hexenyl, and cyclopentylmethyl, the 5-alkylthianthrenium perchlorate ($\mathrm{ThR}^+\mathrm{ClO}_4^-$). When 5-hexenylMgCl was used a mixture of 5-(5-hexenyl)- and 5-(cyclopentylmethyl)thianthrenium perchlorates in the ratio of approximately 2 was obtained. Since the ratio of 5-hexenyl/cyclopentylmethyl in the Grignard reagent was 10.4, it is concluded that the C_6 sulfonium ions were formed by radical trapping by $\mathrm{Th}^{\cdot+}$ after single electron transfer from Grignard to cation radical had occurred, thus allowing for cyclization of 5-hexenyl radical. Formation of $\mathrm{ThBu}^+\mathrm{ClO}_4^-$ is attributed to the trapping of butyl radical by $\mathrm{Th}^{\cdot+}$, while formation of RH and R(−H) is in all cases also attributed to alkyl radical reactions. Reactions in THF (R = Me, i-Pr, Bu, s-Bu, t-Bu, Ph) led almost exclusively to RH and Th. Polymerization of THF was also initiated and took place slowly giving rise to low molecular weight poly(THF). By using THF-d_8 as solvent for reaction between BuMgCl and $\mathrm{Th}^{\cdot+}$, it was possible to find Bu groups (^{1}H-NMR) in the poly(THF-d_8). Polymerization of THF is attributed, in some cases (R = Me, Bu), to alkyl-cation transfer from ThR^+ to THF. In other cases initiation of polymerization by R^+ and THF(−H)$^+$ is considered.

INTRODUCTION

The chemical literature now abounds in discussions of whether or not reactions ordinarily described as electrophilic and nucleophilic are preceded by single electron transfer (SET). The concept of preceding SET is so widespread as to embrace two of the cornerstones of reaction types in organic chemistry: electrophilic aromatic substitution (in which both complete SET and charge-transfer complexation have been invoked)[1a,b] and the S_N2 reaction,[1a,2] and to include many other well-known reactions, far too numerous to document here.

Among reactions in which SET may be involved are those of organic cation radicals with nucleophiles. In this class of reactions documentation concerning SET is not extensive and also not at all clear. Organic cation radicals can undergo substitution or addition reactions with nucleophiles. Much of the published work on such reactions concerns reasonably stable aromatic and heteroaromatic cation radicals reacting with charged and neutral nucleophiles.[1a,3,4] Such reactions usually have the stoichiometry of Eq. 1, in which $\mathrm{ArH}^{\cdot+}$ represents the aromatic or heteroaromatic cation radical. In this equation ArNu represents a substitution product at a ring carbon atom. An analogous reaction can be written for an uncharged nucleophile, say H_2O

$$2\,\mathrm{ArH}^{\cdot+} + \mathrm{Nu}^- \rightarrow \mathrm{ArNu} + \mathrm{ArH} + \mathrm{H}^+ \qquad (1)$$

Many of the reactions which have been studied have involved organosulfur cation radicals, and usually in these cases the product shown here as ArNu is then a sulfonium ion. Such reactions are described later.

The details of the overall reaction of Eq. 1 can be expressed in Eqs 2–4. These equations are not meant to be mechanistically pre-emptive. They signify that the cation radical reacts in a two-electron-bonding way, forming a complex or adduct, which is next oxidized by a second cation radical. In these equations $(\mathrm{ArH/Nu})^{\cdot}$ represents either the π-type complex of Hammerich and Parker's complexation mechanism or the covalently-bound adduct of Blount's half-regeneration mechanism.[1a] A number of these reactions have been documented kinetically and some have been shown to be much more complex than described by these simple equations.[1a]

$$\mathrm{ArH}^{\cdot+} + \mathrm{Nu}^- \rightleftharpoons (\mathrm{ArH/Nu})\cdot \qquad (2)$$

$$(\mathrm{ArH/Nu})\cdot + \mathrm{ArH}^{\cdot+} \rightleftharpoons (\mathrm{ArH/Nu})^+ + \mathrm{ArH} \qquad (3)$$

$$(\mathrm{ArH/Nu})^+ \rightarrow \mathrm{ArNu} + \mathrm{H}^+ \qquad (4)$$

Reaction of a cation radical with a nucleophile can also lead to SET (Eq. 5). Equation 5 is again not pre-emptive, in that electron transfer may occur after complexation (Eq. 6) as is indicated, for example, by kinetics in the reaction of thianthrene cation radical ($\mathrm{Th}^{\cdot+}$) with anisole.[5] The point here is that a radical (Nu· from Nu^-) or another cation radical ($\mathrm{Nu}^{\cdot+}$ from Nu) can be formed by SET to $\mathrm{ArH}^{\cdot+}$. In this way a cation radical ($\mathrm{ArH}^{\cdot+}$) can initiate oxidative chemistry of the nucleophile. This can be a catalytic process, as in

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Diels–Alder cyclizations catalyzed by $(BrC_6H_4)_3N^{\cdot+}$ and reported by Bauld and co-workers,[6] or stoichiometric processes, as with reactions of some azoalkanes and phenylhydrazones initiated by $Th^{\cdot+}$.[7,8] Other examples of cation radical initiated reactions are described by Hammerich and Parker,[1a] and by Eberson.[9,10]

$$ArH^{\cdot+} + Nu^- \rightarrow ArH + Nu^{\cdot} \tag{5}$$

$$(ArH/Nu)^{\cdot} \rightarrow ArH + Nu^{\cdot} \tag{6}$$

A third pathway in the reaction of a cation radical with a nucleophile may also be initiated by SET. This pathway is indicated in Eqs 7–9. It can be seen that the overall result is the same as described by Eq. 1, and that Eqs 7–9 describe a route to ArNu which is quite different from that shown in Eqs 2–4. Again the electron transfer step (Eq. 7) is not pre-emptive of others (e.g. Eq. 6). The key point of this pathway is that the product (ArNu) is formed by the "scavenging" of a neutral radical ($Nu^{\cdot}$) by the cation radical.

$$ArH^{\cdot+} + Nu^- \rightleftharpoons ArH + Nu^{\cdot} \tag{7}$$

$$ArH^{\cdot+} + Nu^{\cdot} \rightarrow (ArHNu)^+ \tag{8}$$

$$(ArHNu)^+ \rightarrow ArNu + H^+ \tag{9}$$

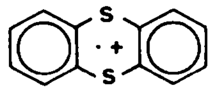
In contrast with other cation radical initiated reactions,[1a,9,10] those described by Eqs 7–9 are not at all well known. The questions of whether nucleophilic reaction (Eq. 2) or SET (Eq. 7) will occur, and of what properties in nucleophiles and cation radicals govern which pathway will be taken, have been discussed extensively by Eberson,[11c] but the answers are still not really clear; nor are there really firm examples of the scavenging reaction shown in Eq. 8. It has been pointed out that anodic cyanation and the homogeneous reaction of cation radicals with cyanide ion may occur in this way,[3] and that reactions of nitrite ion with cation radicals may also involve scavenging of NO_2 by a second molecule of cation radical.[3] The latter reaction is connected with the nitration of aromatics for which, in some cases, the same scavenging reaction was proposed some years ago.[12] But, the nitration question is still very cloudy, with arguments and evidence having been presented both for and against the σ-bond forming reaction of $ArH^{\cdot+}$ with NO_2.[1a,b,13]

Recently, it was proposed that, while the reaction of diaryl mercurials with the thianthrene cation radical (1, designated as $Th^{\cdot+}$) appeared to be a displacement reaction of the customary two-electron kind, the reaction of diethyl mercury with $Th^{\cdot+}$ appeared to involve initial electron transfer and the scavenging of ethyl radicals by $Th^{\cdot+}$ (Eqs 10–12)[14]

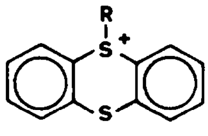
$$Th^{\cdot+} + Et_2Hg \rightleftharpoons Th + Et_2Hg^{\cdot+} \tag{10}$$

$$Et_2Hg^{\cdot+} \rightarrow Et^{\cdot} + EtHg^+ \tag{11}$$

$$Th^{\cdot+} + Et^{\cdot} \rightarrow ThEt^+ \tag{12}$$



1, $Th^{\cdot+}$



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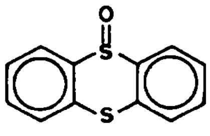

3, ThO

We have followed up this proposal with more extensive studies of analogous R_2Hg reactions and of reactions of $Th^{\cdot+}$ with Grignard reagents, aimed at probing the validity of Eqs 10–12, particularly of Eq. 12. Our studies with Grignard reagents are the subject of this paper, while those with R_2Hg and reconsideration of R_2Hg reactions will be presented separately, later.

