these reactions have been determined. Alternatively, methylene blue sensitized production of singlet oxygen leads to reaction with the diazo precursor, again giving the carbonyl oxide. Rate constants for this reaction for several different diazo compounds have also been determined.

Carbonyl oxides decay almost exclusively by a second-order process involving recombination and ultimately ketone production. Severely hindered carbonyl oxides (IV and especially V) decay more slowly than less hindered species, thus giving indirect support for the recombination mechanism. In addition aldehyde quenching has been shown for I–III in agreement with the results of Criegee.

Finally, we have been interested in the photochemistry of reaction intermediates induced by subjecting photochemically produced transients to a second laser pulse.[31] In a two-laser experiment in which the first laser is used to produce the carbonyl oxide (I) and a dye laser tuned to ~430 nm is used to photolyze I, we observed efficient irreversible bleaching associated with the dye laser pulse. This bleaching indicates that permanent chemical change takes place following excitation of I. Whether the products associated with this bleaching are benzophenone or the aryl ester, phenyl benzoate, will be the subject of future work.

Acknowledgment. Thanks are due to S. E. Sugamori for technical assistance and to Professor W. Sander for the communication of unpublished results (ref 14).

Registry No. I, 20387-24-0; II, 91669-23-7; III, 118797-91-4; IV, 118797-92-5; V, 118797-93-6; VI, 118797-94-7; VII, 118797-95-8; VIII, 118797-96-9; IX, 118797-97-0; X, 118797-98-1; XI, 118797-99-2; O_2, 7782-44-7; diphenyldiazomethane, 883-40-9; bis(4-methylphenyl)diazomethane, 1143-91-5; bis(2,4,6-trimethylphenyl)diazomethane, 61080-14-6; 9-diazofluorene, 832-80-4; diphenylcarbene, 3129-17-7; bis(4-methylphenyl)carbene, 32076-77-0; bis(2,4,6-trimethylphenyl)carbene, 85236-86-8; 9*H*-fluoren-9-ylidene, 2762-16-5; acetaldehyde, 75-07-0; phenylacetaldehyde, 122-78-1; mesitaldehyde, 487-68-3.

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(31) See for example: McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2179. Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 5487.

Reactions of Phenylmagnesium Chloride and Phenyllithium with Thianthrene Cation Radical Perchlorate. Evidence for Electron Transfer: Formation and Decomposition of 5-Substituted Thianthreniumyl Perchlorates

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Reaction of thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$), suspended in either ether or THF, with PhMgCl, and reaction of $Th^{\bullet+}ClO_4^-$, suspended in ether, with PhLi in C_6H_{12}/ether, gave largely benzene and Th. 5-Phenylthianthreniumyl perchlorate (**1a**) was formed in the Grignard reactions but was not obtained in the PhLi reaction. Diphenyl sulfide (Ph_2S) and dibenzothiophene (DBT) were obtained with PhMgCl and PhLi in ether, but not with PhMgCl in THF. Small amounts of ethyl 1-phenylethyl ether and 2-phenyltetrahydrofuran (PhTHF) were also formed. Reaction with PhMgCl in THF-d_8 and with PhLi in $(C_2D_5)_2O$ gave a mixture of C_6H_6 and C_6H_5D. These results show that phenyl radical ($Ph^\bullet$) was formed in the cation radical reactions and abstracted H(D) atom from the solvent. The results suggest also that $Ph^\bullet$ was trapped by $Th^{\bullet+}$, leading to **1a**. However, as shown with control reactions, **1a** reacted further with PhMgCl (slowly) and PhLi (rapidly) and was converted into Ph_2S and DBT. Control reaction of PhLi with **1a** gave Ph_2S and DBT in high, approximately equal yields. Reaction with 5-(*p*-tolyl)thianthreniumyl perchlorate (**1b**) analogously gave phenyl *p*-tolyl sulfide and DBT. Reaction of PhMgCl with **1a** was slow and incomplete and gave not only Ph_2S and DBT but also some 2-phenyl-2′-(phenylthio)diphenyl sulfide (**2a**) and a mixture of 1- and 2-phenylthianthrene (together designated as **3a**). An analogous reaction occurred between PhMgCl and **1b**. Reaction of **1a** with BuMgCl gave BuSPh and DBT, some 2-(phenylthio)diphenyl sulfide (**4**), and some 2-(butylthio)-2′-phenyldiphenyl sulfide (**5a**). In contrast, reaction of PhMgCl with 5-butylthianthreniumyl perchlorate (**1e**) gave mainly benzene and Th, while reaction of BuMgCl with **1e** gave mainly butane, octane, and Th along with a small amount of 2-butyl-2′-(butylthio)diphenyl sulfide (**5e**). Reaction of PhLi with **1e** and its analogues 5-methyl- and 5-ethylthianthreniumyl perchlorate (**1c** and **1d**, respectively) gave benzene, Th, the corresponding alkyl phenyl sulfide and DBT, and small amounts of 2-(alkylthio)-2′-phenyldiphenyl sulfide (**2c–e**). Formation of benzene in these reactions is attributed to deprotonation of the alkyl group in **1c–e** and concomitant formation of an ylide (**6–8**). Ylide **6**, from reaction of PhLi with **1c**, was trapped by reactions with subsequently added water and phenol (reconverting **6** to **1c**) and with added benzophenone, leading to Th and 1,1-diphenyloxirane (**9**). Diphenylmercury did not react with **1a** in acetonitrile solution. The apparent complexity of reactions of $Th^{\bullet+}ClO_4^-$ with PhMgCl and PhLi is better understood in the light of knowledge about reactions of **1a–e**. The comparative simplicity of reaction of $Th^{\bullet+}ClO_4^-$ with Ph_2Hg is also made clearer.

Introduction

Some years ago it was found that thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) reacted with diorgano mercurials (R_2Hg) to give 5-substituted thianthreniumyl perchlorates (1) in excellent yield (eq 1).[2] A question arose as to whether or not the reaction involved electron transfer and formation of radicals, which, being trapped by $Th^{\bullet+}$, gave products 1. Later, evidence for these steps was, in

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(1) On leave from the Institute of Organic and Physical Chemistry, Technical University, Wroclaw, Poland.

(2) Bandlish, B. K.; Porter, W. R., Jr.; Shine, H. J. *J. Phys. Chem.* **1978**, *82*, 1168.

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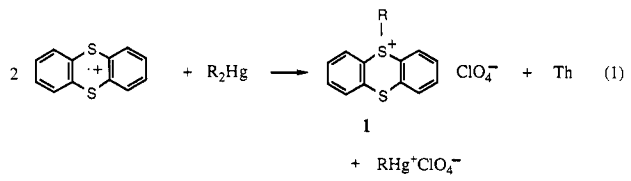


(1)

R = aryl, Me, Et, Bu

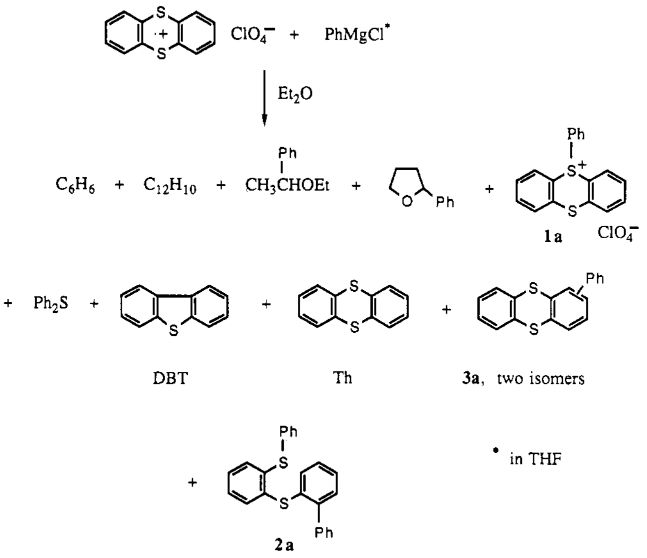
fact, found in the reaction of $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ with diethylmercury.[3] Grignard reagents were also found to undergo electron transfer in reaction with $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$, but in contrast with the reactions with R_2Hg, sulfonium salts (**1**) were not generally found.[4] In particular, reaction of PhMgCl with $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ in THF led to a large amount of benzene (87%), indicating that the primary mode of reaction was electron transfer, from which the phenyl radical ($\mathrm{Ph}^\bullet$) so formed abstracted hydrogen atom from the solvent. The contrast of this reaction with that of $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ with Ph_2Hg[2] was striking and suggested that either free $\mathrm{Ph}^\bullet$ was not formed in the Ph_2Hg reaction, or, if formed, was immediately scavenged by $\mathrm{Th}^{\bullet+}$. It appeared that $\mathrm{Ph}^\bullet$, formed in the Grignard reaction, was not trapped by $\mathrm{Th}^{\bullet+}$, since 5-phenylthianthreniumyl perchlorate (**1a**) was not found. At that time, however, the reaction of $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ with PhMgCl was not examined thoroughly beyond the formation of benzene; other products were not sought. We have now studied that reaction in more detail, in both ether and THF solvents. We have studied also the analogous reaction of $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ with PhLi in ether. We confirm that benzene is the major product in the PhMgCl reaction; it is the major product in the PhLi reaction, too. On the other hand, we have found that **1a** is, in fact, formed and is isolable in the Grignard but not the PhLi reaction. The results of these studies showed the need to study also the reactions of PhMgCl and PhLi with **1a**. We have carried out those studies, and they have led us, in turn, to a more extensive study of reactions of PhLi with a series of 5-substituted thianthreniumyl perchlorates, **1b**–**e**, in which R = *p*-tolyl, methyl, ethyl, and butyl. We have studied also the reactions of PhMgCl with **1b** and **1e** and of butylmagnesium chloride (BuMgCl) with **1a** and **1e**.

Results

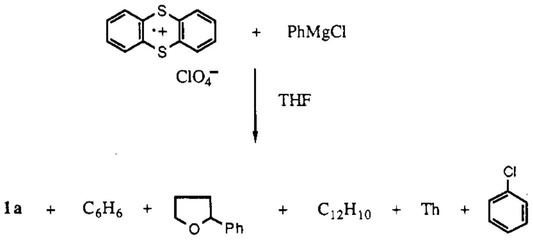
Reactions of $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ with PhMgCl and PhLi. $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ is insoluble in the solvents, ether and THF, in which reactions of PhMgCl and PhLi can be carried out. Reactions were therefore carried out in suspension, under argon. Two ratios of reactants were used, namely approximately 2:1 and 1:1 of $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$/organometallic. Products were analyzed and assayed with combinations of gas chromatography (GC) and preparative-scale thin-layer chromatography (TLC). The structures of some products (**2**–**5**) were assigned on the basis of mass spectrometry and the probable pathways of reaction. Quantitative data are listed in Tables I–III, while the reactions and products are shown in Schemes I–III.

