Reactions of Phenols with Thianthrene Cation Radical

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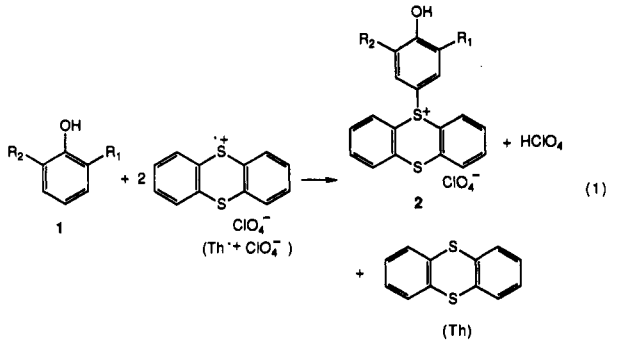
The phenols 2-R_1-6-R_2-phenol **1a–g** in which R_1 = R_2 = *tert*-butyl, methyl, isopropyl, Cl, Br, F, and H reacted with thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) to give 5-(4-hydroxyaryl)thianthreniumyl perchlorates **2a–g** in good yield. *o*-Allylphenol (**1i**) behaved similarly. *o*-*tert*-Butylphenol (**1h**) gave both 5-(3-*tert*-butyl-4-hydroxyphenyl)thianthreniumyl perchlorate (**2h**) and a quinonoidal perchlorate (**3**), namely, 5-(3-thianthreniumyl-5-*tert*-butyl-6-oxo-2,4-cyclohexadien-1-ylidene)-5,5-dihydrothianthrene perchlorate. The 2,6-di-*tert*-butyl-4-R_3-phenols **4a–c**, R_3 = *tert*-butyl, methoxy, and methyl, reacted with $Th^{\bullet+}ClO_4^-$ in nitrile solvents (RCN) to give 2-R-5-R_3-7-*tert*-butylbenzoxazoles **5a–e**. The *tert*-butyl group that was displaced by RCN in forming **5** was converted into *t*-BuNHCOR (**8**), *tert*-butyl alcohol, and isobutene. In contrast, 2-*tert*-butyl-4,6-dimethylphenol (**9**) gave, in CH_3CN, 4-*tert*-butyl-2,5,7-trimethylbenzoxazole (**11**), that is, with migration of the displaced *tert*-butyl group. The reactions of 4-*tert*-butylphenol (**14**) and 2,4-di-*tert*-butylphenol (**17**) are also described.

Introduction

The reactions of benzene derivatives with thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) were reported some years ago.[1,2] When the benzene ring carried an electron-donating group, substitution by $Th^{\bullet+}$ took place para to that group, and a 5-arylthianthreniumyl perchlorate was formed. Among the benzene derivatives were phenol (**1g**, R_1 = R_2 = H), *o*-*tert*-butylphenol (**1h**, R_1 = *t*-Bu, R_2 = H), and *o*-chlorophenol (**1j**, R_1 = Cl, R_2 = H). In those cases the products were 5-(4-hydroxyaryl)thianthreniumyl perchlorates **2**, eq 1. No further work of this kind was carried



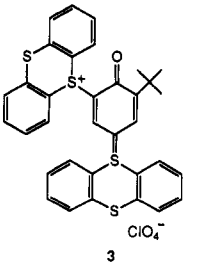
out, but the kinetics of reaction with phenol were studied by Parker. From those studies[3] and related ones with anisole[4] came the complexation mechanism of reaction that has become generally accepted in describing cation-radical reactions of this and similar kinds. It was shown that the complexation mechanism with phenol prevailed, provided that the solution was acidic. In neutral solution, the sulfonium salt **2g** (R_1 = R_2 = H) became deprotonated, a step that, in fact, was rate-determining in those circumstances.

We have recently returned to the reactions of phenols with $Th^{\bullet+}ClO_4^-$ among studies of the competition that can occur between oxidation of a reactant and substitution within it in its reactions with $Th^{\bullet+}ClO_4^-$. The reactions we report now are of phenol itself, and of some of its 2-substituted, 2,6-disubstituted, and 2,4,6-trisubstituted derivatives.