REACTION OF $Th^{\cdot+}$ WITH GRIGNARD REAGENTS

In 1978 Eberson drew attention to the analogy between homolytic aromatic substitution ($R^{\cdot} + Ar$) and the corresponding reaction of a carbanion with the aromatic cation radical ($R^- + Ar^{\cdot+}$). He commented on the possibility of SET in the latter case in the following way. "In view of the ease of oxidation of carbanions (in the form of organometallics, say RLi or RMgX) one would predict that the reaction between a carbanion and a radical cation of even low oxidizing power would lead to very rapid initial electron transfer and hence that products would be derived from attack of $R^{\cdot}$ on Ar. Somewhat surprisingly, such studies have to our knowledge not been performed before but should be of considerable interest . . ."[15]

We have investigated the reaction of $Th^{\cdot+}$ with a number of RMgCl. Our results, presented here in detail, will provide evidence for electron transfer and for radical scavenging. They will implicate the involvement of the solvent in hydrogen-atom abstraction reactions, and in cationic polymerization induced by preceding cation radical reactions. Some of our results will be attributable to electron transfer and validate the scavenging reaction (Eq. 12), but in others of our results the possibility of SET will still remain ambiguous.

Organomagnesium chlorides (RMgCl) were used in all of the following work. The reason for this was to avoid in the use of RMgBr and RMgI the greater possibility of oxidizing the halide ion with $Th^{\cdot+}$.[3] The oxidation potential of Th is 1.3 V vs SCE. Oxidation potentials of RMgCl appear not to have been reported, but an impression of the likely ease of SET from RMgCl to $Th^{\cdot+}$ can be gained from the oxidation potentials of some alkylMgBr which are in the range of −0.25 to −1.16 V vs NHE in ether solution relative to a $Pt/Mg/MgBr_2$ cathode,[16] and of EtMgBr with a peak potential of −1.73 V vs Ag/0.01 M Ag^+ in THF relative to a Pb cathode.[17] Again, Chevrot *et al.* have reported that in THF a number of RMgCl can reduce some polynuclear aromatic hydrocarbons but not others to their anion radicals. For example, pentacene with a reduction potential of −2.05 V (vs Ag/0.1 M Ag^+), was reduced, but naphthacene (−2.44 V) was not reduced when R = t-Bu, i-Pr, Et and vinyl.[18] The data indicate that these RMgCl are powerful SET agents, and that SET to $Th^{\cdot+}$ should, from the point of view of oxidation and reduction potentials, be facile.

Table 1. Products of reaction of Grignard reagents with $Th^{\cdot +}ClO_4^-$ in ether

RMgCl		$Th^{\cdot +}ClO_4^-$	H_2O	Products, mmol[a]						Account, %[b]	
R	mmol	mmol	ml	RH	R(−H)	RR	Th	ThO	$ThR^+ClO_4^-$	$Th^{\cdot +}$	RMgCl
Bu	1.2	3.00	—	0.29	0.032	0.048	1.88	0.54	0.58	100	82
Bu	1.2	—	0.25	1.24	0.000	0.008	—	—	—	—	104
s-Bu[e]	1.6	2.00	—	0.73	0.290	0.050	1.77	0.084	—	93	76[c]
s-Bu[e]	1.6	—	0.25	1.58	0.008	0.007	—	—	—	—	100
t-Bu[f]	1.0	3.00	—	0.63	0.240	0.015	2.04	0.970	—	100	104[d]
t-Bu[f]	1.0	—	0.50	1.10	0.024	0.007	—	—	—	—	114

[a] Identified and assayed as described in Experimental.

[b] Sum of product yields based on each reactant and adjusted for the amount of RR, R(−H) (and a presumed equivalent amount of RH) already in the RMgX solution (see reaction with water).

[c] s-BuCl, 0.13 mmol, was also obtained and is included.

[d] t-BuCl, 0.20 mmol, was also obtained and is included.

[e] s-Butyl.

[f] t-Butyl.

In proceeding to the details of our results and our conclusions, we shall designate RMgCl as if it were always the monomer in our reactions. This is not far from the truth in THF solutions but is not correct in ether solutions for which, in the concentrations used, it is more likely that RMgCl is dimeric.[19] However, we must simplify our discussions by treating RMgCl as the monomer in its reactions.

PRODUCTS OF REACTION

Products of reaction of $Th^{\cdot +}$ with Bu-, s-Bu- and t-BuMgCl in ether are listed in Table 1. Those of 5-hexenyl- and cyclopentylmethylMgCl are in Table 2, while products from a series of RMgCl in THF are listed in Table 3. Product yields are listed in mmol rather than as percentage yield. The reason for this is to allow for comparison with control reactions with water, and also to avoid ambiguities in accounting for both reactants, $Th^{\cdot +}$ and RMgCl.

In all cases a large amount of thianthrene (Th) was formed, sometimes amounting to 100% of the $Th^{\cdot +}$ used. Thianthrene oxide (ThO) appears in Tables 1 and 2, and arose from reaction of $Th^{\cdot +}$ with water adventitiously present in the solvent in which $Th^{\cdot +}ClO_4^-$ was suspended, although only small amounts of ThO could have been formed in this way, and from quenching unused $Th^{\cdot +}$ in workup, particularly when an excess of $Th^{\cdot +}$ over RMgCl was used. ThO is not listed in the THF reactions (Table 3) since only traces were found. Alkane (RH) was always formed, particularly in large amounts from reactions in THF. Alkene, R(−H), was formed in significant amounts only from reactions with s-Bu and t-BuMgCl in ether. Only traces of alkene were found from reactions in THF, and therefore R(−H) does not appear in Table 3. Alkenes were not found in reactions of cyclopentylmethylMgCl. In the case of 5-hexenylMgCl we cannot rule out the formation of alkene since the authentic product (1,5-hexadiene) was not available for GC comparison.

Dimer (RR) was found in significant amounts only in reactions of Bu- and s-BuMgCl in ether. Small

Table 2. Products of reaction of 5-hexenylMgCl and cyclopentylmethylMgCl with $Th^{\cdot +}ClO_4^-$ in ether

Reactants				Products,[a] mmol							
RMgCl		$Th^{\cdot +}ClO_4^-$	H_2O	RH		ThR^+ClO_4				Acct, %[h]	
R	mmol	mmol	ml	1-hexene	MCP[d]	5-hex[e]	CPM[c]	Th	ThO	$Th^{\cdot +}$	RMgCl
5-Hex[b]	1.0	3.0	—	0.24	0.039	0.36[f]	0.20[f]	1.88	0.58	101	84
5-Hex[b]	1.0	—	0.25	0.98	0.094	—	—	—	—	—	107
CPM[c]	1.2	3.0	—	0.0	0.31	—	0.56[g]	1.97	0.50	101	73
CPM[c]	1.2	—	0.25	0.0	1.24	—	—	—	—	—	103

[a] Identified and assayed as described in Experimental.

[b] 5-Hexenyl, but a mixture of 5-hexenyl and cyclopentylmethyl assayed by reaction with water (line 2) as being in the ratio of 10.4 : 1.

[c] Cyclopentylmethyl.

[d] Methylcyclopentane.

[e] 5-Hexenyl only.

[f] Assay by ^1H-NMR. A second assay by GLC after conversion to RCl gave 0.27 mmol and 0.12 mmol, respectively; Th (0.51 mmol) was also obtained.

[g] Isolated yield. A second assay by GLC after conversion to RCl gave 0.52 mmol; Th (0.50 mmol) was also obtained.

[h] Sum of product yields based on each reactant.