Substantial amounts of benzene were formed in all reactions. We emphasize that this occurred particularly in reactions having an excess of $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$. That is, the benzene could not have come from later workup of unused organometallic, but was a primary product, whose formation is attributed to abstraction of hydrogen atom from solvent by phenyl radical ($\mathrm{Ph}^\bullet$).

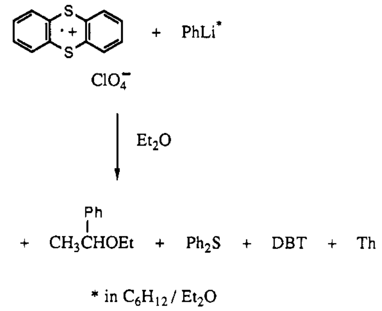
Scheme I



Scheme II



Scheme III



5-Phenylthianthreniumyl perchlorate (**1a**) was isolated from reactions with PhMgCl. It is noticeable (Table I) that more **1a** was obtained in the 2:1 than in the 1:1 reactant ratios, a result that is attributable to loss of **1a** in the latter because competition for reaction of PhMgCl with **1a** rather than $\mathrm{Th}^{\bullet+}$ was the greater. Three products of the contraction and opening of the thianthrene ring are listed in Table I: diphenyl sulfide (Ph_2S), dibenzothiophene (DBT), and 2-phenyl-2′-(phenylthio)diphenyl sulfide (**2a**). Of these, Ph_2S and DBT go hand in hand. They should, as is shown later, have been obtained in equimolar amounts and for the most part this is borne out in Table I. They arose from reaction of PhMgCl with **1a**. Product **2a** is also a product of reaction of PhMgCl with **1a**. These two reactions, that is, one giving Ph_2S and DBT and the other giving **2a**, are general reactions of 5-substituted thianthreniumyl ions, as is shown later. Ph_2S and DBT were obtained from reaction of PhLi with $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$, too (Table III). There, they are not listed in equimolar amounts. Instead, the amount of Ph_2S obtained was close to three times (runs 1–3) that of DBT. We do not know the reason for that. Control experiments showed that PhLi did not react with DBT in the same conditions, and although control experiments showed that $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ did react with DBT, reaction was far too slow to account for the loss of

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[3] Sugiyama, K.; Shine, H. J. *J. Org. Chem.* **1982**, *48*, 143.
[4] Soroka, M.; Shine, H. J. *Tetrahedron* **1986**, *42*, 6111.

Table I. Products of Reaction of $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ with PhMgCl in Ether

	reactants, mmol		products, mmol and %[a]											totals,[b] %	
run no.	$\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$	PhMgCl	C_6H_6[c]	PhEtOEt[d]	PhTHF[e]	$C_{12}H_{10}$[f]	Ph_2S	DBT	Th	ThO	**2a**[g]	**3a**[h]	**1a**[i]	Ph	Th
1	1.70	0.85	0.482	0.029	0.013	0.026	0.018	0.030	1.11	0.224	0.013	0.008	0.216	0.83	1.60
			56.7	3.4	1.5	1.1	2.1	1.8	65.5	13.2	1.5	0.94	25.4	93.7	94.4
	j	0.85	0.866			0.017									
2	1.71	0.85	0.37	0.027	tr	0.055	0.031	0.032	1.12	*k*	0.050	0.065	0.114	0.77	*l*
			43.5	3.2		12.9	3.6	1.9	65.5		5.9	7.6	13.4	90.5	
	j	0.85	0.83			tr									
3	1.64	0.85	0.33	0.029	tr	0.016	0.063	0.065	1.06	*k*	0.031	0.039	0.120	0.64	*l*
			38.8	3.4		3.8	7.4	4.0	64.6		3.6	4.6	14.1	75.7	
4	1.73	1.70	0.77	0.053	0.035	0.082	0.258	0.223	1.10	tr	0.149	0.126	0.026	1.58	1.62
			45.3	3.1	2.1	9.6	15.2	13.1	64.7		8.8	7.4	1.5	93.0	95.5
	j	1.70	1.75			tr									
5	1.71	1.70	0.63	0.058	tr	0.073	0.210	0.178	1.16	tr	0.11	0.051	0.09	1.30	1.59
			37.0	3.4		8.6	12.4	10.4	67.8		6.5	3.0	5.3	76.1	93.0

[a] The percent data are entered below the mmol data. [b] These percent data represent the sum of Ph groups from PhMgCl and Th groups from $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ in all products; the percent biphenyl is corrected for the amount of biphenyl in the control reaction. [c] Average of assays on columns A and B. [d] Ethyl 1-phenylethyl ether. [e] 2-Phenyl-THF. [f] Biphenyl. [g] 2-phenyl-2′-(phenylthio)diphenyl sulfide. [h] Two isomers of phenylthianthrene. [i] 5-Phenylthianthreniumyl perchlorate. [j] Control reaction with water; no $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$. [k] Not measured. [l] Summation is not possible because of absence of ThO yield.

Table II. Products of Reaction of $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ with PhMgCl in THF[a]

	reactants, mmol		products, mmol and %							totals, %	
run no.	$\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$	PhMgCl	C_6H_6	C_6H_5Cl	PhTHF	$C_{12}H_{10}$	Th	ThO	**1a**	Ph	Th
1[b]	2.50	1.70	0.935	0.047	0.056	0.082	1.79	0.035	0.367	1.57	2.19
			55.0	2.8	3.3	9.6	71.6	1.4	21.6	92.4	87.6
	c	1.70	1.65			tr					
2[b]	1.00	0.51	*d*	*e*	0.016	0.023	0.887	0.035	0.100	*f*	1.02
					3.1	9.0	88.7	3.5	19.6		102
3[g]	1.70	0.85	*h*		0.005	0.06	1.34	0.066	0.137		1.54
					0.59	14.1	78.8	3.9	8.1	*f*	90.8
4[g]	1.71	1.70	*h*		0.018	0.129	1.48	0.011	0.04		1.53
					1.1	15.2	86.5	0.64	2.3	*f*	89.5

[a] For the key to abbreviations and expressions of mmol and percent data, see Table I. [b] In 3 mL of solvent THF. [c] Control reaction with water; no $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$. [d] Large errors in measurement were caused by the overlap of benzene and THF peaks in the GC output, caused by the relatively large amount of THF used. [e] Not measured. [f] Summation not possible owing to absence of benzene yield. [g] In 25 mL of solvent THF. [h] Solvent and product benzene were evaporated prior to workup.

Table III. Products of Reaction of $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ with PhLi in Ether[a]

	reactants, mmol		products, mmol and %							totals, %	
run no.	$\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$	PhLi[b]	C_6H_6	PhEtOEt	$C_{12}H_{10}$[c]	Ph_2S	DBT	Th	ThO	Ph	Th
1	1.17	1.28	0.892	0.113	0.058	0.081	0.028	0.936	0.031	1.20	1.00
			69.6	8.8	9.1	6.3	2.4	80.0	2.6	93.8	85.0
	d	1.28	1.28		tr						
2	1.23	1.36	0.912	0.109	0.056	0.107	0.037	1.04	0.013	1.24	1.10
			67.0	8.0	8.2	7.9	3.0	84.5	1.0	91.1	89.4
	d	1.36	1.36								
3	1.22	0.675	0.50	0.020	0.010	0.031	0.011	0.795	0.210	0.561	1.02
			74.1	3.0	3.0	4.6	0.90	65.2	17.2	83.1	84.6
	d	0.675	0.675		0.015						
4	1.20	0.712	0.485	0.032	0.025	0.053	0.024	0.952	0.051	0.62	1.03
			68.1	4.5	7.0	7.4	2.0	79.3	4.3	87.1	85.8
	d	0.712	0.712		0.024						

[a] For the key to abbreviations and percent data, see Table I. [b] The mmol of PhLi that are listed are equated to the amount of C_6H_6 obtained in the control reaction. [c] Corrected for the amount of $C_{12}H_{10}$ obtained in the control reaction. [d] Control reaction with water; no $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$.

Table IV. Products of Reaction of 1a and 1b with PhLi in Ether

compd		reactants, mmol			products, mmol				totals,[a] %	
no.	Ar	H_2O	$\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$	PhLi	C_6H_6	$C_{12}H_{10}$[b]	PhSAr	DBT	Ph	1
1a	phenyl		0.51	0.68	0.20[c]	0.022[d]	0.437	0.431	99.6	84.5
		e		0.68	0.66	tr				
1b	*p*-tolyl		0.60	0.62	0.085[c]	0.018[d]	0.529	0.525	105	87.5
		e		0.62	0.62	tr				

[a] The sum of the Ph groups from PhLi found in all products, and the conversion of 1 into DBT. [b] Biphenyl. [c] It is believed that most, if not all, of this is due to the excess of PhLi which was used. [d] It is believed, on the basis of the control experiments, that most of this is a real product of reaction. [e] Control experiment.

DBT in the much faster reaction of $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ with PhLi.

Compound **1a** is, but Ph_2S, DBT and **2a** are not, listed in Table II for reaction of $\mathrm{Th}^{\bullet+}\mathrm{ClO}_4^-$ with PhMgCl in THF. It would appear that in THF PhMgCl does not react with **1a**. However, that is not the case; it was found by direct experiment that that reaction does occur, albeit very

Table V. Products of Reaction of 1a with PhMgCl and BuMgCl and of 1b with PhMgCl

			reactants, mmol		products, mmol								
Ar in 1	R in RMgCl	solvent	1	RMgCl	RH	RAr	RSAr	DBT	Th	2	5a	1[a]	total, %
Ph	Ph	Et_2O	0.506[b]	0.54	0.155[c]	0.157[d]	0.135	0.122	0.144	0.113[e]		0.164[b]	107[f]
Ph	Ph	THF	0.305[b]	0.34	0.174[c]	0.020	0.034	0.033	tr	0.098[e]		0.166[b]	97[f]
p-Tol	Ph	Et_2O	0.413[g]	0.408	0.093[c]	0.005[h]	0.244	0.242	0.007	0.054[i]		0.107[g]	99[f]
Ph	Bu	Et_2O	0.30[b]	0.36	0,095	0.028	0.127	0.133	0.042		0.096		103[j]

[a] Recovered. [b] **1a**, Ar = phenyl. [c] The amount of C_6H_6 represents mostly later decomposition of PhMgCl with workup water. The unused PhMgCl arose from the excess that was used and from incomplete reaction with 1. [d] Believed to be too high. [e] **2a**. [f] The sum of DBT, Th, **2**, and recovered 1. [g] **1b**, Ar = *p*-tolyl. [h] 0.048 mmol of biphenyl was obtained, too, approximately equal to the amount (0.40 mmol) in the aged PhMgCl solution. [i] **2b**. [j] The sum of DBT, Th, **5a**, and (assumed on the basis of GC–MS, M^+, 294) 0.039 mmol of **4**.

slowly, and that not only Ph_2S and DBT but also **2a** are formed (Table V). Therefore, we do not know why these products were not found in the reaction of $Th^{\bullet+}ClO_4^-$ with PhMgCl in THF. A striking feature of the reaction in THF was its relative speed, whether reaction occurred in concentrated (3 mL) or dilute (25 mL) solution. It is evident that the major reactions in THF are those of $Ph^\bullet$, leading (run 1) to benzene, PhTHF, biphenyl, and **1a**.