Results

Mono- and Disubstituted Phenols. Six 2,6-disubstituted phenols (**1a–f**, R_1 = R_2 = *t*-Bu, Me, *i*-Pr, Cl, Br, and F) gave the sulfonium salts **2a–f**. The results are listed in Table I. Listed also are the amounts of thianthrene (Th) and thianthrene 5-oxide (ThO) that were obtained. ThO was formed from the hydrolysis of $Th^{\bullet+}$ by water that was either present in the reaction medium or was added in the workup procedure. High yields of **2** were obtained with the substituents *t*-Bu, Me, and *i*-Pr. The data show that the stoichiometry of eq 1 prevailed. Reactions with **1d–f** were slow and incomplete, resulting in the workup hydrolysis of unused $Th^{\bullet+}$ and the formation of substantial amounts of ThO. Analysis of the data after compensation for unused $Th^{\bullet+}$ (0.26 mmol in each case) showed that the formation of **2d–f** even in diminished yield, followed the stoichiometry of eq 1.

Table I lists phenol (**1g**) and *o*-allylphenol (**1i**) each of which gave **2** in good yield. Reaction with *o*-*tert*-butylphenol (**1h**) is also listed, but this varied in one respect from the other reactions. Although **2h** was formed in good yield, the presence of a second sulfonium salt was detected in the reaction mixture. Formation of the second salt (**3**) was enhanced by carrying out the reaction with a 4:1 ratio of $Th^{\bullet+}$/**1h**. A mixture of **2h** and **3** was obtained, the composition of which was determined by ^1H NMR as being 0.11 mmol (55%) of **2h** and 0.053 mmol (27%) of **3**. The monoperchlorate **3** was separated from its mixture with **2h** by selective precipitation of **2h** with ether from a solution of the mixture in dichloromethane. It is probable that phenol and *o*-allylphenol would behave similarly but these reactions were not explored.



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Trisubstituted Phenols. In contrast with **1a–i**, the trisubstituted phenols **4a–c**, having *tert*-butyl groups in the 2- and 6-positions, underwent oxidative loss of a *tert*-butyl group in reaction with $Th^{\bullet+}$, Scheme I. The phenol was converted into a benzoxazole (**5**) by reaction with solvent nitrile, while the *tert*-butyl group, displaced as t-Bu^+, was found as isobutene, *tert*-butyl alcohol, and an *N*-*tert*-butylamide (**8**) derived from the solvent. Thus, in the solvents acetonitrile, propionitrile, and acrylonitrile, 2,4,6-tri-*tert*-butylphenol (**4a**) gave, respectively, 2-methyl- (**5a**), 2-ethyl- (**5b**), and 2-vinyl-5,7-di-*tert*-butyl-1,3-benz-

(1) Silber, J. J.; Shine, H. J. *J. Org. Chem.* **1971**, *36*, 2923.
(2) Kim, K. K.; Hull, V. J.; Shine, H. J. *J. Org. Chem.* **1974**, *39*, 2534.
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(4) Svanholm, U.; Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 101.

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Table I. Reactions of 2-R_1- and 2-R_1-6-R_2-Phenols 1 with $Th^{\cdot+}ClO_4^-$ and Formation of 5-(4-Hydroxyaryl)thianthreniumyl Perchlorates 2

				products,[b] %				
run[a]	1	R_1	R_2	2[c]	Th	ThO	ThO_2	other
1	**a**	*t*-Bu	*t*-Bu	91	46	6.5		*d*
2	**b**	Me	Me	92	43	2.3		
3	**c**	*i*-Pr	*i*-Pr	94	45	3.8	1.1	
4	**d**	Cl	Cl	60	48	18	1.8	*e*
5	**e**	Br	Br	58	50	19	1.3	*f*
6	**f**	F	F	53	49	22	1.0	*g*
7	**g**	H	H	86	44	2.9	1.0	
8	**h**	*t*-Bu	H	79	56			*h*
9	**h**	*t*-Bu	H	58	49	20		*i*
10	**i**	allyl	H	98	40	5.4	1.8	