Table 3. Products of reaction of Grignard reagents with $Th^{\cdot+}ClO_4^-$ in THF

RMgCl		$Th^{\cdot+}ClO_4^-$	H_2O	Products,[a] mmol			Account, %[e]	
R	mmol	mmol	ml	RH	RR	Th	$Th^{\cdot+}$	RMgCl
Me	1.9	3.82	—	1.33	0.018	4.1	107	72
Me	1.9	—	0.3	1.93	0.0	—	—	102
i-Pr	1.9	3.74	—	1.25	0.034	3.5	94	69
i-Pr	1.9	—	0.3	1.87	—	—	—	98
Bu	1.9	3.72	—	1.46	[f]	3.9	105	77
Bu	1.9	—	0.3	2.03	[f]	—	—	107
s-Bu[b]	1.9	3.74	—	1.26	[f]	3.8	102	66
s-Bu[b]	1.9	—	0.3	1.87	[f]	—	—	98
t-Bu[c]	1.9	3.83	—	1.59	0.01	4.0	104	84
t-Bu[c]	1.9	—	0.3	1.91	0.0	—	—	101
Ph[d]	1.8	3.64	—	1.57	[f]	[f]	—	87
Ph[d]	1.8	—	0.3	1.82	[f]	[f]		101

[a] Identified and assayed as described in Experimental. R(−H) was not found.
[b] s-Butyl.
[c] t-Butyl.
[d] Phenyl.
[e] Sum of product yields, based on each reactant. Loss of alkyl group from RMgCl is attributed to incorporation in poly(THF).
[f] Not determined.

amounts were found in some reactions in THF. A small amount of (presumed) dimer was observed by GLC in reactions of cyclopentylmethylMgCl. Dimers were not sought in reactions of 5-hexenylMgCl although minor peaks in the GLC of product mixtures may have been caused by dimers.

A sulfonium salt ($ThR^+ClO_4^-$) was obtained only from reactions of Bu-, 5-hexenyl-, and cyclopentylmethylMgCl in ether (Tables 1 and 2). Sulfonium salt could not be found in any of the reactions in THF carried out in the usual way and documented in Table 3, not even from reactions of MeMgCl and BuMgCl. This apparent anomaly is discussed later. $ThBu^+ClO_4^-$ was obtained when reaction of $Th^{\cdot+}$ with BuMgCl in THF was quenched and worked up without delay. This also is discussed later.

For the most part product recovery (i.e. material balance) was good. We were able to account for all of the $Th^{\cdot+}$, allowing for experimental error, in almost all cases. Accounting for RMgCl was not quite so good. Errors in quantitative analysis of gas and other volatile products were probably larger than errors in assaying solid products containing the Th group. Reactions in THF led to poly(THF) and, as is shown later, this involved incorporation of R groups from RMgCl. Incorporation of R in poly(THF) in reactions of some RMgCl was detected by ^1H-NMR, and was confirmed with the use of BuMgCl in THF-d_8 as solvent. Consequently, the account for RMgCl in reactions in THF was always low (Table 3).

The possibility that a sulfonium salt ($ThR^+ClO_4^-$), once formed in solution, might react with RMgCl as the latter was being added in increments had to be investigated. Results from reaction of $ThBu^+ClO_4^-$ with BuMgCl in ether are described later.

In the sections that follow we shall consider evidence piece by piece in sequence. Because the several reactions that occurred are inter-related, however, the discussions of one piece of evidence will necessarily overlap with discussions of another.

EVIDENCE FOR ELECTRON TRANSFER

Formation of thianthrene (Th)

Both in ether and THF, most of the $Th^{\cdot+}$ used was converted into Th (Tables 1–3). To a large extent the Th was formed by SET from RMgCl, but we cannot ascribe all of the Th to this reaction. We illustrate and clarify the complexities with some examples from the tables.

SET appears to be exclusive in the case of t-BuMgCl in ether, in which an excess of $Th^{\cdot+}$ (3.0 mmol) was used over the amount of Grignard (1.0 mmol). The stoichiometry of the reaction of $Th^{\cdot+}$ with water requires that equal amounts of Th and ThO be formed. Since 0.97 mmol of ThO was obtained, 0.97 mmol of Th must also have been formed in the workup hydrolysis of unused $Th^{\cdot+}$. The stoichiometry requires, then, that after reaction of $Th^{\cdot+}$ with t-BuMgCl, 1.94 mmol of $Th^{\cdot+}$ remained for workup hydrolysis. Consequently, in the initial reaction the Grignard reagent (1.0 mmol) reduced the balance of $Th^{\cdot+}$ (1.06 mmol) by SET. The data are in reasonable experimental agreement. These reactions can be described, then, with Eqs 13 and 14. A similar analysis can be made of the reaction of s-BuMgCl, although an excess of $Th^{\cdot+}$ was not used in this case.

$$Th^{\cdot+} + RMgCl \rightarrow Th + R\cdot + MgCl^+ \tag{13}$$

$$2Th^{\cdot+} + H_2O \rightarrow Th + ThO + 2H^+ \tag{14}$$

Reaction of BuMgCl with $Th^{\cdot+}$ in ether gave some $ThBu^+$ (Table 1). We shall argue, with the help of evidence from using 5-hexenylMgCl, that $ThBu^+$ was formed by trapping Bu· with $Th^{\cdot+}$. In that light, our view is that SET is the initial reaction of BuMgCl with $Th^{\cdot+}$, too, and we can get a reasonable impression of reactions and material balance with the help of Eqs 15–17, in which millimolar amounts, taken in part (Eqs 15 and 16) from Table 1, are written under the reactants. If SET and trapping of Bu· proceeded as shown (Eqs 15 and 16), 1.22 mmol of $\mathrm{Th}^{\cdot+}$ would have been left for workup hydrolysis. Our assay of ThO (0.54 mmol) requires that 1.08 mmol be left. These data are in reasonable agreement.

$$\underset{1.2}{\mathrm{Th}^{\cdot+}} + \underset{1.2}{\mathrm{BuMgCl}} \rightarrow \underset{1.2}{\mathrm{Th}} + \underset{1.2}{\mathrm{Bu}\cdot} + \mathrm{MgCl}^+ \qquad (15)$$

$$\underset{0.58}{\mathrm{Th}^{\cdot+}} + \underset{0.58}{\mathrm{Bu}\cdot} \rightarrow \underset{0.58}{\mathrm{ThBu}^+} \qquad (16)$$

$$\underset{1.22}{2\mathrm{Th}^{\cdot+}} + \mathrm{H_2O} \rightarrow \underset{0.61}{\mathrm{Th}} + \underset{0.61}{\mathrm{ThO}} + 2\mathrm{H}^+ \qquad (17)$$

The data in Table 3 suggest that in THF all RMgCl undergo 100% SET. In no case listed in Table 3 was a sulfonium salt ($\mathrm{ThR^+ClO_4^-}$) found. Herein lies a complication. Sulfonium ion was, we feel, undoubtedly formed from the use of MeMgCl and BuMgCl, but was consumed in initiating polymerization of THF. Initiation of polymerization by $\mathrm{ThBu^+}$ was, in fact, achieved separately, with isolated $\mathrm{ThBu^+ClO_4^-}$. Further, $\mathrm{ThBu^+ClO_4^-}$ was isolated, in other experiments, by rapid workup, from reaction of $\mathrm{Th}^{\cdot+}$ with BuMgCl in THF. Thus, the data in Table 3 are, at first sight, likely to be misleading. When BuMgCl was used the reactions ensuing may be summarized, then, with Eqs 15, 16, 18 and 19. In this case the ultimate fate of $\mathrm{Th}^{\cdot+}$ is conversion into Th, but only part of the total Th will have been formed directly by SET. The same may be said of MeMgCl in THF.

$$\mathrm{ThBu^+ + THF \rightarrow Th + THF{-}Bu^+} \qquad (18)$$

$$\mathrm{THF{-}Bu^+ + nTHF \rightarrow poly(THF)} \qquad (19)$$

Can we rule out analogous reactions with the branched RMgCl? We are not certain of the answer, but our inclination is that trapping of the branched alkyl radicals does not occur. We discuss this further below.

Formation of RH, R(−H) *and* RR

Hydrocarbons RH, R(−H) and RR were formed from reactions of Bu-, s-Bu-, and t-BuMgCl in ether. If we assume that the R(−H) already present in the Grignard solution (water reaction data) arose from alkyl-radical disproportionation in preparing RMgCl, and compensate for that as well as RR already present, we can compute the following for the $\mathrm{Th}^{\cdot+}$ reactions. SET gave alkyl radicals which ended up as alkane plus alkene plus dimer to the total extent of 33.5, 68.2 and 83.8%, respectively, from Bu-, s-Bu, and t-BuMgCl. In the case of BuMgCl 48.3% of Bu groups ended up as $\mathrm{ThBu^+}$, so that we can account for 81.8% of all Bu groups in that reaction.