Small amounts of two isomers of phenylthianthrene were obtained from reaction with PhMgCl (Table I). The isomers were separable on the column (A) used for assaying products, and their integrated peaks were in the ratio 7:10. For convenience, however, they are listed together as **3a** in Table I. Assignment of them as phenylthianthrenes was made on the basis of GC–MS data. Separation was achieved on the mass spectrometer column, each isomer having *m*/*e* 292.

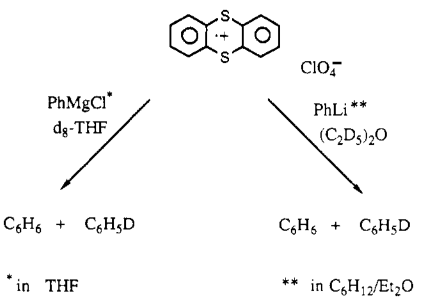
Small amounts of phenylated solvent were formed in each reaction. 2-Phenyltetrahydrofuran (PhTHF) was obtained from reaction with PhMgCl in THF. Both PhTHF and ethyl 1-phenylethyl ether (PhEtOEt) were obtained from reaction with PhMgCl in ether. The reason for that is that PhMgCl was used as a solution in THF. PhEtOEt was obtained from reaction with PhLi. These products are significant even if formed in small amounts. They are indicative of the combination of $Ph^\bullet$ and solvent-derived radicals.

Finally, small but significant amounts of biphenyl are listed in each of Tables I–III. Biphenyl was present in the PhMgCl and PhLi solutions but in much smaller amounts than the small quantities found in the cation radical reactions. (It was noticed that the amount of biphenyl in these commercial solutions increased with usage.) These amounts (Tables I–III) then are believed to be from the reactions themselves and are indicative again of $Ph^\bullet$ reactions, either with $Ph^\bullet$ itself or with product benzene.

Thianthrene 5-oxide (ThO) is listed in each of the tables. This can have been formed reasonably only by reaction of $Th^{\bullet+}$ with water either present in the solvent before addition of the organometallic or added in workup. The amount of ThO obtained should have been particularly high when an excess of $Th^{\bullet+}$ was used and remained unused at the end of reaction. It should be noted that this would apply especially to runs in which significant amounts of **1a** were not formed, because formation of **1a** requires an excess (a 2:1 ratio) of $Th^{\bullet+}$ over organometallic (cf. eq 1).

Table III reports the formation of chlorobenzene. That is an artifact of having chloride ion present in a reaction of $Th^{\bullet+}$;[5] we do not know why chlorobenzene was found only in reaction in THF. Last, each table reports an accounting of the total of Ph and Th units found in the products. The totals have built-in errors in that authentic samples of some of the products were not available, and therefore GC assays were made with assumed concentration factors (CF). However, those errors could not have been large. The product totals are in the range of 75–95%, the more significant losses being in the account of Ph groups.

Scheme IV



Reactions in Perdeuterio Solvents (Scheme IV). Reactions were carried out between $Th^{\bullet+}ClO_4^-$, suspended in THF-d_8, and PhMgCl in THF, and between $Th^{\bullet+}ClO_4^-$, suspended in ether-d_{10}, and PhLi in cyclohexane/ether. Thus, the reactions were in a mixture of perdeuterio and ordinary solvents of known proprotions. It was considered impractical to prepare solutions of the organometals in purely perdeuteriated solvents. The reactions therefore gave mixtures of C_6H_6 and C_6H_5D in which the ratio C_6H_6/C_6H_5D was measured with a quadrupole mass spectrometer. The relative intensities of the ions having *m*/*e* 78 and 79 were measured and compared with those having *m*/*e* 77, 78 and 79 from a control reaction. By knowing the normalized (M − 1), M, and (M + 1) ratios for ordinary benzene it was possible to calculate the ratio of C_6H_6/C_6H_5D obtained from the reactions in mixed solvents. These were 83.5% C_6H_6 and 16.5% C_6H_5D from reaction of PhMgCl in THF-d_8/THF and 41% C_6H_6 and 59% C_6H_5D from reaction of PhLi in $(C_2D_5)_2O/Et_2O/$cyclohexane. The proportion of H/D atoms in the solvents was 17/83 for the THF mixture and (by treating the H contents of C_6H_{12} and Et_2O as equivalent) approximately 15/85 for the ether/cyclohexane mixture. These proportions would represent the ratio of C_6H_6/C_6H_5D in each product if H(D) atom abstraction were nonselective. The measurements of relative abundances are likely to have contained not insignificant errors because they were made with a few scans only and by GC–MS. The C_6H_6/C_6H_5D ratios in the present work are significant nevertheless in that they are diagnostic of H(D) atom abstraction by $Ph^\bullet$.

Reactions of 5-Substituted Thianthreniumyl Perchlorates (1a–e) with Organometals. These reactions were studied in order to understand the formation of some of the products of reaction of $Th^{\bullet+}ClO_4^-$ with organometals. A series of 5-R-thianthreniumyl perchlorates, R = Ph, *p*-tolyl, Me, Et, and Bu (**1a–e**), was prepared by reaction of $Th^{\bullet+}ClO_4^-$ with R_2Hg.[2] Reactions of **1a–e** variously with PhLi, PhMgCl, and BuMgCl were studied in ether and

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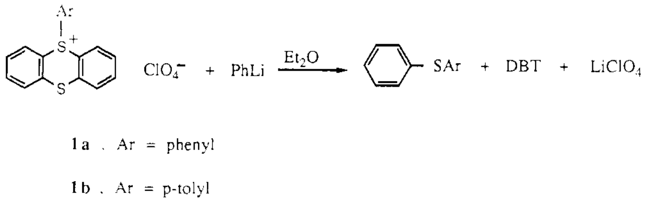
[5] Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 155.

Table VI. Products of Reaction of 1e with PhMgCl and BuMgCl in Ether

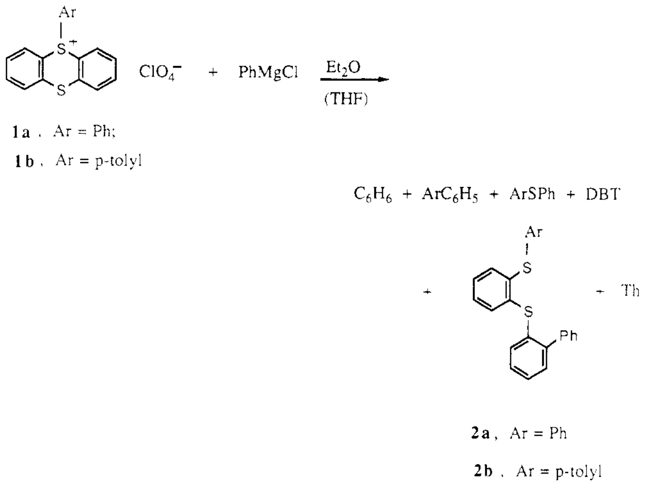
	reactants, mmol		products, mmol											totals, %	
R in RMgCl	**1e**	RMgCl	C_4H_{10}	C_6H_6	C_8H_{16}	C_8H_{18}	$C_{12}H_{10}$	RC_6H_5	Th	**2e**	**3e**	**5e**	**1e**[a]	R	**1e**
Bu	0.291	0.30	0.099			0.163			0.257		0.007	0.042		104[b]	103[c]
Ph	0.180	0.185		0.183	tr		tr	0.029	0.148	*d*			0.015	116[e]	91[f]

[a] Recovered. [b] Sum of Bu groups from BuMgCl in all products. Half of the Bu groups in C_8H_{18} is included in the sum. [c] Sum of Th, **3e**, and **5e**. [d] Not found. [e] Sum of Ph groups from PhMgCl in all products. [f] Sum of Th and recovered **1e**.

Scheme V



Scheme VI

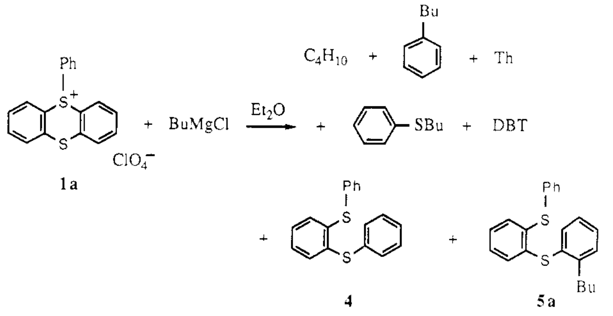


THF. The products of these reactions varied with the organometallic and the nature of R in 1.

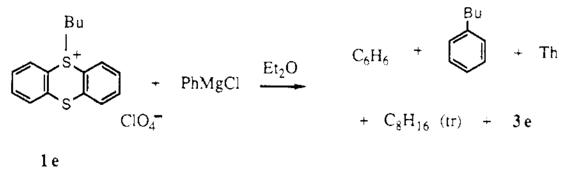
PhLi with 1a,b in Ether. These reactions were rapid. Insoluble **1a** and **1b** disappeared quickly and were converted into dibenzothiophene (DBT) and diaryl sulfide in equal and high yields. That is, 85% of **1a** was converted into Ph_2S and DBT, while 88% of **1b** was converted into phenyl *p*-tolyl sulfide and DBT (Scheme V). In each case small amounts of biphenyl were formed (Table IV). Benzene was produced, too, but its origin is believed to be the later workup decomposition of the excess of PhLi which had been used.