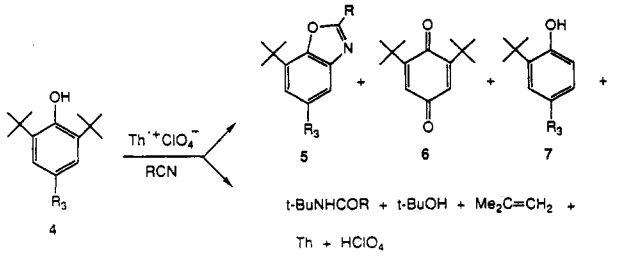
[a] $Th^{\cdot+}ClO_4^-$ (0.80 mmol) and 1 (0.40 mmol) were used in all runs except in run 9 (0.80 mmol of $Th^{\cdot+}ClO_4^-$ and 0.20 mmol of **1h**). [b] All products except **2a–i** were assayed by GC on column A. [c] Isolated yields, based on 1. [d] *t*-BuNHAc (2.5% based on **1a**) was also obtained. [e] **1d** (0.13 mmol, 33%) was recovered. [f] **1e** (0.13 mmol, 33%) was recovered. [g] **1f** (0.13 mmol, 33%) was recovered. [h] **1h** (0.017 mmol, 4.3%) was recovered. [i] The bis(thianthreniumyl) monoperchlorate (**3**, 0.053 mmol, 27% based on **1h**) was obtained as a mixture with **2h**.

Table II. Products of Reaction of 2,6-Di-*tert*-butyl-4-R_3-phenols 4 with $Th^{\cdot+}ClO_4^-$ in Nitrile Solvents (RCN) and Formation of Benzoxazoles 5

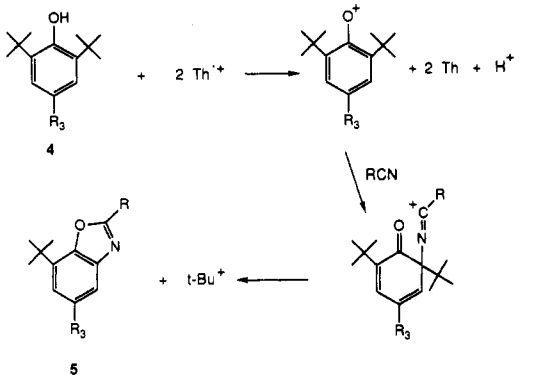
	phenol		R in	products,[b] %							
run[a]	no.	R_3	RCN	5	6	7	8	*t*-BuOH	$Me_2C{=}CH_2$	Th	ratio[c]
1[d]	**4a**	*t*-Bu	Me	**a**, 80	2.2	4.5	17	62	12	95	0.95
2[e]	**4a**	*t*-Bu	Et	**b**, 77	4.3	6.3	40	33	20	94	0.94
3[f]	**4a**	*t*-Bu	vinyl	**c**, 54	9.8	8.5	17	44	25	95	0.84
4[g]	**4b**	OMe	Me	**d**, 80	9.4		31	39	6.3	99	1.1
5[h]	4c	Me	Me	**e**, 43		5.6	18	53	6.3	94	0.63[i]

[a] $Th^{\cdot+}ClO_4^-$ (0.80 mmol) and 4 (0.40 mmol) were used in each run. [b] All products except *t*-BuOH and isobutene were assayed by GC on column A. *t*-BuOH was assayed on column B and isobutene on column C. The % yields of products, except Th, are based on 4. [c] (Yields of 5 + 6 + 7)/(yields of 8 + *t*-BuOH + isobutene). [d] 1.3% of **4a** was recovered and 0.60% of ThO was obtained, also. [e] 2.0% of **4a** was recovered. [f] 6.0% of **4a** was recovered, and 2.0% of ThO was obtained. [g] 1.0% of ThO and 1.3% of ThO_2 were obtained. [h] 2.4% of ThO was obtained. [i] (Yields of 5 + 7)/(yields of 8 + *t*-BuOH + isobutene); the reason for the low value (≪1.0) is not known.