When alkyl radicals were formed by SET and were not trapped as $\mathrm{ThR^+}$, they appear to have undergone H-atom abstraction from solvent, disproportionation, and recombination with the following distributions, respectively, Bu· (64, 16 and 20%), s-Bu· (40, 52 and 8%), and t-Bu· (46, 52 and 2%). These analyses may be in error because we were unable to account for all of the alkyl groups in the RMgCl used. But, they signify that alkyl-radical reactions ensued from the reaction of RMgCl with $\mathrm{Th}^{\cdot+}$ in ether.

Hydrogen-atom abstraction from solvent ether must have led to solvent radicals ($\mathrm{EtOCHCH_3}$)·. We were unable to trace the fate of these radicals. We assume, though, that further H-atom abstraction led to ethyl vinyl ether (EVE) and that this was polymerized by $\mathrm{Th}^{\cdot+}$. Our reasoning here is based on separate polymerization of EVE (see Experimental) and analogy with THF reactions, discussed later. In summary, the reactions we identify thus far are: SET (Eq. 13), radical trapping by $\mathrm{Th}^{\cdot+}$ (Eq. 16), the hydrocarbon producing reactions (Eqs 20–22) and the (presumed) solvent polymerization sequence (Eqs 23 and 24)

$$\mathrm{R\cdot + Et_2O \rightarrow RH + CH_3\dot{C}HOEt} \qquad (20)$$

$$\mathrm{R\cdot + R\cdot \rightarrow RH + R(-H)} \qquad (21)$$

$$\mathrm{R\cdot + R\cdot \rightarrow RR} \qquad (22)$$

$$\mathrm{R\cdot + CH_3\dot{C}HOEt \rightarrow RH + CH_2{=}CHOEt} \qquad (23)$$

$$\mathrm{Th^{\cdot+} + CH_2{=}CHOEt \rightarrow poly(EVE)} \qquad (24)$$

Reactions in THF led almost exclusively to alkane as the hydrocarbon product. When PhMgCl was used 87% of the phenyl groups ended up as benzene. The results reflect the greater ease of abstracting hydrogen atom from THF as compared with ether.[20] In all of these reactions poly(THF) was also formed, and this is discussed in more detail below. The simplest representation of these findings is that SET (Eq. 13) and H-atom abstraction (Eq. 25) occurred exclusively. Solvent polymerization would then follow (e.g. Eqs 26 and 27), accounting, thereby, for the final complete conversion of $\mathrm{Th}^{\cdot+}$ into Th. However, it is virtually certain that, when BuMgCl was used, some Bu· must initially have been trapped as $\mathrm{ThBu^+}$. Probably, some Me· and possibly some i-Pr· may also have been trapped as the corresponding $\mathrm{ThR^+}$. Thereafter, polymerization of THF by alkyl-cation transfer must have occurred. The overall result is stoichiometrically the same as that in Eqs 13 and 25–27, however. It is possible also that branched radicals, e.g. t-Bu·, and even THF(−H)·, could be oxidized by $\mathrm{Th}^{\cdot+}$ leading to polymer-initiating cations and Th. Again the overall result is the same stoichiometrically. These points are discussed further below.

$$\mathrm{R\cdot + THF \rightarrow RH\cdot + THF(-H)\cdot} \qquad (25)$$

$$\mathrm{THF(-H)\cdot + Th^{\cdot+} \rightarrow Th(THF)^+} \qquad (26)$$

$$\mathrm{Th(THF)^+ + nTHF \rightarrow poly(THF) + Th} \qquad (27)$$

Cyclization of the 5-hexenyl radical

Evidence for radical trapping by $\mathrm{Th}^{\cdot+}$. The products of reaction of $\mathrm{Th}^{\cdot+}$ with 5-hexenylMgCl in ether are listed in Table 2. The composition of the Grignard reagent was shown, by decomposition with water, to be a mixture of 5-hexenyl- and methylcyclopentylMgCl in the ratio 10.4 : 1. This ratio is in reasonable agreement with the literature.[21] We shall refer to this ratio as L/C (linear to cyclic group). Table 2 reports also the reaction of cyclopentylmethylMgCl with $\mathrm{Th}^{\cdot+}$. This reaction led to two major products, methylcyclopentane and the sulfonium salt ($\mathrm{ThR^+ClO_4^-}$, R = cyclopentylmethyl). The latter was isolated as an oil and characterized by ^{1}H-NMR for use in assaying the mixture of sulfonium salts obtained from 5-hexenylMgCl. The CPM-sulfonium salt was also converted into cyclopentylmethyl chloride

(93%) and thianthrene (89%) by reaction with LiCl in acetone, so as to check this method of assaying a sulfonium salt.† Reaction of 5-hexenylMgCl with $Th^{\cdot+}$ gave two major types of product, the mixture of hydrocarbons 1-hexene and methylcyclopentane (27.9%, L/C approx 6.2) and the mixture of sulfonium salts (56%, L/C approx 2). Together, these products accounted for 84% of the Grignard reagent. The oily mixture of sulfonium salts was assayed by ^{1}H-NMR and also as the corresponding alkyl chlorides after conversion by reaction with LiCl in acetone, giving L/C ratios of 1.80 and 2.3, respectively. These ratios when compared with L/C 10.4 show, without doubt, that the 5-hexenyl radical was liberated from the Grignard reagent by SET and underwent cyclization before being trapped by $Th^{\cdot+}$. We know of no other reasonable way of explaining this result. Recently, Bailey and co-workers have shown that 5-hexenyllithium undergoes rather rapid cyclization to (cyclopentylmethyl)lithium, but have noted the earlier reports by others of the relatively slow cyclization of the Grignard reagent.[23] Therefore, we feel that the L/C result obtained now is diagnostic of radical trapping by $Th^{\cdot+}$.

The L/C ratio for the hydrocarbons is 6.2. At face value this would suggest that the 5-hexenyl radical may react with solvent somewhat faster in competition with cyclization, than it reacts with $Th^{\cdot+}$ (suspended as $Th^{\cdot+}ClO_4^-$) in competition with cyclization. This is an attractive idea because solvent molecules are nearby the radical, that is complexed with the Grignard reagent from which the 5-hexenyl radical is formed, and are also in greater concentration than $Th^{\cdot+}$. However, the hydrocarbon ratio may be misleading since 16% of the Grignard's alkyl groups were lost from our accounting. It is less likely that we are in error with sulfonium salt recovery than in hydrocarbon assay. Also, small amounts of protonation of Grignard by acid from pre-reaction hydrolysis of $Th^{\cdot+}$ would affect the hydrocarbon L/C ratio. Therefore, we report our data (Table 2), but place significance only in the sulfonium salt part.

POLYMERIZATION OF SOLVENT

Polymerization of THF

Polymerization of THF occurred in all of the reactions of $Th^{\cdot+}$ with RMgCl in this solvent. Polymerization was very slow, but continuous, occurring at room temperature or when sealed reaction mixtures were placed in the refrigerator for periods of weeks. After standing for several weeks a reaction mixture would become a gel. Polymerization would continue if more THF was added. Thus, the polymerizations had the characteristics of a living polymer. Polymers isolated from such mixtures by preparative TLC had rather low average molecular weights, for example 2300 when MeMgCl was used.

Polymerization of THF by $Th^{\cdot+}ClO_4^-$ alone has been reported to give high-molecular-weight polymer (100,000) in 2 d at 30°.[24] We were unable to polymerize THF in this way over a period of 6 d. An analogous polymerization of THF by perylene cation radical perchlorate has been reported but took place very slowly.[25] Polymerization of THF by cation radical alone is somewhat ambiguous, since there is no way of ruling out initiation by protons formed by adventitious hydrolysis of the cation radical. In connection with the ambiguity of cation-radical-induced polymerization, crystalline perylene cation perchlorate is prepared by anodic oxidation of perylene in THF.[26]

Cationic polymerization of THF can be initiated in three ways: protonation, hydride-ion abstraction (a rare occurrence, attributed to initiation by Ph_3C^+), and by alkyl-cation addition to the oxygen atom of THF.[27] The last method, illustrated, for example, by initiation with $Me_3O^+BF_4^-$, [28] has been well documented. Anion and free-radical polymerization do not occur.