PhMgCl and BuMgCl with 1a and 1b. In contrast with the cleanliness and speed of reaction of PhLi, PhMgCl in both ether and THF reacted slowly with **1a** and produced a more complex mixture of products (Scheme VI). After 18 h of contact, 32% (ether) and 54% (THF) of the initial **1a** remained unused (Table V). DBT and Ph_2S were again formed in equal but smaller amounts, namely 29% (ether) and 24% (THF) of the **1a** that reacted. Part of the reacting **1a** underwent ring cleavage into 2-phenyl-2′-(phenylthio)diphenyl sulfide (**2a**), namely 28% in ether and 71% in THF. Table V lists substantial amounts of benzene from each reaction with PhMgCl, but each is approximately equal to the amount of recovered **1a** and, hence, unused PhMgCl. The benzene is thus not a primary reaction product. On the other hand, reaction with PhMgCl in ether gave a substantial amount (33% of **1a** used) of Th, meaning that 33% of the phenyl groups in **1a** was displaced. This must account, in fact, for the surprisingly large yield of biphenyl in that reaction.

Scheme VII



Scheme VIII



That is, in the reaction of PhMgCl with **1a** it is likely that only 0.385 mmol (0.54 – 0.155) of PhMgCl was used. The sum of phenyl groups in the products then becomes 0.135 mmol in Ph_2S, 0.113 mmol in **2a**, and, by difference, 0.137 in biphenyl. This is equatable, then, to the amount of Th formed (0.144 mmol) and suggests that the biphenyl was formed by combination of Ph from **1a** with Ph from PhMgCl. The biphenyl (0.157 mmol reported) could not have come from PhMgCl alone, for in that case 0.314 mmol of phenyl groups from PhMgCl would have been needed, an obvious impossibility.

The reaction of PhMgCl with **1a** in ether is closely paralleled by the analogous reaction with **1b** (Table V, Scheme VI). Again, reaction was very slow, and much (26%) of the **1b** remained unused. The major reaction paths were ring contraction (RSAr + DBT, 79.1%) and ring opening (**2b**, 17.6%), accounting for 96.7% of the **1b** which reacted. The amount of Th obtained (0.007 mmol) is surprisingly small but equatable to the product (0.005 mmol) 4-methylbiphenyl, whose identity was assumed on the basis of GC–MS. Unused **1b** in this case accounts for the amount of benzene (0.093 mmol) that was obtained. Based on the initial amount of PhMgCl and the amount (0.107 mmol) of recovered **1b**, we should have obtained approximately 0.10 mmol of benzene, which compares well with the amount (0.093 mmol) measured.

BuMgCl also caused the disruption of the ring of **1a** (Scheme VII). Reaction was slow but complete after 15 h of contact; 43% of **1a** was converted into DBT and butyl phenyl sulfide, 13% was converted into 2-(phenylthio)diphenyl sulfide (**4**), and 32% was converted into 2-butyl-2′-(phenylthio)diphenyl sulfide (**5a**). Butylbenzene and Th (9% and 14% of **1a**) were roughly equivalent and have apparently the same origin, that is removal of Ph from **1a** by BuMgCl. Butane (26% of BuMgCl) must have been formed largely by the excess (0.06 mmol) of BuMgCl present. It is probable that some of the butane (about 10% of BuMgCl) was a primary product.

Table VII. Products of Reaction of $ThR^+ClO_4^-$ (1c–e)[a] with PhLi in Ether

compd		reactants, mmol		products, mmol							totals, %	
1	R in 1	1	PhLi	C_6H_6[b]	RC_6H_5	RSPh	DBT	Th	2	3	Ph[c]	1[d]
1c	Me	0.300	0.344	0.260	tr	0.079	0.093	0.162	tr	0.01	101	88
1d	Et	0.200	0.258	0.110	tr	0.076	0.082	0.070	0.017	tr	79	85
1e	Bu	0.302	0.344	0.135	0.009	0.212	0.195	0.031	0.015		128[e]	103[e]

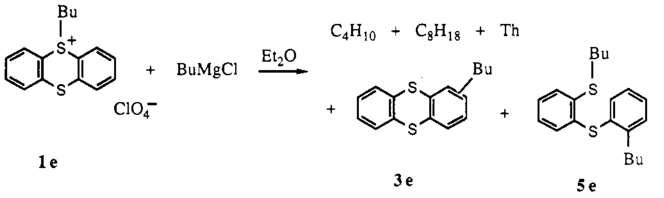
[a] 5-R-thianthreniumyl perchlorate. [b] Compensated for conversion of excess of PhLi into benzene in workup. [c] The sum of Ph groups in all products; based on the amount of PhLi equivalent to reactant **1**. [d] The sum of DBT, Th, **2**, and **3**, based on the initial amount of **1**. [e] Includes 0.07 mmol of butyldibenzothiophene (BuDBT); structure assumed on the basis of GC–MS.

Table VIII. Products of Reaction of 1c with PhLi: Effect of Addition of Phenol and of Water

reactants, mmol				products, mmol and %						totals, %	
1c	PhLi	phenol[a]	H_2O[a]	C_6H_6	MeSPh	DBT	Th	**1c**[b]	phenol[b]	**1c**	Me
0.299	0.344	0.30		0.230	0.123	0.079	0.096	0.113	0.186		
				66.8[c]				37.8	62.0	96[d]	78[e]
0.709	0.817		0.56	*f*	0.112[g]	0.170	0.125	0.358			
								50.5		92[d]	62[e,g]

[a] Added after **1c** and PhLi had reacted. [b] Recovered. [c] Based on PhLi. [d] Sum of DBT, Th, and recovered **1c**. [e] Sum of methyl groups in MeSPh and recovered **1c**. [f] Not measured. [g] Some loss occurred in workup.

Scheme IX

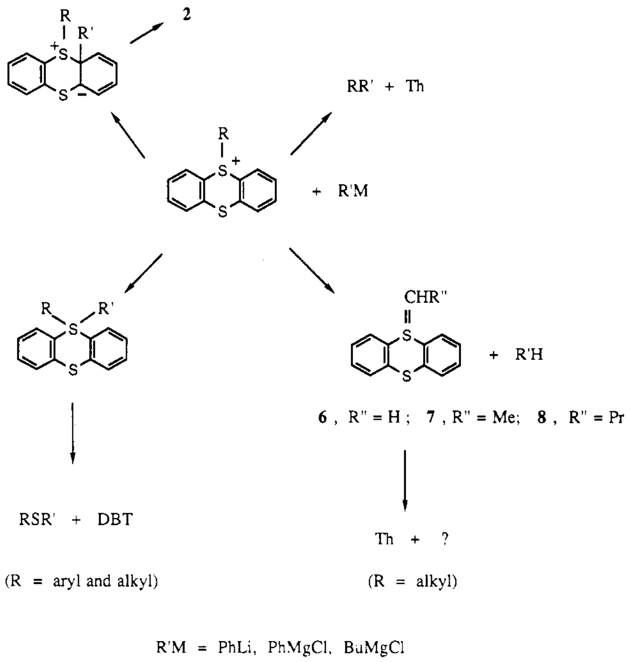


PhMgCl and BuMgCl with 1e. PhMgCl reacted with **1e** slowly, 8% of **1e** remaining unused after 20 h of contact (Table VI). In contrast with reaction with **1a**, DBT and the corresponding sulfide were not formed. Instead, most of the **1e** was deprotonated, accounting for most of the benzene listed in the table. Both butylbenzene and butylthianthrene (**3e**) were formed (Scheme VIII), amounting to approximately 18% and 5% of Bu groups in the reacting **1e**, respectively. Deprotonation of **1e** must have given an ylide (**8**) that did not survive later decomposition. In concordance with the loss of Bu group, 90% of the reacting **1e** was converted into Th. Ring-opened product **2e** was not found. Formation of ylides from 5-alkylthianthrenium ions is described in more detail later.

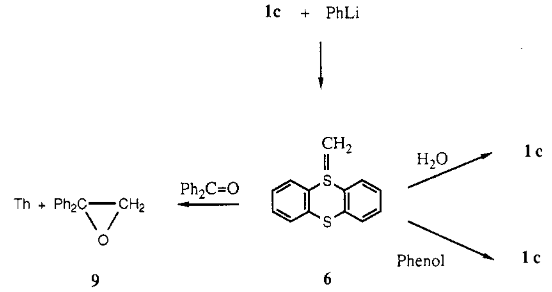
Loss of Bu group from **1e** was the principle fate of reaction of **1e** with BuMgCl. Reaction was complete within 3 h and led mainly to Th (88% of **1e**), butane, and octane (Scheme IX). The butane is attributed to deprotonation of **1e**, accounting thus for 33% of BuMgCl and, by subsequent decomposition of the ylide thus formed, accounting for 39% of the **1e** and Th. Octane formation is attributed to combination of butyl groups from **1e** and BuMgCl. In that way it would account for 56% of **1e** and 54% of BuMgCl. The accounting of loss of Bu groups from **1e** and formation of Th by these routes is reasonably good. A small amount (2.4%) of **1e** ended as butylthianthrene (**3e**) and some (14%) underwent ring cleavage, forming 2-butyl-2′-(butylthio)diphenyl sulfide (**5e**).

Reactions of PhLi with 1c–e. PhLi reacted rapidly with **1c–e**. Two major reactions occurred in each case, deprotonation with formation of benzene and an ylide and ring contraction with formation of DBT and the corresponding sulfide, RSPh (Scheme X). The accounting of products (Table VII) is quite good and indicates that the ylide (**6–8**) that must have been formed in the generation of benzene decomposed later into Th. An account of groups R was not made, however. Table VII shows that DBT and RSPh were formed in roughly equal amounts.

Scheme X



Scheme XI



By averaging the two products in each case, we see that 29%, 40%, and 67% of **1c**, **1d**, and **1e**, respectively entered into the ring-contraction reaction. In contrast, their conversions into benzene was, respectively, 72%, 26%, and 31%. Ring cleavage occurred with **1d** and **1e**, giving, respectively, **2d** (8.5%) and **2e** (5%).

Trapping of Ylide 6 from Reaction of PhLi with 1c. Three methods of trapping the ylide were used. One hour after reaction between PhLi and **1c** was complete, as in-

Table IX. Products of Reaction of 1c with PhLi: Formation of 2,2-Diphenyloxirane (9)

reactants, mmol			products,[a] mmol and %						totals, %	
1c	PhLi	Ph_2CO[b]	$C_{12}H_{10}$	PhSMe	DBT	Th	9	Ph_2CO[c]	1c	Me
0.50	0.60	0.50	0.016	0.144 28.8[d]	0.198 39.6[d]	0.305 61.0[d]	0.282 56.4[d]	0.212 42.4	101[e]	85[f]

[a] C_6H_6 was not assayed. [b] The Ph_2CO was added after 1c and PhLi had reacted. [c] Recovered (GC). [d] Based on 1c. [e] Sum of DBT and Th; based on initial amount of 1c. [f] Me groups as a sum of PhSMe and 9; based on initial amount of 1c.

dicated by the disappearance of insoluble 1c, water was added to regenerate 1c from the ylide (6). Regeneration was carried out also by adding phenol (Scheme XI). The results are given in Table VIII, where it can be seen that 51% (water) and 38% (phenol) of 1c was recovered. The products of ring contraction, MeSPh and DBT, are listed, too, but their equivalence is not as good as obtained earlier (Table VII). The third method of trapping 6 was more direct, by the addition of benzophenone 5 min after reaction between PhLi and 1c appeared to be complete. The result (Table IX) was the formation of 1,1-diphenyloxirane (9, Scheme XI) in 56% yield. The amount of Th formed (61%) and benzophenone used (58%) are in excellent agreement with the trapping reaction. Ring-contraction products, DBT and MeSPh, were formed but to the lesser extent (40% for DBT) than ylide formation. The results parallel those reported in Table VII in which ylide formation, measured as the yield of benzene, is 67% and ring contraction is 29%.