Scheme I



Scheme II



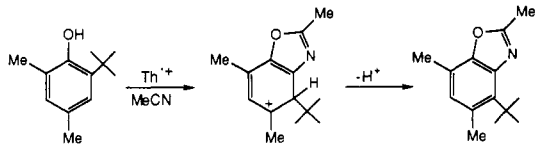
oxazole (**5c**). At the same time *N*-*tert*-butylacetamide (**8a**), *N*-*tert*-butylpropionamide (**8b**), and *N*-*tert*-butylacrylamide (**8c**) were formed, respectively. The structure of **5c** was confirmed by hydrogenation of its vinyl group to form **5b**. Formation of a benzoxazole (R = Me) occurred also in reactions of **4b** (R_2 = OMe) and **4c** (R_2 = Me) in acetonitrile, with the concomitant trapping of the *tert*-butyl cation, as described. The yields of these several products are listed in Table II.

Loss of a *tert*-butyl group occurred to a smaller extent in these reactions in two other ways. Protonolysis of an *o*-*tert*-butyl group occurred with **4a** and **4c**, as indicated by the formation of the 2-*tert*-butyl-4-R_3-phenols **7a** (R_3 = *tert*-butyl) and **7b** (R_3 = methyl). The acid needed for protonolysis could have been generated in one of the other product-forming reactions, for example, in the formation of **5** (Scheme II). Loss of the *tert*-butyl group also from the para position occurred to some extent in the reactions of **4a**. This loss must have been initiated by reaction of the oxidized phenol with water, because it resulted in the formation of 2,6-di-*tert*-butylbenzoquinone (**6**). It is presumed that the necessary water was either present in the solvent or was added in the workup procedure. Hydrolytic loss of the 4-methoxy group and formation of **6** occurred also in the reaction of **4b**; presumably, the methoxy group was ejected as methanol.

In principle, there should be a balance between the amounts of the phenol-derived products in which *tert*-butyl-group loss occurred and the amounts of amide, *tert*-butyl alcohol, and isobutene. This was found to be the case in reactions of **4a** and **4b**, as is seen in Table II (runs 1–4), where the balance is expressed as a ratio. The data for the reaction of **4c** are not as quantitatively good, the ratio (run 5) being only 0.63 instead of the theoretical 1.0. The reason for the loss of phenol-derived products is not known.

2-*tert*-Butyl-4,6-dimethylphenol (9). Surprisingly, **9** did not lead to 2,5,7-trimethylbenzoxazole, corresponding in type to the products **5**. Instead, a 2,5,7-trimethyl-*tert*-butylbenzoxazole (14%) was formed. ^1H NMR spectroscopic data were consistent with the *tert*-butyl group's, being located in the 4- (i.e., **11**) or 6-position (i.e., **12**) of the benzoxazole. We have chosen the 4-position

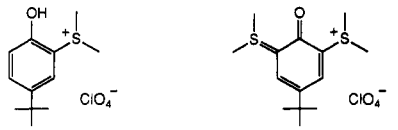
Scheme III



10 11

solely on the basis that its formation represents a simple 1,2-shift of the *tert*-butyl group (i.e., **10**, Scheme III). Apart from forming **11**, the reaction of **9** with $Th^{\bullet+}ClO_4^-$ gave 2,4-dimethylphenol (**13**, 5.8%), **8a** (6.5%), and isobutene (25%). A quantitative balance of products was not achieved.

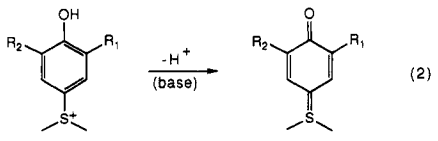
4-*tert*-Butylphenol (14). This phenol reacted with $Th^{\bullet+}ClO_4^-$ in a reactant ratio $Th^{\bullet+}$/phenol of 2:1 to give the sulfonium salt **15** (86%) and in a ratio of 4:1 to give the quinonoidal salt **16** (89%).



15 16

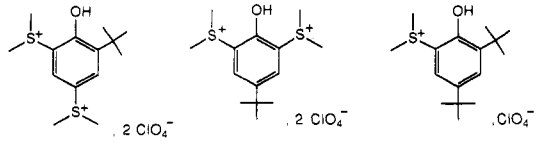
2,4-Di-*tert*-butylphenol (17). The expected 2-methyl-5-*tert*-butylbenzoxazole was not obtained from the reaction of **17** with $Th^{\bullet+}$. Instead, reaction at the 6-position occurred and gave the quinonoid **18** in 11% yield (based on **17**). Also, loss of the 4-*tert*-butyl group and formation of *N*-acetyl-2-*tert*-butyl-4-aminophenol (**19**) occurred (Scheme IV). Formation of **19** rather than isomeric 2-acetamino-4-*tert*-butylphenol (**20**) was confirmed by direct synthesis of **19** and **20** (see Experimental Section).