It is improbable that the polymerizations initiated by the Grignard reactions were proton catalyzed. The polymerizations appear in some cases to be initiated by alkyl-cation transfer from a sulfonium ion. Indications that this was an initiating source were given by our failure, initially, to isolate sulfonium salts, e.g. $ThMe^+ClO_4^-$ and $ThBu^+ClO_4^-$, from the Grignard reactions in THF even though these salts were known to us, from work with dialkyl mercurials, to be stable,[22] and even though isolation of $ThBu^+ClO_4^-$ from reaction of BuMgCl with $Th^{\cdot+}$ in THF was achieved finally, by working up the products as soon as the $Th^{\cdot+}$ had disappeared. Subsequently, poly(THF-d_8) was obtained by reaction of BuMgCl with $Th^{\cdot+}$ in THF-d_8, and isolated by preparative TLC. The presence of butyl groups in the polymer was identified by ^{1}H-NMR, signals being obtained at δ 3.25, 1.3 and 0.8. The transfer of Bu^+ to THF-d_8 from $ThBu^+ClO_4^-$ itself was also followed by ^{1}H-NMR. Reaction was carried out in CD_2Cl_2 and the change in the α-CH_2 signal from δ 3.5 in the sulfonium ion to δ 3.25 in the polymer was followed over a period of many days.‡ It follows that, if $ThBu^+$ is the initiator in the Grignard reaction, transfer of Bu^+ from $ThBu^+$ to bulk solvent THF occurs relatively quickly (otherwise we would have been able to isolate $ThBu^+$ more easily), and that polymerization goes rather slowly. We are not certain of why polymerization should be so slow, but suggest that, perhaps, chain carrying THF oxonium ions were in relatively low concentration, being, instead, in equilibrium with open chain, covalently bonded perchlorate ester (Eq. 28), as has been documented by others.[30]

Is polymerization initiated by a sulfonium ion, e.g. the 5-t-butylthianthrenium ion, when the Grignard reagent has secondary and tertiary alkyl groups? We do not know the answer to that question. Such thianthrenium ions, to our knowledge, have not been made. It may be that when a secondary or tertiary alkyl radical approaches $Th^{\cdot+}$ the radical is oxidized to the cation. Perhaps this may be the fate of the

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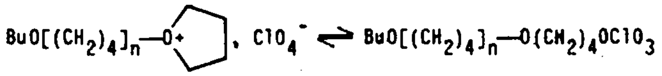
† The reaction of chloride ion with 5-alkylthianthrenium ions reported here has a bearing on our earlier work with dialkyl mercurials. In that work aqueous LiCl was added to the reaction mixture after reaction between R_2Hg and $Th^{\cdot+}$ was complete in order to convert RHg^+ to covalent, isolable RHgCl.[14,22] It may be that in that way some of the sulfonium ion, present in solution as the perchlorate, was destroyed.

‡ The multiplet at 3.25 ppm is attributed to the α-CH_2 in initial group $CH_3CH_2CH_2CH_2O$— in the polymer. Pruckmayr and Wu[29] assigned 3.41 ppm to these protons in poly(THF) in benzene solution. The broad signals at 0.81 and 1.3 ppm in our group are assigned to the CH_3 and β,γ-CH_2CH_2—(cf. 1.65 ppm),[29] respectively.

THF(−H)· radical too.[27a–c] These cations may then alkylate THF at its O atom. Answers to these questions have yet to be found.



(28)

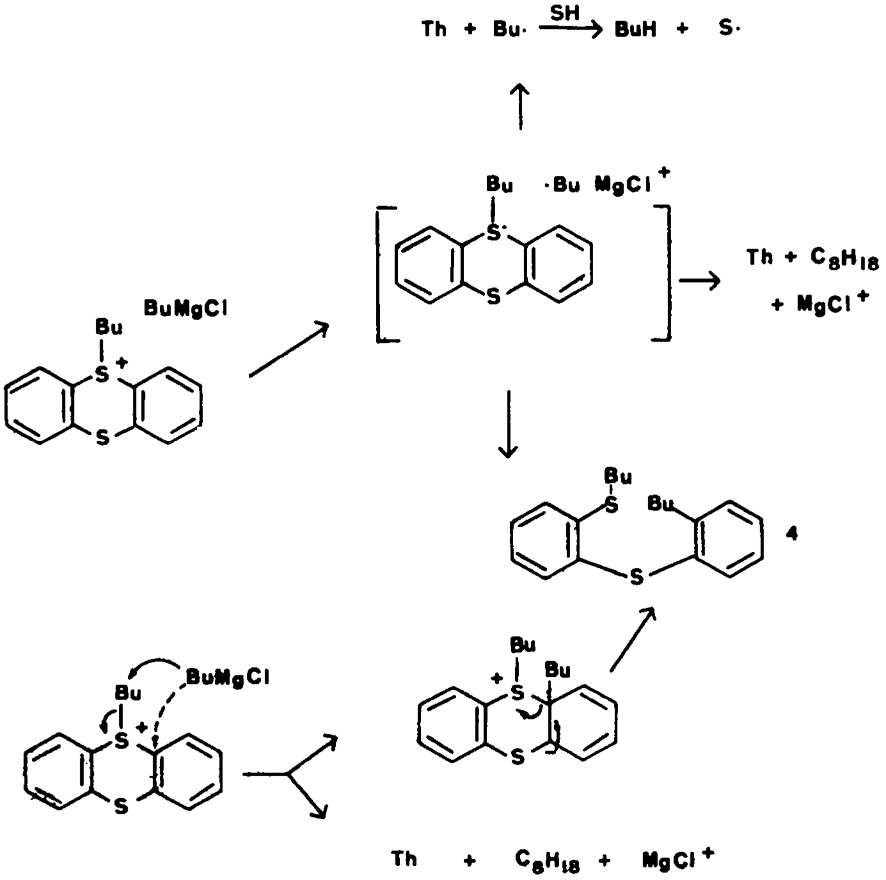
Polymerization of ethyl vinyl ether

We have no direct evidence that EVE was formed in the reactions which were carried out in diethyl ether. All attempts to find EVE by GLC were negative. On the other hand, it was also impossible to find EVE by GLC when it was introduced repeatedly in increments into a suspension of $Th^{\cdot+}ClO_4^-$ in diethyl ether. Instead, poly(EVE) was isolated. The amount of poly(EVE) that could be formed in the Grignard reactions (Table 1) is very small, since the EVE itself could come only from dehydrogenation of the solvent by radicals from the Grignard reagent, itself in only 1–2 mmolar amounts. Therefore, we propose only with the help of circumstantial evidence that EVE may have been formed in those reactions and then polymerized by $Th^{\cdot+}$.

REACTION OF $ThBu^+ClO_4^-$ WITH BuMgCl

Displacement of R^+ from ThR^+ by chloride ion in acetone was facile. Initiation of polymerization by transfer of Bu^+ from $ThBu^+$ to THF can also be looked upon as the nucleophilic displacement of Bu^+ by THF. Therefore, it was necessary to know if nucleophilic displacement of R^+ from ThR^+ also occurred by RMgCl in the Grignard reactions in which ThR^+ was formed. The reaction of $ThBu^+ClO_4^-$ with BuMgCl in ether gave butane, 1-butene and octane in the mmolar ratio 0.12, 0.02 and 0.32, respectively, accounting for 97.5% of the butyl groups in the reactants. The relative amount of octane is quite unlike that obtained from the reaction of $Th^{\cdot+}$ with BuMgCl in ether (mmolar ratio 0.29, 0.032, 0.048, Table 1) so that it seems unlikely that reaction of $ThBu^+$ with BuMgCl is important in the Grignard reaction. This is understandable because an excess of $Th^{\cdot+}$ was used in that reaction, allowing for preferential SET between $Th^{\cdot+}$ and RMgCl as the latter was added.