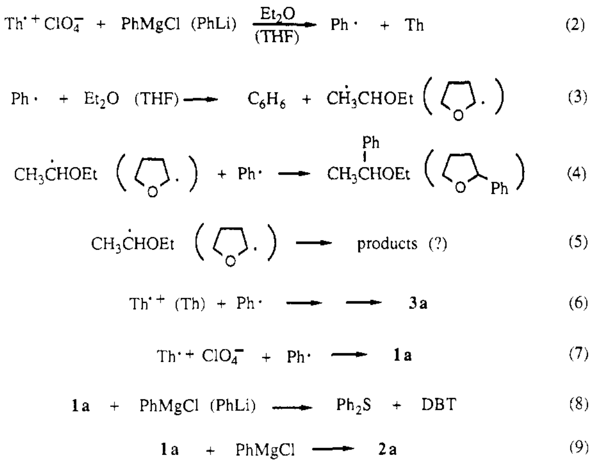
Identification and Assay of Products 2-5. Ring-cleavage products (2, 4, and 5) and substituted thianthrenes (3) were characterized by GC-MS but isolated in only one case (2a). The structures of 2, 4, and 5 were assigned only on the basis of the GC-MS data and the probable paths of reaction between thianthreniumyl ion and the Grignard reagents and PhLi. In principle, both 1- and 2-substituted thianthrenes may be formed in the reactions of $Th^{\bullet+}ClO_4^-$ and 1 with the organometals. The GC analyses showed only one peak, however, for some of these products, which are therefore listed as a unit (3) in the tables. In one case, that of the reaction of $Th^{\bullet+}ClO_4^-$ with PhMgCl (Table I), the two isomers, 1- and 2-phenylthianthrene, were separated and assayed on the GC column as well as separated and identified by GC-MS.

Compound 2a was isolated as an oil in 14% yield by preparative-scale TLC from reaction of PhMgCl with 1a. ^1H NMR and GC-MS data were consistent with the structure assigned.

Discussion

Reactions of $Th^{\bullet+}ClO_4^-$. There is no doubt that the primary reaction with PhMgCl and PhLi is an electron transfer (Scheme XII, eq 2). The evidence for the formation of $Ph^\bullet$ is several fold. First is the formation, in high yield, of benzene (eq 3), supported itself with the use of deuterated solvents and the formation of C_6H_5D (Scheme IV). Second is the formation of phenylated solvents, PhEtOEt and PhTHF (eq 4). It does not seem possible that these products could have been formed by any other reaction than combination of $Ph^\bullet$ and solvent radical, the latter itself being a product of a $Ph^\bullet$ reaction. The amounts of phenylated solvent are understandably not large. The fate of the major portions of solvent-derived radical, corresponding with the large yields of benzene, is not known (eq 5). Third is the formation of biphenyl, attributable to combination of two $Ph^\bullet$ derived from the organometal. Fourth is the formation of phenylthianthrenes (3a, Table I), attributable to either reaction of $Ph^\bullet$ with thianthrene (Th) itself or with $Th^{\bullet+}$ (eq 6). Two isomers of phenylthianthrene were detectable and were assayed by GC.

Scheme XII



They must be, then, 1- and 2-phenylthianthrene, and we believe the latter to be dominant.

Last, as evidence for formation of $Ph^\bullet$, is possibly the formation of 1a (eq 7). In the light of so much other evidence for $Ph^\bullet$ we attribute the formation of 1a to the trapping of $Ph^\bullet$ by $Th^{\bullet+}$. We cannot claim this as a certainty, but note only that the circumstances support this view. Trapping would have to occur in the surface of insoluble, crystalline $Th^{\bullet+}ClO_4^-$, a circumstance that has been discussed earlier with regard to 5-hexenyl radical.[4] Probably, it is phenyl radicals that are not trapped in this way that diffuse from the surface and react with solvent. The yields of 1a are not large. They are larger in the 2:1 than in the 1:1 molar ratio reactions (Table I), being in the range 13-25% in ether and 20% in THF medium. A reason for the low yields of 1a is primarily the intrinsic difficulty of trapping $Ph^\bullet$ with solid $Th^{\bullet+}ClO_4^-$ in media that can so easily donate an H atom. Another reason, however, is the reactivity of 1a itself toward PhMgCl and PhLi. The occurrence of two types of reaction between 1a and the organometals can be deduced from the products of reaction and is confirmed with evidence from direct reactions of 1a. One type of reaction caused ring contraction and the formation of Ph_2S and DBT (eq 8). The other type caused ring scission (eq 9) and the formation of 2-phenyl-2′-(phenylthio)diphenyl sulfide (2a). As judged by the relative yields of 2a, DBT, and isolable 1a (Table I), reaction of 1a with PhMgCl was more extensive when the ratio of reactants $Th^{\bullet+}ClO_4^-$ and PhMgCl was 1:1 than 2:1. An example can be seen by comparing, say, run 1 with run 4, and expressing the extent of ring contraction by the amount of DBT. In run 1, we see (% DBT + % 2a)/1a to be 3.3/25.4 (i.e., 0.13/1) whereas in run 4 we see 21.9/1.5 (14.6/1). These data are understandable in that in the 2:1 reactions, there was an excess of $Th^{\bullet+}ClO_4^-$ available for reaction with PhMgCl, limiting the availability of PhMgCl for reaction with 1a as it was formed.

Reactions of $Th^{\bullet+}ClO_4^-$ with PhMgCl and PhLi are markedly different from that with Ph_2Hg, which leads to 1a in high yield.[2] The difference raises again the question of whether or not electron transfer, leading to formation and trapping of $Ph^\bullet$, occurs in the reaction with Ph_2Hg.[3,4]

Evidence for formation of free Ph$^\bullet$, in the way of formation of benzene and/or biphenyl, is absent from the Ph_2Hg reaction. If electron transfer does occur in that reaction, the Ph$^\bullet$ thus generated must be trapped extraordinarily efficiently by $Th^{\bullet+}$, a possibility that is increased, however, as compared with reactions with PhMgCl and PhLi, by the solubility of $Th^{\bullet+}ClO_4^-$ in the solvent, acetonitrile, used in the Ph_2Hg reaction. Notably, also, Ph_2Hg did not react with **1a** in acetonitrile solution (eq 10).

$$\mathbf{1a} + Ph_2Hg \xrightarrow{CH_3CN} \text{No Reaction} \tag{10}$$

Reactions of 1a–e with PhMgCl, PhLi, and BuMgCl. Connections with Reactions of $Th^{\bullet+}ClO_4^-$. Four major reactions occurred when **1a–e** reacted with the organometals, the relative extents of these reactions varying with the nature of the organometal and the substituent in the 5-substituted thianthreniumyl ion. The reactions were ring contraction, ring opening, deprotonation, and displacement of a substituent.

Ring contraction is illustrated in Scheme X, in which interaction of a sulfuranyl intermediate is proposed. Ring contraction occurred rapidly and cleanly in reactions of **1a** and **1b** with PhLi (Table IV). In contrast, other reactions competed with ring contraction in the reactions of PhLi with **1c–e** and of PhMgCl and BuMgCl with **1a** and **1e**. That is, reaction of PhMgCl with **1a** led not only to ring contraction but also to ring opening, with the formation of **2a** (Scheme VI), to either almost equal (in ether) or greater (in THF) extent (Table V). Ring opening occurred also in reactions of BuMgCl with **1a** and **1e** with the formation of **5a** (Table V, Scheme VII) and **5e** (Table VI, Scheme IX). In the latter case, however, deprotonation (giving butane) and displacement (giving octane) of the Bu group from **1e** were the important reactions. Again, deprotonation (giving benzene) and displacement (giving butylbenzene) were the prominent reactions of **1e** with PhMgCl, and ring opening was not observed (Table VI, Scheme VIII).

Patterns of competition between deprotonation and ring contraction can be seen in reactions of **1a–e** with PhLi (Scheme X). As noted before, **1a** and **1b** gave ring contraction cleanly (Table IV), whereas deprotonation was a severe competition for ring contraction with **1c** and to a smaller but significant extent with **1d** and **1e** (Table VIII). Deprotonation must give an ylide (Scheme X), the fate of which is decomposition, but in an unknown way, to Th. Formation of an ylide was validated in reactions of **1c** with PhLi. In that case, the ylide (**6**) was converted into **1c** a short time after being formed, and its methylene group was trapped as an oxirane in reaction with benzophenone (Table IX, Scheme XI). It is notable that ring contraction occurred along with each of these trapping reactions, indicating that ring contractions and deprotonation followed parallel, independent pathways. Conversion of methylene ylides into **9** by reaction with benzophenone has been documented by Corey.[6]

The deprotonation of 5-alkylthianthrenium ions by PhLi and PhMgBr is regarded as an acid–base reaction. How do the ring-contraction and ring opening reactions occur? Are they, simply, the nucleophilic attack of carbanionic phenyl on the sulfur and ring positions of the cation (as shown in Scheme X), or do they involve, first, an electron transfer and next the rapid combination of Ph$^\bullet$ and the sulfuranyl radical? We are unable to answer these questions. There are small evidences for the probable formation of radicals in these reactions. For example, the formation of biphenyl, methylbiphenyl, and butylbenzene (RC_6H_5, Table V) and formation of butylthianthrene (**3e**, Table VI) may be radical combination reactions. But, the evidence is slender. Whereas the reactions of PhLi, PhMgCl, and BuMgCl with $Th^{\bullet+}$ appear certainly to begin with electron transfer, there is no firm evidence for such a step in the reactions of the thianthreniumyl ions.