Deprotonation of Sulfonium Salts. Formation of Quinonoids 24. In some cases already noted a quinonoidal product was isolated rather than a 5-(hydroxyaryl)thianthreniumyl salt. That is, **3** was obtained rather than the bis(thianthreniumyl) diperchlorate **21**, **16** rather than **22**, and **18** (Scheme IV) rather than **23**. It is apparent that the products that were isolated were formed by deprotonation of their precursors during workup. Deprotonation of all of the isolated 5-(hydroxyaryl)-thianthreniumyl perchlorates **2a–i** was also carried out deliberately (eq 2) and the corresponding quinonoids **24a–i** were isolated. The interconversion of **2** and **24** in solution was also monitored with UV spectroscopy. Absorption and melting point data for **2a–i** and **24a–i** are listed in Table III (supplementary material).



(2)

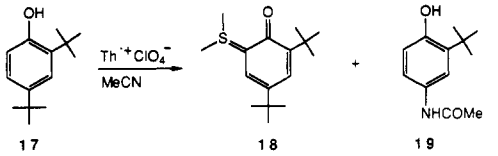
2 24



21 22 23

Identification of Products. The sulfonium salts **2a–i** gave well-resolved, first-order ^1H NMR spectra. These have been reported elsewhere.[5] In contrast, the ^1H NMR spectra of most of the quinonoids **24a–i** were not well-enough resolved to allow for complete analysis. Elemental analysis of each **2** or, more conveniently, the corresponding **24**, is listed in Table IV (supplementary material). Also listed in Table IV are the elemental analyses for the new benzoxazoles (**5b,d,e**) and compounds **11**, **15**, and **16**. Known compounds **2g** and **5a** were not identified further; known **2h** (Table IV) was analyzed because its melting point (219–221 °C) was different from that reported earlier (205–206 °C[2]); **5c** was an oil and was identified as **5b** after hydrogenation of the vinyl group.

Scheme IV

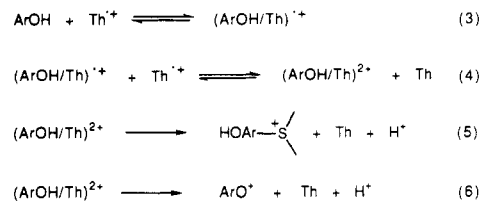


17 18 19

+ t-BuNHCOMe

8a

Scheme V



(3) (4) (5) (6)

Discussion

The oxidation of phenols by chemical[6–9] and anodic[10] methods has received much attention. Particularly pertinent are anodic oxidations in acidic solution and in the absence of oxygen. Among these, studies especially of di- and trisubstituted phenols have led to a general understanding that a phenoxonium ion is formed first. Depending on the circumstances, this may react with a nucleophile at a free position in the ring, or, in cases of trisubstituted phenols such as **4a–c**, may react with solvent nitrile to form a benzoxazole as shown in Scheme II. Our results with the mono- and disubstituted phenols suggest, however, that in reaction with $Th^{\bullet+}$ a free phenoxonium ion may not be formed from those phenols. If a free phenoxonium ion were formed, reaction with the solvent at an unsubstituted position would be expected. The fact that sulfonium ions (e.g., **2**) were formed in good yield suggests then that Parker's complexation mechanism may be followed. This is represented with ArOH in Scheme V. In that scheme, eq 5 represents the formation of a 5-(hydroxyaryl)thianthrenium ion (i.e., as in **2**), while eq 6 represents the formation of a phenoxonium ion (i.e., as in Scheme II). The former route (eq 5) would be followed by phenols in which room for substitution by a thianthreniumyl group existed in the phenolic ring. The latter