The question arises whether the reaction of $ThBu^+$ with BuMgCl involves SET, too. The answer cannot be given clearly. The formation of butane suggests that Bu· is formed (Eq. 29). The sulfuranyl radical (ThBu·), also formed by this SET would then decompose into Th and Bu·. The butyl radicals formed from two sources in solvent-cage proximity could combine to form octane or diffuse away to abstract H atom



Scheme 1.

from the solvent.

$$\mathrm{ThBu^+ + BuMgCl \rightarrow ThBu^{\cdot} + Bu^{\cdot} + MgCl^+} \qquad (29)$$

Sulfuranyl radicals, formed by cathodic reduction of aryl dialkyl sulfonium ions, have been shown to be very unstable. Loss of an alkyl radical occurs so rapidly as to suggest that bond cleavage may be concerted with one-electron reduction.[31] The loss of sulfur-bound butyl radical in an SET reaction of $\mathrm{ThBu^+}$ with the Grignard agent (Scheme 1) would be consistent with such sulfuranyl radical instability. Diazotization of 2-aminophenyl 2-R-thiophenyl sulfide (R = Me, Ph) resulted in ring closure giving Th and $\mathrm{R^{\cdot}}$,[32] also attesting to the relative instability of sulfuranyl radicals such as shown in Scheme 1.

An interesting product, identified by mass spectrometry and ^{1}H-NMR as 2-butyl-2′-(butylthio) diphenylsulfide (4), was also obtained, albeit in small yield (7.5%). In the context of SET we might envisage this product as arising from attack of butyl radical on the sulfuranyl radical (Scheme 1). However, we cannot distinguish this pathway and the radical pathway for forming octane, too, from those involving direct nucleophilic attack of RMgCl on $\mathrm{ThBu^+}$, at the ring (for 4) and α-carbon atom (for octane).

EXPERIMENTAL

Analytical methods. GLC analyses were made with a Varian model 3700 gas chromatograph equipped with a Varian CDS-111 or 4270 integrator. Concentration factors were established by using solns of standards; internal standards were not used. Columns used for GLC analyses were 20% BEEA on Chromosorb PAW, 60–80 mesh (glass, 6.5 ft and 12 ft × 1/8 in), 5% OV-101 and 10% OV-101 on Chromosorb WHP, 80–100 mesh; the former was 1.5 ft × 1/8 in stainless steel and the latter 3 ft × 1/8 in stainless steel. The columns were used isothermally or under programmed heating as necessary. Woelm (ICN) silica gel (Cat. No. 402809) was used for column chromatography. Preparative TLC was carried out with E. Merck (Cat. No. 5717-7) 20 × 20 cm plates, coated with 2 mm of silica gel. Analytical TLC was carried out with Merck (5761) 0.25 mm silica gel plates. Low resolution mass spectra were obtained with a Hewlett-Packard model 5995 spectrometer, while high resolution mass spectra were recorded at the Midwest Center for Mass Spectrometry.[†] Gaseous hydrocarbons were from Matheson Gas Products, Inc. Standard solutions of the gases were prepared by dissolving a known volume of gas from a gas burette in a known volume of solvent, and checking the amount of solute by weighing. Aliquots of standard solns were sealed in 1 ml ampules at 0° and stored in the refrigerator for periodic use. The following compounds, also used as standards and controls in GLC analyses, were obtained from Aldrich Chemical Co.: 2,3-dimethylbutane, hexamethylethane, cyclohexane, methylcyclopentane, methylenecyclopentane, octane, 1-hexene, cyclohexene, 1-methylcyclopentene, 5-hexen-1-ol, cyclopentylmethanol, 2,3-dihydrofuran, and ethyl vinyl ether. Butyl-, s-butyl, and t-butylchloride were from Aldrich. Diethyl ether and tetrahydrofuran (THF) for Grignard reactions were distilled three times over $\mathrm{LiAlH_4}$ under argon and were stored under argon. Polymer (solvent) molecular weights were determined by gel permeation.[‡]

Grignard reagents. s-ButylMgCl and t-butylMgCl in ether, and all Grignard reagents in THF were from Aldrich. Other Grignard solns were prepared immediately before use under argon. Assays were carried out either by titration[33] or by measuring the volume of alkane obtained by decomposing an aliquot with water.

Reagents and products. 6-Chloro-1-hexene was prepared in 70% yield by the reaction of 5-hexen-1-ol with $\mathrm{Ph_3P}$ and $\mathrm{CCl_4}$; b.p. 128–129° (685 mmHg). Lit. b.p. 128–130° (760 mmHg).[34] Cyclopentylmethylchloride was prepared in 60% yield from cyclopentylmethanol in the same manner; b.p. 137–138° (685 mmHg). Lit. b.p. 141–143° (755 mmHg).[35] 2,3-Diethoxybutane was obtained as a mixture of *dl* and *meso* forms in 32% yield by reaction of diethyl ether with di-t-butyl peroxide,[36] and had b.p. 42–45° (21 mmHg). The *meso* and *threo* isomers have b.p. 138° (745 mmHg) and 139.8° (747 mmHg), respectively.[37] The dimer of THF, octahydro-1,1′-bifuran, was prepared similarly in 68% yield from THF,[36] and had b.p. 76–80° (12 mmHg). Lit. b.p. 73–76° (12.5 mmHg).[38]

Reactions of Grignard reagents with thianthrene cation radical perchlorate

In ether solution. The method in general was to add the Grignard soln dropwise by syringe to a suspension of $\mathrm{Th^{\cdot +}ClO_4^-}$ being vigorously stirred magnetically in a septum-capped vial cooled in an ice bath to 0°. Products were identified, assayed and, in some cases, isolated, by combinations of GLC, TLC, and column chromatography. Results are tabulated in Table 1, while each run is described more specifically below. An aliquot of each Grignard soln was also decomposed in a septum-capped vial by adding water by syringe, and the hydrocarbon products were assayed by GLC. Results are listed in Table 1.

BuMgCl (*run* 1). Reactants were 948 mg (3.00 mmol) of $\mathrm{Th^{\cdot +}ClO_4^-}$ in 7 ml of ether and 0.50 ml (1.2 mmol) of BuMgCl. After addition of the BuMgCl (5 min) the excess of $\mathrm{Th^{\cdot +}ClO_4^-}$ had become deposited on the wall of the vial as a grey–black mixture. The supernatant soln was analyzed directly on the smaller BEEA column after 1.5 h of stirring. Results are listed in Table 1. After GLC analysis, 2 ml of water and 5 ml of $\mathrm{CH_2Cl_2}$ were injected into the vial and stirring was continued until all of the $\mathrm{Th^{\cdot +}ClO_4^-}$ had disappeared. The water layer was removed, and extracted with 5 × 10 ml of $\mathrm{CH_2Cl_2}$. The collected $\mathrm{CH_2Cl}$ soln was dried over $\mathrm{MgSO_4}$ and evaporated. The residue was separated with $\mathrm{CH_2Cl_2}$ on 2 mm TLC plates to give, in order of decreasing R_f, 406 mg (1.88 mmol) of thianthrene (Th), 126 mg (0.54 mmol) of thianthrene 5-oxide (ThO), and 218 mg (0.58 mmol) of an oil which was identified by ^{1}H-NMR as 5-butylthianthrenium perchlorate ($\mathrm{ThBu^+ClO_4^-}$). Th and ThO were removed from the plate material with $\mathrm{CH_2Cl_2}$, while $\mathrm{ThBu^+ClO_4^-}$ was removed with dry acetone. The $\mathrm{ThBu^+ClO_4^-}$ was crystallized three times by precipitation from $\mathrm{CH_2Cl_2}$ with dry ether and had m.p. 121–123°, ^{1}H-NMR ($\mathrm{CH_2Cl_2}$) δ: 0.8 (t, 3H, $\mathrm{C\underline{H}_3}$, J = 6 Hz), 1.5 (m, 4H, $\mathrm{—C\underline{H}_2C\underline{H}_2—}$), 3.7 (t, 2H, $\mathrm{—C\underline{H}_2S^+}$, J = 6.5 Hz), 7.8 (m, 6H), 8.2 (m, 2H). The product was identical with that obtained earlier from the reaction of $\mathrm{Th^{\cdot +}ClO_4^-}$ with $\mathrm{Bu_2Hg}$.[22b]

s-BuMgCl (*run* 2). The reactants were 0.63 ml (1.60 mmol) of Grignard soln and 632 mg (2.00 mmol) of $\mathrm{Th^{\cdot +}ClO_4^-}$ in 9 ml of ether. Volatile materials were pumped off and analyzed as described in run 1, and the results are listed in Table 1. The residue left in the reaction vial was extracted directly with $\mathrm{CH_2Cl_2}$, however, and the products were separated by column chromatography (silica gel, Woelm) rather than by TLC. Elution with $\mathrm{CH_2Cl_2}$ gave 383 mg (1.77 mmol) of Th and 20 mg (0.084 mmol) of ThO. Elution with $\mathrm{CH_2Cl_2}$/acetone gave 23 mg of an unidentifiable substance.

t-BuMgCl (*run* 3). Reactants were 0.53 ml (1.0 mmol) of a 1.9 M soln of t-BuMgCl and 948 mg (3.00 mmol) of

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[†] An NSF regional facility, University of Nebraska, Lincoln, Nebraska. We thank Drs Frank Crow and Ken Tomer for their help.