The studies of LaRochelle and Trost[7] of the reactions of triarylsulfonium ions with organolithiums have a bearing on our work and our discussions. These workers found, for example, that reaction of $Ph_3S^+BF_4^-$ with vinyllithium gave quantitative yields of Ph_2S and styrene. Analogously, $(p\text{-tolyl})_3S^+BF_4^-$ gave 92% of $(p\text{-tolyl})_2S$ and 80% of 4-methylstyrene. The involvement of radicals or radicaloid intermediates in such reactions was ruled out, particularly from results of stereochemical studies in the reactions of *cis*- and *trans*-propenyllithium with $Ph_3S^+BF_4^-$. LaRochelle and Trost argued also against pathways involving nucleophilic attack of the organolithium at *ipso*-carbon atoms in the aryl groups, particularly from results of the reactions of phenyl- and vinyllithium with *S*-phenyldibenzothiophene tetrafluoroborate. The first of these reactions gave 2-phenyl-2′-(phenylthio)biphenyl exclusively. This product corresponds in type with our ring-opening reaction. The second reaction gave DBT (60%), styrene (60%), 2-(phenylthio)-2′-vinylbiphenyl (8%), and 2-(vinylthio)-2′-phenylbiphenyl (5%). The first two of these products correspond with our ring-contraction and the second two with our ring-opening reactions. The argument against ipso attack was that PhLi would have to have reacted at an ipso position of the DBT ring of the *S*-$PhDBT^+$ ion, whereas vinyllithium would have to have reacted at the ipso position of the phenyl group in that ion. The latter route was considered to be an unfavorable and hence improbable one. Consequently, LaRochelle and Trost concluded that in these reactions *all* products are derived from the formation and various modes of collapse of a sulfurane. How a sulfurane is formed was not discussed. In that connection, though, if electron transfer preceded the formation of a sulfurane, the *cis*- and *trans*-propenyl radicals would have had to bond to the sulfuranyl radical before undergoing inversion.

At the same time, it is to be noted that Kim and Bae[8] reduced the thianthreniumyl perchlorate **1f** (R = 2-thianthrenyl) with sodium naphthalenide in the presence of thiophenol. The major products were Th and naphthalene with a trace of 2-(R-thio)diphenyl sulfide, a product analogous to our **4** (Scheme VII, Table V). The most likely source of this and Th must have been the sulfuranyl radical corresponding with **1f**.

Sulfuranyl radicals of the type Ar$\dot{S}$Me(R) have a very fleeting life when formed by cathodic reduction of the corresponding sulfonium ions.[9] The sum of all of these indications is that if an electron-transfer step precedes the formation of the sulfuranes responsible for our products and those reported by others, the resulting sulfuranyl radical and its partner must combine extremely rapidly.

In summary, the course of reaction of $Th^{\bullet+}ClO_4^-$ with PhMgCl and PhLi becomes clear. Electron transfer occurs, and in principle should lead to **1a**. However, complexity arises from the reactions of Ph$^\bullet$ with solvent, solvent-derived radicals and, possibly, Th. Complexity arises also because the primarily sought product (**1a**) reacts with the organometals, too. The difference between reactions of $Th^{\bullet+}ClO_4^-$ with PhMgCl and PhLi and with Ph_2Hg be-

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(6) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.

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(8) Kim, K.; Bae, H. K. *Bull. Korean Chem. Soc.* **1987**, *8*, 165.

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comes clearer. That is, the comparatively high yield of **1a** from the last reaction can be attributed in part to the lack of reaction of **1a** with Ph_2Hg. At the same time, evidence for the involvement of $Ph^{\bullet}$ in the reactions with PhMgCl and PhLi is absent from the reaction with Ph_2Hg.

Experimental Section

Gas chromatographic (GC) analyses were made with a Varian gas chromatograph, Model 3700, attached to a Varian integrator, Model 4270. Two columns were used: (A), 6 ft, $^1/_8$ in. 5% SE-30 on Supelcoport, and (B), 3 ft, $^1/_8$ in 20% Carbowax-20 M on 60–80 mesh Chromosorb. The columns were used isothermally or with programmed heating, as necessary. An internal standard (naphthalene) was used for analyses on column A, while predetermined concentration factors were used with column B. Analytical thin-layer chromatography (TLC) was carried out on Kodak chromogram silica gel sheets, while preparative-scale TLC was carried out on Analtech Uniplates of silica gel GF. Mass spectra were obtained with a Hewlett-Packard Model 5995 mass spectrometer, either by GC–MS or with a direct insertion probe.

Tetrahydrofuran (THF) was distilled over lithium aluminum hydride under argon and was stored under argon. Acetonitrile was distilled over phosphorus pentoxide and stored under argon. Dry ether was kept over sodium wire. Phenylmagnesium chloride (PhMgCl) was a 2 M solution in THF from Aldrich. The molarity was reassayed by decomposition of an aliquot with water each time PhMgCl was used in reaction with thianthrene cation perchlorate ($Th^{\bullet+}ClO_4^-$). The amount of benzene formed was measured by GC with column B. In this way the effective molarity was found to be 1.70 M. Phenyllithium (PhLi) was a 2 M solution in cyclohexane/ether (70:30) from Aldrich. Assayed by benzene formation it was found to be effectively 2.15 M. Butylmagnesium chloride, 2.0 M in ether, from Aldrich was not reassayed. Perdeuteriodiethyl ether and perdeuterio THF were from Cambridge Isotope Laboratories. Thianthrene (Th) (Fluka AG) was purified by chromatography on silica gel with petroleum ether as eluent, recrystallized from acetone, and had mp 155–156 °C. Dibenzothiophene (DBT) was from Eastman Organic Chemicals. Ethyl 1-phenylethyl ether,[10] for use in GC control, was prepared by alkylation of 1-phenylethanol with ethyl iodide in a dimethyl sulfoxide (DMSO) solution of sodium hydroxide. The product had bp 88–90 °C (30 mmHg) and had satisfactory ^1H NMR and GC–MS data. $Th^{\bullet+}ClO_4^-$ was prepared essentially as described earlier.[11]

Dimethyl-, diethyl-, dibutyl-, diphenyl-, and di-*p*-tolylmercury were from Eastman Organic Chemicals and were used without further purification.

Authentic Sulfides. Diphenyl sulfide was from Aldrich and was distilled before use: bp 104–105 °C (1 mmHg). Methyl, ethyl, and butyl phenyl sulfide were prepared by reaction of sodium thiophenoxide (prepared in situ from thiophenol and sodium hydroxide in ethanol) with the appropriate alkyl iodide. They were distilled before use, and had, respectively, bp 183–185 °C (683 mmHg), 202–205 °C (683 mmHg), and 133–135 °C (20 mmHg). Each product had an acceptable ^1H NMR spectrum. Phenyl *p*-tolyl sulfide was prepared by addition of *p*-tolyldiazonium tetrafluoroborate to a solution of thiophenol and sodium hydroxide in ethanol. The product, bp 115–116 °C (2 mmHg), had an acceptable ^1H NMR spectrum.

Authentic Thianthreniumyl Perchlorates (1a–e). 5-Phenyl- (**1a**), 5-*p*-tolyl- (**1b**), 5-methyl- (**1c**), 5-ethyl- (**1d**), and 5-butylthianthreniumyl perchlorate (**1e**) were made by reaction of the appropriate diorgano mercurial with $Th^{\bullet+}ClO_4^-$ essentially as described earlier[2] and had acceptable melting points and ^1H NMR spectra after purification by reprecipitation from methylene chloride solution with ether.

2,2-Diphenyloxirane (9), for use as a GC and GC–MS standard, was prepared as described earlier[6] as a viscous oil, which solidified partly on long standing. Its ^1H NMR spectrum in carbon tetrachloride corresponded well with that in deuteriochloroform.[6] Mass spectrum, *m*/*e* (relative intensity, %): 196 (M^+, 4.3), 168 (13.0), 167 (100), 166 (15.3), 165 (49.3), 152 (25.0), 139 (6.1), 115 (9.1), 89 (8.7), 65 (8.7), 63 (17.3), 51 (19.4), 50 (12.4), 39 (24.9).

Reactions of $Th^{\bullet+}ClO_4^-$ with PhMgCl in Ether. Reactions were carried out with 2:1 and 1:1 ratios of reactants. An example of each is given.

(I) Run 1. A suspension of 537 mg (1.7 mmol) of $Th^{\bullet+}ClO_4^-$ in 9 mL of ether was prepared in a septum-capped, 10-mL volumetric flask and purged with argon. To this was added dropwise by syringe through the septum and while stirring magnetically 0.50 mL (0.85 mmol) of PhMgCl solution. The mixture was stirred for 1 h, at which time unreacted $Th^{\bullet+}ClO_4^-$ remained. This was then quenched with 0.1 mL of 4 M aqueous potassium carbonate solution. Potassium carbonate solution was used instead of water because it caused decomposition of $Th^{\bullet+}ClO_4^-$ faster than water. A precipitate of magnesium and sulfonium salts formed. A weighed portion of naphthalene was added, the solution was made up to 10 mL with ether, and the supernatant solution was analyzed for products on column A. These products consisted of ethyl 1-phenylethyl ether, small amounts of 2-phenyl-THF, biphenyl, Th, diphenyl sulfide, DBT, 2-phenyl-2′-(phenylthio)diphenyl sulfide (**2a**), and two isomers of phenylthianthrene (**3a**). All of the products except 2-phenyl-THF and the last three listed were identified and assayed in the GC with the use of authentic compounds. 2-Phenyl-THF was characterized by GC–MS (M^+, *m*/*e* 148). The last three products were characterized by GC–MS (M^+, *m*/*e*, 370, 292, and 292, respectively), but assayed by GC with concentration factors assumed to be the same as that of Th. The two isomers of phenylthianthrene were separable on column A, and their integrated peaks were in the ratio 7:10. They are reported as a unit (**3a**), however, in Table I.

After GC analysis, the precipitate was filtered off, washed with ether, dried, and shaken with 20 mL of methylene chloride. The methylene chloride solution was evaporated to dryness to give 84.8 mg (0.216 mmol) of crude 5-phenylthianthreniumyl perchlorate (**1a**), mp 240–250 °C. This was purified by reprecipitation from methylene chloride with ether, giving 40 mg, mp 250–253 °C (lit.[2] mp 259–261 °C). The original reaction filtrate (ether) was evaporated to dryness, and the residue was used in preparative-scale TLC for isolation and assay of thianthrene 5-oxide (ThO). The plate was developed with methylene chloride, and the ThO band was removed with the same solvent, giving 51.9 mg (0.224 mmol), mp 135–140 °C.

(II) Run 4. Reaction was carried out in a 25-mL flask essentially as in run 1, with 546 mg (1.73 mmol) of $Th^{\bullet+}ClO_4^-$ and 1.0 mL (1.70 mmol) of PhMgCl solution in 24 mL of ether. This mixture was stirred under argon for 6 h, after which time a gray-white precipitate was present. The solution was made up to volume and assayed for benzene on column B. Next, 0.15 mL of potassium carbonate solution and naphthalene were added. The supernatant solution was assayed again on column B for benzene and column A for benzene and other products. Only traces of ThO were found by GC and were not assayed by TLC.