[‡] We thank Dr Richard W. Tock and Mr Bernard Young, Department of Chemical Engineering, Texas Tech University, for these measurements.

$\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ in 8 ml of ether. After stirring for 3 h, all volatile materials were transferred under vacuum to a 10 ml volumetric flask cooled in a liq N_2 trap. The distillate was diluted to 10 ml at 0° with ether and analyzed on the smaller BEEA column. To the residue in the vial was added by syringe 0.5 ml of water and 8 ml of ether. The ether layer was again analysed on the BEEA column. Results are listed in Table 1. Thereafter, 10 ml of CH_2Cl_2 was added to the vial and the contents were worked up for column chromatography. Elution with CH_2Cl_2 gave only 441 mg (2.04 mmol) of Th and 226 mg (0.97 mmol) of ThO. No other substances were found.

5-HexenylMgCl (*run* 4). The name 5-hexenylMgCl means here a mixture of 5-hexenyl- and cyclopentylmethylMgCl prepared in the usual way from 6-chloro-1-hexene. The relative amounts of the two alkyl groups in the Grignard was determined by decomposing the Grignard with water and measuring the amounts of 1-hexene and methylcyclopentane by GLC. The result is listed in Table 2.

To the suspension of 948 mg (3.00 mmol) of $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ in 7 ml of ether was added 0.50 ml (1.00 mmol) of a 2.0 M 5-hexenylMgCl soln. Again, a black–grey inclusion precipitate of the excess of $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ was formed and stirring was continued for 2 h. Thereafter the ether soln was assayed for 1-hexene and methylcyclopentane on the smaller BEEA column. Neither 1-methylcyclopentene nor methylenecyclopentane were found.

After GLC analysis of 2 ml of water and 10 ml of CH_2Cl_2 were injected into the vial and stirring was continued until all of the $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ had disappeared. Workup followed as in run 1, and gave 407 mg (1.88 mmol) of Th, 134 mg (0.58 mmol) of ThO, and 224 mg (0.56 mmol) of an oil, shown to be a mixture of 5-(5-hexenyl)- and 5-(cyclopentylmethyl)thianthrenium perchlorates. Analysis of the mixture was carried out in two ways. Integration of the ^{1}H-NMR ($CDCl_3$) signals of the $\underline{H}_2C{=}CH(CH_2)_4S^+$ and cyclopentyl $C\underline{H}_2S^+$ protons gave respectively 0.36 mmol of the 5-hexenyl and 0.20 mmol of the cyclopentylmethyl salts; thus the ratio L/C (linear/cyclic) was 1.80. Then, the $CDCl_3$ was evaporated and the oily residue was dissolved in 3 ml of dry acetone. To the soln was added 300 mg of LiCl. Stirring was continued overnight, whereupon some Th had precipitated. Therefore, 4 ml of CH_2Cl_2 was added for complete solubility and the soln was analyzed by GLC on the 5% OV-101 column, giving 0.27 mmol of 5-hexenyl-, 0.12 mmol of cyclopentylmethylchloride, and 0.51 mmol of Th. Thus, the ratio L/C by this method was 2.3.

*Cyclopentylmethyl*MgCl (*run* 5). Reaction with $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ (948 mg, 3.00 mmol) and 0.50 ml (1.2 mmol) of a 2.4 M soln of Grignard was carried out as in run 4. Assay of methylcyclopentane (on the 5% OV-101 column) gave 0.31 mmol: no other hydrocarbon was found. TLC of the non-volatile products gave 427 mg (1.97 mmol) of Th, 112 mg (0.48 mmol) of ThO, and 220 mg (0.56 mmol) of 5-(cyclopentylmethyl)thianthrenium perchlorate. The sulfonium salt was dissolved in 3.0 ml of dry acetone to which 300 mg of LiCl was added. The soln was stirred overnight, diluted with 4.0 ml of CH_2Cl_2 to dissolve Th and analyzed by GLC (5% OV-101). Results are listed in Table 2.

Reaction of $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ *with ethyl vinyl ether*

To a suspension of 316 mg (1.00 mmol) of $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ in 8 ml of ether at 0° was added dropwise 96 μl (1.00 mmol) of ethyl vinyl ether. A vigorous reaction occurred, but a large amount of $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ remained. Therefore, three more 96 μl aliquots of ethyl vinyl ether were added, but again, much $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ remained. This was destroyed by addition of 1.0 ml of 2 M NaOH soln. Volatile materials were pumped off into a 10 ml volumetric flask and analyzed by GLC as described earlier. Neither ethyl vinyl ether nor any other volatile product could be found. The non-volatile residue was taken up in CH_2Cl_2 and its components were separated by preparative TLC giving, in order of decreasing R_f, 132 mg (0.61 mmol) of Th, 88 mg (0.38 mmol) of ThO, and (extracted with methanol) 177 mg of a honey-like oil. This had a ^{1}H-NMR spectrum consistent with poly(vinyl ethyl ether) and a weight average mol. wt of 1200.

Reaction of BuMgCl *with 5-butylthianthrenium perchlorate* ($\mathrm{ThBu}^+\mathrm{ClO}_4^-$) *in ether*

To a stirred suspension of 149 mg (0.40 mmol) of $\mathrm{ThBu}^+\mathrm{ClO}_4^-$ in 5 ml of ether (a sufficient volume to dissolve Th as it was formed) was added dropwise 0.17 ml (0.4 mmol) of BuMgCl soln. The mixture was sampled periodically by syringe for GLC monitoring. After 3 h no further increase in the amount of Th was found. GLC analysis of the volatile products on the smaller BEEA column gave butane (0.12 mmol), butene (0.02 mmol), and octane (0.31 mmol). The non-volatile products were chromatographed on 2 mm plates with a 5 : 1 (v/v) mixture of CH_2Cl_2 and acetone. Two bands were obtained. The lower, near the origin, was unreacted $\mathrm{ThBu}^+\mathrm{ClO}_4^-$ (0.02 mmol). The upper was a mixture of thianthrene and what is believed from mass spectrometry to be 2-butyl-2′-(butylthio)diphenyl sulfide. This mixture was assayed by GLC on the 10% OV-101 column and gave 0.37 mmol of Th and 0.03 mmol of 2-butyl-2′-(butylthio)diphenyl sulfide. The concentration factor which was used for assaying this compound by computer integration was taken to be the sum of the concentration factors of Th and octane. High resolution mass spectrometry† gave M^+ 330.1488 (calc for $C_{20}H_{20}S_2$: 330.1476). Low resolution GC/MS spectrometry gave principal ions (%) 330 (23), 274 (7), 241 (6), 199 (5), 198 (24), 197 (24), 165 (6), 153 (7), 142 (10), 140 (14), 135 (11), 133 (21), 123 (6), 91 (100), 77 (11), 57 (11).

Reactions of Grignard reagents with thianthrene cation radical perchlorate

In THF soln. A series of reactions was carried out between RMgX and $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ in which R = Me, i-Pr, Bu, s-Bu, t-Bu and Ph (phenyl). A general description for this series follows and the results are listed in Table 3. More detailed descriptions are then given only for particular reactions.

General procedure. A weighed amount of $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$, a stirring bar and 20 ml of THF were placed under argon in a septum-capped 40 ml vial in a bath at 20°. The vial was connected through the septum by a small length of 1/8 in. Tygon tubing to a gas burette. The Grignard soln was added slowly dropwise via the septum from a 1.0 ml calibrated syringe while the suspension of $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ was stirred vigorously. Addition was stopped when all of the $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ had disappeared. Vigorous evolution of gas was observed only with addition of MeMgCl and i-PrMgCl. In other cases gaseous products were sufficiently soluble in THF so that gas evolution was not observed. After addition of the Grignard soln the mixture was stirred for 1 h before the gas volume, where appropriate, was measured. Thereafter, samples of gas and soln were taken via the septum for analysis and assay by GLC on the larger BEEA column. After GLC analysis the THF soln was monitored for products by analytical TLC. Only Th and traces of ThO were found. The amount of Th in soln was measured, therefore, by ^{1}H-NMR. Results of analyses and assays are listed in Table 3.

Polymerization of THF by MeMgCl. A suspension of 632 mg (2.00 mmol) of $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ in 9 ml of THF was stirred as described above. When the gas burette was stabilized, 0.325 ml (0.94 mmol) of a 2.9 M soln of MeMgCl was added dropwise during 2 min. Evolution of gas (methane) during addition was vigorous. All of the $\mathrm{Th}^{\cdot+}\mathrm{ClO}_4^-$ had disappeared after 15 min of stirring. The amount of gas formed, corrected to standard conditions was 0.55 mmol. The vial was disconnected from the burette and stored in the refrigerator for 6 weeks, at which time the soln had the consistency of honey. The growth of polymer (assumed to be "living" polymer) was stopped by addition of 1 ml of 2 N NaOH soln. Extrac-

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† See footnote†, p. 6018.

tion with 50 ml of CH_2Cl_2 gave a very viscous product, which was chromatographed on a column of silica gel. Elution with CH_2Cl_2 gave 426 mg (1.57 mmol, 98.5%) of Th, and elution with acetone gave 3.1 g of viscous poly(THF), weight average mol. wt 2300.

Reaction of BuMgCl *with* $Th^{\cdot+}ClO_4^-$ *in* THF *isolation of* $ThBu^+ClO_4^-$

Dropwise addition during 2 min of 0.50 ml of 2.2 M BuMgCl soln to a suspension of 948 mg (3.0 mmol) of $Th^{\cdot+}ClO_4^-$ in 7 ml of THF at 0° gave a dark brown mixture. This was immediately poured into a well-stirred mixture of 2 ml of water and 10 ml of CH_2Cl_2. The water phase was separated and extracted with 4 × 10 ml of CH_2Cl_2. To the combined, dried ($MgSO_4$) CH_2Cl_2 solns was added 60 ml of dry ether. A dark, gummy precipitate formed. This was separated by decanting the soln, taken up in a few ml of CH_2Cl_2 and placed on 2 mm TLC plates. Development with CH_2Cl_2–acetone (2 : 1 v/v) gave two bands, one being Th and the other (lower) $ThBu^+ClO_4^-$. Extraction gave 89 mg (0.22 mmol, 22% based on BuMgCl) of oily product, identified as $ThBu^+ClO_4^-$ by ^{1}H-NMR.

Polymerization of THF *by* $ThBu^+ClO_4^-$ *in* CH_2Cl_2. A soln of 100 mg (0.268 mmol) of $ThBu^+ClO_4^-$ in 0.4 ml of CH_2Cl_2 was sealed with 1.6 ml of THF in a glass ampule. The ampule was heated for 3 h in boiling water, and opened after cooling in ice. GLC on the smaller BEEA column showed the presence of 1-butene (0.009 mmol, 3.3% of butyl groups used) but not of butane. Five ml of water was added to the ampule, and the organic products were extracted with 5 × 10 ml of CH_2Cl_2. Workup and separation on 2 mm plates with CH_2Cl_2–acetone (10 : 1 v/v) gave 58 mg (0.268 mmol, 100%) of Th and 416 mg of very viscous poly(THF).

Polymerization of THF-d_8 *by* $ThBu^+ClO_4^-$ *in* CH_2Cl_2 *at* 75°. The THF-d_8 was dried by distillation from sodium benzophenone ketyl under argon. A soln of 110 mg (0.295 mmol) of $ThBu^+ClO_4^-$ in 200 mg of CH_2Cl_2 and 430 mg of THF-d_8 was sealed in a 5 mm NMR tube. The soln was heated in a bath at 75° and the ^{1}H-NMR spectrum was recorded periodically. The triplet signal from the $—CH_2S^+$ protons at δ 3.7 disappeared in time while a triplet signal from $—CH_2O—$ at δ 3.3 grew in intensity. The tube was opened after 24 h and to the viscous product was added 2 ml of CH_2Cl_2 and 100 μl of water. The CH_2Cl_2 was dried over $MgSO_4$ and evaporated to give 377 mg of a viscous mixture. Separation on a 2 mm plate gave 58 mg (0.268 mmol, 91%) of Th and poly(THF-d_8). The latter was again chromatographed on a 2 mm plate and gave 4 mg of Th, 2 mg of ThO, and 290 mg of poly(THF). The Th and ThO thus represented 98% of the original $ThBu^+ClO_4^-$.

The poly(THF-d_8) had ^{1}H-NMR ($DCCl_3$) δ: 0.93 (t, 3H, $C\underline{H}_3$), 1.4 (m, 4H, $—C\underline{H}_2C\underline{H}_2—$) and 3.33 (t, 2H, $—C\underline{H}_2O—$, $J = 7$ Hz). Assay, using HMDSO as an internal standard, gave 0.27 mmol (91.5%) of butyl groups, from which, with the amount of polymer used, the average mol wt of the poly(THF-d_8) was calculated to be 960.

Reaction of $ThBu^+ClO_4^-$ *with* THF-d_8 *in* CD_2Cl_2 *at* 20°

Transfer of the butyl group from S to O was followed by ^{1}H-NMR. A soln of 34.5 mg (0.093 mmol) of $ThBu^+ClO_4^-$ in 475 mg of CD_2Cl_2 was placed in a septum-capped NMR tube. THF-d_8 (70 mg) was added dropwise until $ThBu^+ClO_4^-$ showed signs of precipitation. The soln was kept at room temp (approx 20°) for several weeks, during which the ^{1}H-NMR was recorded periodically. The signal at δ 3.2 ($—CH_2C\underline{H}_2—O—$) slowly increased while the signal at δ 3.5 ($—CH_2C\underline{H}_2S^+$) slowly decreased, eventually (68 d) reaching the ratio 4 : 1.

Reaction of BuMgCl *with* $Th^{\cdot+}ClO_4^-$ *in* THF-d_8

A soln of BuMgCl was prepared by stirring overnight under argon a mixture of 313 μl (3.0 mmol) of BuCl, 97 mg (4.0 mmol) of Mg and 1.0 ml of THF-d_8. Grignard soln was added dropwise from a calibrated syringe to a stirred suspension of 126 mg (0.4 mmol) of $Th^{\cdot+}ClO_4^-$ in 2 ml of THF-d_8 under argon in a septum-capped vial at 0°. When all of the $Th^{\cdot+}ClO_4^-$ had disappeared (7 min), 88 μl (9.2 mmol) of BuMgCl soln had been added. The presence of $ThBu^+ClO_4^-$ could not be detected by TLC and ^{1}H-NMR. After 3 d at room temp all volatile products and solvent were pumped off and trapped in a liq. N_2 bath. GLC analysis of the distillate gave butane (0.138 mmol, 69%), 1-butene (tr.) and octane (0.0029 mmol). The residue was taken up in 2 ml of CH_2Cl_2 and separated on a 2 mm plate, giving 81 mg (0.375 mmol, 93.7%) of Th, 6.0 mg (0.026 mmol, 6.5%) of ThO and 40 mg of poly(THF-d_8). The presence of butyl groups in this polymer was detected by ^{1}H-NMR signals (poorly resolved) at δ 3.25, 1.3 and 0.8.

Attempted polymerization of THF *by* $Th^{\cdot+}ClO_4^-$

A stirrer bar and 316 mg (1.0 mmol) of $Th^{\cdot+}ClO_4^-$ were placed in a 20 ml septum-capped ampule. The ampule was evacuated to low pressure through the septum for 4 h, after which 10 ml of THF was introduced by syringe. The ampule was sealed and the suspension of $Th^{\cdot+}ClO_4^-$ was stirred for 6 d. No change in viscosity was noticed. The mixture was allowed to stand, whereupon 0.5 ml for ^{1}H-NMR spectroscopy and 5.0 ml for evaporation were withdrawn. ^{1}H-NMR showed no sign of Th, while evaporation left no significant amount of residue. The $Th^{\cdot+}ClO_4^-$ was then filtered, washed with CCl_4, giving 310 mg (98%) recovery.

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Notes added in proof

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