The gray-white precipitate was removed for extraction of 10.4 mg (0.026 mmol) of crude **1a**, mp 250–253 °C, after reprecipitation from methylene chloride. Results from all runs are given in Table I.

Reaction of $Th^{\bullet+}ClO_4^-$ with PhMgCl in THF. The reactions were very fast as compared with those in ether, all of the $Th^{\bullet+}ClO_4^-$ disappearing within 5 min. In contrast with reaction in ether, diphenyl sulfide and DBT were not formed, but chlorobenzene was found.

Four runs are listed in Table II. Two of these were carried out in a small (3 mL) and two in larger (25 mL) volume of THF. The use of the small volume was to avoid the overlap of THF and benzene GC peaks and thus allow for GC assay of benzene. The assay was successful only in one run (run 1). The larger volume (25 mL) was used for better comparison of the reaction in THF with that in ether.

Run 1. In a 25-mL volumetric flask was placed 791 mg (2.50 mmol) of $Th^{\bullet+}ClO_4^-$ and 3 mL of THF. The flask was purged with argon, capped with a septum, and to it was added 1.0 mL (1.70 mmol) of PhMgCl solution. The $Th^{\bullet+}ClO_4^-$ disappeared quickly, and a gray precipitate formed. The mixture was stirred for 1 h, naphthalene was added, and the solution was made up to volume with ether. The supernatant solution was analyzed on column A before and after quenching with 0.1 mL of water.

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(10) Mislow, K. *J. Am. Chem. Soc.* **1951**, *73*, 4043.

(11) Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368. The warning on explosiveness should be noted.

Removal of the precipitate and workup gave 144 mg (0.367 mmol) of crude **1a**, mp 240–250 °C. Results are given in Table II.

Run 4. Reaction was carried out with 540 mg (1.71 mmol) of $Th^{\bullet+}ClO_4^-$ suspended in 24 mL of THF. Into this 1 mL (1.70 mmol) of PhMgCl solution was injected. The $Th^{\bullet+}ClO_4^-$ disappeared within 2 min. After 1 h of stirring, the solution was quenched with 0.1 mL of 4 M aqueous potassium carbonate, and the solution was evaporated to dryness on a rotary evaporator. The residue was treated with 50 mL of methylene chloride to separate inorganic material. The filtered methylene chloride solution was concentrated to small volume and diluted with 50 mL of ether. Product **1a** (15.8 mg, 0.04 mmol) was obtained; crude mp 240–250 °C. The solution was evaporated to dryness, and the residue was dissolved in 25 mL of ether for GC assay on column A. Results are given in Table II.

Control Reactions with PhMgCl Alone. Decomposition of an aliquot of PhMgCl solution in the appropriate solvent (ether or THF) was carried out in parallel with each $Th^{\bullet+}ClO_4^-$ reaction. After quenching with water, benzene was assayed on column B, while both benzene and biphenyl were assayed on column A. Biphenyl was present in trace amounts only. Results are given in Tables I and II.

Reaction of $Th^{\bullet+}ClO_4^-$ with PhMgCl in THF-d_8. Reaction was carried out in a 10-mL volumetric flask containing 318 mg (1.0 mmol) of $Th^{\bullet+}ClO_4^-$ and 2.0 mL of THF-d_8, into which 0.40 mL (0.68 mmol) of PhMgCl in THF was injected. The $Th^{\bullet+}ClO_4^-$ disappeared within 2 min, and a gray precipitate formed. After 1 h of stirring 0.05 mL of water was added, and the mixture was made up to volume with ether. The supernatant solution was used for GC–MS, which showed the presence of benzene (*m/e* 78), C_6H_5D (*m/e* 79), 2-phenyl-THF-d_7, and Th. The relative intensities of ions having *m/e* 78 and 79 were measured five times and averaged 100:25.6.

A control experiment was carried out with 0.40 mL of PhMgCl solution, 2.0 mL of THF-d_8, and 0.05 mL of water. Relative intensities of ions having *m/e* 77, 78, and 79 were measured five times and averaged 24.6, 100 and 7.47, respectively. The measured ratio of masses M/(M + 1) is reasonably close to that of natural abundances in benzene, namely 100:6.73.[12]

The relative amounts of C_6H_6 and C_6H_5D that were formed in the reaction of $Th^{\bullet+}ClO_4^-$ with PhMgCl in THF-d_8 were calculated from these data. That is, the contribution ($0.0747x$) made by C_6H_6 ($=x$) to the abundance of *m/e* 79 and the contribution ($5/6 \times 0.246y$) made by C_6H_5D ($=y$) to the abundance of *m/e* 78 were computed, to give the ratio of C_6H_6/C_6H_5D ($=x/y$) 421:83.3. The result is very much greater than the ratio of H/D in the solvent mixture, namely 16.7:83.3, indicative of a substantial KIE in H(D) abstraction.

Reactions of $Th^{\bullet+}ClO_4^-$ with PhLi in Ether. Reactions were carried out with reactant ratios $Th^{\bullet+}ClO_4^-$/PhLi of ca. 1.75:1 and 1:1.1. In the latter cases $Th^{\bullet+}ClO_4^-$ was completely consumed, leaving a presumed small excess of PhLi. However, this small excess of PhLi is assumed to have been used up in the formation of Ph_2S and DBT (see Discussion).

(I) Run 1. $Th^{\bullet+}ClO_4^-$ (370 mg, 1.17 mmol) and 15 mL of ether were placed in a 25-mL volumetric flask. The flask was capped with a septum and purged with argon, and to it was added by syringe 0.60 mL (1.28 mmol) of PhLi solution. The $Th^{\bullet+}ClO_4^-$ disappeared within 10 min, but stirring was continued for 1 h, after which 0.05 mL of water was added, causing a colorless precipitate to form. The solution was made up to volume with ether, and a 5-mL aliquot was removed. To this aliquot was added 5.32 mg (0.415 mmol) of naphthalene as a GC standard. The solution was assayed for benzene on column A and for other products on column B. These products consisted of ethyl 1-phenylethyl ether, biphenyl, diphenyl sulfide, and DBT.

The precipitate in the major (20 mL) portion of reaction solution was removed, washed with methylene chloride, and dried, giving 161 mg (1.01 mmol, 79%) of (assumed) $LiClO_4{\cdot}3H_2O$. This solid melted in a flame but did not burn.

The filtrate (20 mL) was evaporated to dryness to give 230 mg of solid residue. This was dissolved in 3.0 mL of methylene chloride and used for preparative-scale TLC. Only Th and ThO were removed (with methylene chloride) from the plate. Quantitative results are given in Table III.

(II) Run 3. Reaction was carried out as described for run 1, but with 385 mg (1.22 mmol) of $Th^{\bullet+}ClO_4^-$ and 0.32 mL (0.68 mmol) of PhLi solution. $Th^{\bullet+}ClO_4^-$ remained after 1 h of stirring. After addition of 0.05 mL of water the mixture was stirred until the $Th^{\bullet+}ClO_4^-$ had disappeared. The remaining treatment was as in run 1.

Control Reactions with PhLi Alone. Decomposition of an aliquot of PhLi solution with water was carried out in parallel with each $Th^{\bullet+}ClO_4^-$ reaction. Thus, 0.60 mL (1.28 mmol) of PhLi solution was used in 25 mL of ether and decomposed with 0.05 mL of water. Analysis for benzene on column B and for biphenyl on column A was made. Initially, biphenyl was not found in the freshly opened bottle of reagent. Small amounts of biphenyl were found in later usage.

Reaction of $Th^{\bullet+}ClO_4^-$ with PhLi in Diethyl-d_{10} Ether. $Th^{\bullet+}ClO_4^-$ (314 mg, 0.993 mmol) and 2.0 mL of diethyl-d_{10} ether were placed in a 10-mL volumetric flask. After septum-capping and purging with argon, 0.35 mL (0.744 mmol) of PhLi solution was added by syringe. The mixture was stirred for 1 h after which the excess of $Th^{\bullet+}ClO_4^-$ that was present was decomposed with 0.10 mL of water. The solution was made up to volume with ether, and the solution above the (assumed) $LiClO_4{\cdot}3H_2O$ was analyzed qualitatively by GC. Products found were benzene, cyclohexane (from the PhLi solution), biphenyl, diphenyl sulfide, DBT, Th, and ThO.

The solution was then analyzed by GC–MS for the relative amounts of C_6H_6 and C_6H_5D. The relative intensities of ions having *m/e* 78 and 79 were found to be 100/117. These intensities were compared with those obtained for ions 77, 78, and 79 measured earlier, namely 24.6, 100, and 7.47. The ratio of C_6H_6/C_6H_5D from reaction of $Th^{\bullet+}ClO_4^-$ with PhLi was calculated to be 60:85 in comparison with an H/D ratio in the solvent mixture of 15:85. Thus, a KIE of 4 was exhibited in the H(D) abstraction reaction.

Reaction of 1a and 1b with PhLi in Ether. In a 25-mL argon-filled volumetric flask were placed 200 mg (0.51 mmol) of **1a** and 24 mL of ether. The flask was capped with a septum, and the suspension of **1a** was purged with argon. To the vigorously stirred suspension was added 0.33 mL (0.68 mmol) of PhLi solution by syringe. The **1a** disappeared within 1–2 min, and a yellow solution was formed. Stirring was continued for 1 h when 0.05 mL of water was injected to decompose the excess of PhLi. A yellow-white precipitate formed. The mixture was made up to volume with ether, and the supernatant solution was analyzed for product by GC. Benzene was assayed with column B, and all other products were assayed with column A. Naphthalene was used as an internal standard. The ether-insoluble precipitate was recovered to give 79.5 mg (0.495 mmol, 72.8%) of (assumed) $LiClO_4{\cdot}3H_2O$. Reaction of **1b** was carried out in the same way. A control experiment with PhLi (0.30 mL, 0.615 mmol) was run in the same way. All results are listed in Table IV.

Reaction of 1a with PhMgCl in Ether. The procedure with 199 mg (0.506 mmol) of **1a** and 0.32 mL (0.544 mmol) of PhMgCl solution was the same as that used for the PhLi reaction. However, reaction was comparatively slow. Stirring was continued for 18 h, after which time some **1a** was still unused and suspended in the solution. Addition of 0.1 mL of water caused further precipitation of solid. GC analysis was carried out as earlier. The ether-insoluble solid (162 mg) was removed and treated with 20 mL of methylene chloride. The methylene chloride solution was evaporated to dryness to give 64.6 mg (0.164 mmol, 32.4%) of **1a**, mp 249–253 °C.

GC results are given in Table V. They show the formation of the same products as obtained from reaction of **1a** with PhLi, but with the addition of another product assumed from GC–MS data to be 2-phenyl-2′-(phenylthio)diphenyl sulfide (**2a**). GC–MS showed also the presence of yet another product, *m/e* 294, which is assumed on this basis to have been 2-(phenylthio)diphenyl sulfide (**4**).

Reaction of 1a with PhMgCl in THF. In this reaction 120 mg (0.305 mmol) of **1a** and only 2 mL of THF (to allow for assay of benzene by GC) were used in a 10-mL volumetric flask. The amount of PhMgCl solution was 0.20 mL (0.34 mmol). Reaction

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[12] Beynon, J. H. *Mass Spectrometry and its Applications to Organic Chemistry*; Elsevier: Amsterdam, 1960; p 297. The ratio has been calculated on the basis of revised atomic masses.

was again comparatively slow. After 18 h of stirring 0.1 mL of 4 M aqueous potassium carbonate solution was added to the suspension. Workup as described above gave 65.3 mg (0.166 mmol, 54.4%) of unused **1a**, and the GC results that are listed in Table V.

Reaction of 1a with BuMgCl in Ether. To a suspension of 118 mg (0.30 mmol) of **1a** in 9 mL of ether in a septum-capped 10-mL volumetric flask was added 0.18 mL (0.36 mmol) of BuMgCl solution. The **1a** disappeared slowly during 15 h of stirring. After 20 h the mixture was quenched with 0.1 mL of potassium carbonate solution and worked up as usual. Results are given in Table V.

GC analysis showed a measurable amount of not only (assumed) 2-butyl-2′-(phenylthio)diphenyl sulfide (**5a**) but also of **4** (assumed). The basis of these assumptions was the GC–MS data. Mass spectrometry data for **4**, *m/e* (relative intensity): 294 (M$^+$, 100), 186 (7.9), 185 ($C_{12}H_9S^+$, 44.4), 184 (DBT$^+$, 59.6), 152 (10.1), 139 (7.8), 77 (10.7), 51 (18.9). Data for **5a**, *m/e* (relative intensity): 351 (23.4), 350 (100, M$^+$), 317 (2.33), 294 (3.29), 293 (3.50), 229 (1.71), 218 (23.0), 216 (2.54), 198 (12.5), 197 (38.2), 186 (4.13), 185 (7.51), 184 (15.0), 165 (6.62).

Isolation of 2-Phenyl-2′-(phenylthio)diphenyl sulfide (2a). Reaction of 173 mg (0.44 mmol) with 0.35 mL (0.59 mmol) of PhMgCl solution was carried out in 3 mL of THF. After 3 days of stirring the mixture was quenched and made up to 10 mL with ether. Qualitative GC analysis showed the usual products to be present. The filtered solution was evaporated to dryness in a rotary evaporator at room temperature to give 109 mg of a viscous oil. The oil was separated into its component products by preparative-scale TLC, using pentane as developer. The band containing **2a** was removed, and the product was extracted with methylene chloride, giving 23 mg (0.062 mmol) of an oil, representing 14.1% based on **1a**.

GC–MS data, *m/e* (relative intensity): 371 (29.3), 370 (M$^+$, 100), 261 ($C_{18}H_{13}S^+$, 9.7), 260 (7.7), 185 (14.8), 184 (DBT$^+$, 22.0), 152 (7.5).

The ^{1}H NMR ($CDCl_3$) spectrum of **2a** consisted of two multiplets at δ 7.046–7.095 and 7.215–7.420. The multiplets from a solution of 34 mg (0.092 mmol) of **2a** in $CDCl_3$ were integrated against an added aliquot (25 μL) of CH_2Cl_2, from which the number of protons in the molecule **2a** was computed as 18.

Reactions of 1e with BuMgCl and PhMgCl in Ether. (I) With BuMgCl. Reaction was carried out in a 10-mL volumetric flask between 109 mg (0.291 mmol) of **1e** in 9 mL of ether and 0.15 mL (0.30 mmol) of BuMgCl solution. The **1e** disappeared within 3 h of stirring, but stirring was continued for 5 h, after which 0.05 mL of water was added. Workup and GC analysis (Table VI) on column A followed. The concentration factor (CF) of butane was assumed to be 1.0 while CF's of 2-butyl-2′-(butylthio)diphenyl sulfide (**5e**) and butylthianthrene (**3e**) were assumed to be the same as that of thianthrene. The structures given to **3e** and **5e** are assumed on the basis of GC–MS data. Data for **3e**, *m/e* (relative intensity): 272 (M$^+$, 91.9), 230 (19.4), 229 (100), 216 (13.8), 198 (12.5), 197 (80.3), 185 (18.7), 184 (18.7), 171 (11.6), 165 (12.4), 152 (15.5), 68 (21.5), 63 (17.6), 51 (10.7), 44 (50.0), 43 (10.7), 42 (27.2), 41 (35.5), 40 (39.1), 39 (27.1). Data for **5e**, *m/e* (relative intensity): 330 (M$^+$, 21.0), 274 (7.3), 217 (5.4), 198 (20.0), 197 (20.0), 91 (C_7H_7, 100), 57 (14.8), 55 (10.6), 44 (15.0), 41 (56.8), 38, (14.9).

(II) With PhMgCl. Reaction was carried out in a 5-mL volumetric flask between 671 mg (0.180 mmol) of **1e** in 45 mL of ether and 0.11 mL (0.187 mmol) of PhMgCl solution. Some unreacted **1e** remained after 20 h of stirring when 0.07 mL of potassium carbonate solution was injected. GC analysis on column A followed, and the unreacted **1e** was recovered. Results are given in Table VI.

Reactions of 1c–e with PhLi in Ether. Reactions were carried out in the usual way in a 10-mL volumetric flask. A control reaction was run with PhLi alone along with each reaction with **1**. An example with **1c** is given. Addition of 0.16 mL (0.34 mmol) of PhLi solution to the stirred suspension of 98.5 mg (0.30 mmol) of **1c** in 9 mL of ether caused the **1c** to disappear within a few minutes and the formation of a yellow-orange solution. After 1 h of stirring, 0.05 mL of water was injected, dispersing the orange color and precipitating a white solid. GC analysis (Table VII) followed in the usual way on column A. Products 2-(methylthio)-2′-phenyldiphenyl sulfide (**2c**) and methylthianthrene (**3c**) were detected by GC and by GC–MS but were not assayed.

After GC analysis the mixture was poured into 20 mL of water, and the aqueous suspension (Th) was extracted with methylene chloride. The methylene chloride solution was stirred, concentrated, and made up to 10 mL for quantitative assay of Th by preparative-scale TLC (Table VII).

Reactions with **1d** and **1e** were carried out similarly (Table VII). Products **2d** and **3d** and **2e** and **3e** were assayed by GC, with the assumption that they had the CF of Th, and were assigned structures based on GC–MS data. The following data, *m/e* (relative intensity) were obtained.

2d: 322 (M$^+$, 100), 294 (8.5), 293 (11.1), 261 (10.8), 260 (20.1), 258 (8.8), 215 (7.8), 185 (6.0), 184 (22.0), 152 (6.5).

2e: 350 (M$^+$, 100), 296 (7.1), 295 (13.7), 294 (56.9), 293 (8.1), 261 (13.7), 260 (16.0), 215 (5.7), 185 (11.0), 184 (27.3), 154 (43.9), 153 (10.4), 140 (16.3).

3c: 230 (M$^+$, 100), 229 (10.9), 216 (7.7), 198 (24.1), 197 (61.3), 184 (9.6), 152 (9.5), 69 (16.3), 39 (15.6).

3d: 244 (M$^+$, 100), 230 (10.6), 229 (66.4), 216 (8.2), 211 (14.5), 197 (20.4), 184 (11.5), 69 (8.3).

Effect of Phenol and of Water on Products of Reaction of 1c with PhLi. (I) Phenol. Reaction between 99.0 mg (0.30 mmol) of **1c** and 0.16 mL (0.34 mmol) of PhLi solution was carried out as described. After 1 h of stirring a solution of phenol (0.30 mmol) in 1 mL of ether was injected. A white precipitate formed immediately. After 20 h of stirring, the supernatant solution was analyzed by GC on column B for benzene and column A for other products (Table VIII). The white precipitate was collected, washed with ether, and dried, giving 37.3 mg (0.113 mmol, 37.7% recovery) of **1c**, mp 185–190 °C.

(II) Water. Quenching the reaction (see I, above) with 0.1 mL of water caused precipitation of both **1c** and $LiClO_4 \cdot 3H_2O$. The mixture of these solids was removed after GC analysis, and the **1c** was extracted with methylene chloride and reprecipitated with ether. Results are given in Table VIII.

Trapping of Ylide (6) and Formation of 1,1-Diphenyloxirane (9) in Reaction of 1c with PhLi. Reaction between 165 mg (0.50 mmol) of **1c** and 0.28 mL (0.60 mmol) of PhLi solution was carried out in the usual way. After 5 min of stirring, 0.50 mmol of benzophenone in 0.50 mL of ether was injected. The yellow color of the solution gradually faded; no precipitate formed. After 20 h of stirring, GC and GC–MS analyses were performed (Table IX). The presence of **9** in the mixture was confirmed by GC and use of authentic **9**, and by exact correspondence of the GC–MS spectrum with that of authentic **9**.

Evaporation of the solvent gave 240 mg of yellow, oily solid. The ^{1}H NMR (CCl_4) spectrum of this mixture had a singlet (CH_2) at 3.12 ppm, corresponding with that for authentic **9**. Attempts to separate **9** by preparative-scale TLC failed because bands for **9** and benzophenone overlapped. TLC controls confirmed the presence of **9**.

Attempted Reaction of 1a with Diphenylmercury (Ph_2Hg) in Acetonitrile. A mixture of 77.9 mg (0.198 mmol) of **1a**, 72.0 mg of Ph_2Hg, and 1.0 mL of acetonitrile was stirred in the usual conditions in a 10-mL volumetric flask. After 72 h of stirring the solution was diluted to volume with ether. A precipitate formed. GC analysis on column A showed none of the products to be present that were obtained in the PhLi and PhMgCl reactions. The precipitate was recovered, giving 71.1 mg (0.181 mmol, 91.3%) of **1a**, mp 248–253 °C.

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Registry No. **1a**, 65886-50-2; **1b**, 30882-99-6; **1c**, 65886-47-7; **1d**, 65886-49-9; **1e**, 110547-52-9; $Th^{\cdot +}ClO_4^-$, 35787-71-4; PhMgCl, 100-59-4; PhLi, 591-51-5; BuMgCl, 693-04-9.