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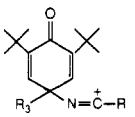
route would be followed by trisubstituted phenols. In those, replacement of, for example, a *tert*-butyl group by nucleophilic thianthrene would appear to be sterically encumbered. Consequently, the main fate of the phenoxonium ion is reaction with the solvent nitrile. This, incidentally, occurs at an ortho position, leading to **5**, rather than at a para position. The reason for this we believe is that attack by RCN at the para position of the phenoxonium ion is not fruitful. That is, the attack would be reversible because it would lead only to an ion, e.g., **25**,



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which cannot easily end in a stabilized aromatic product as is seen in Scheme II. Yet, there are some elaborations on this general concept that are not easily understood. The phenol **17** gave some 4-acetamino-2-*tert*-butylphenol (**19**, Scheme IV) but no 2-methyl-5-*tert*-butylbenzoxazole, which would have been formed by displacement of the *o*-*tert*-butyl group from **17**. With phenol **9**, the *o*-*tert*-butyl group migrated to a neighboring position in the formation of a benzoxazole (**11**, Scheme III). Possibly, the latter behavior can be attributed to the favorable formation of intermediate **10** in which stabilization of the positive charge by the two Me groups occurs.

Experimental Section

Acetonitrile (Eastman Kodak), acrylonitrile, and propionitrile were dried by distillation over phosphorus pentoxide under dry argon. Preparative-scale thin-layer chromatography (TLC) was carried out on plates made from MN-Kieselgel (Catalog No. 816-38), Brinkman Instrument Co. Silica gel (Baker, 3405R, 60–200 mesh) was used for column chromatography. Gas chromatographic (GC) analyses were made with a Varian Associates gas chromatograph (3700 series) attached to a Varian Associates integrator (Model 4270). The following $^1/_8$ in. stainless steel columns were used: (A) 10% OV-101 on 80–100-mesh Chrom-WHP, 2 ft; (B) 20% Carbowax-20M on 80–100-mesh Supelcoport, 3 ft; (C) 20% BEEA on 60–80-mesh Chrom-PAW, 13 ft. Quantitative GC analyses were made with the use of authentic materials and their predetermined response factors. Naphthalene was used as an internal standard with column A (except when phenoxathiin was used, run 4, Table I). Cyclohexane was used as an internal standard with columns B and C. Thianthrene (Th) was from Fluka and was purified by column chromatography with petroleum ether (40–60 °C) as eluent followed by crystallization from acetone: mp 158–159 °C. Thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) was prepared as described earlier.[11] All phenols were obtained from commercial sources and were used as received, except for 2-allyl- (**1i**) and 2-*tert*-butylphenol (**1h**), which were distilled under vacuum, and for 2,4,6-tri-*tert*-butylphenol (**4a**), which was crystallized from ethanol.

Reaction of $Th^{\bullet+}ClO_4^-$ with Phenols 1a–i. General Procedure. The phenol (0.40 mmol, usually) and $Th^{\bullet+}ClO_4^-$ (250 mg, 0.80 mmol, usually) were placed under argon in a septum-capped, 50-mL, round-bottomed flask into which was injected 20 mL of acetonitrile. The solution was stirred either until the color of the cation radical had disappeared or for 2 d (**1d–f**). The solution was then diluted with 5 mL of water and extracted with 3 × 50 mL of dichloromethane. The dichloromethane solution was dried and worked up to give a solid residue. In order to recover the sulfonium salt **2**, the residue was dissolved in 10 mL of dichloromethane and to that solution was added 50 mL of ether. The mixture was placed in the refrigerator overnight, after which the precipitated salt was removed by filtration, weighed, and reprecipitated from dichloromethane with ether (1:5, v/v) for melting point measurement, ^1H NMR and IR spectroscopy, elemental analysis (in some cases), and conversion into the corresponding quinonoid (**24**). Results are given in Tables I and III. The filtrate from recovery of **2** was concentrated and made up to 10 mL for GC analysis on column A. Each reaction was carried out twice. The averaged results are given in Table I.

Reaction of $Th^{\bullet+}ClO_4^-$ with Phenols 4a–c. General Procedure. The phenol and $Th^{\bullet+}ClO_4^-$ were placed in a septum-capped, 25-mL volumetric flask. The flask was evacuated through a needle in the cap and was filled with argon, after which 20 mL of acetonitrile was injected. The mixture was stirred until the color of $Th^{\bullet+}$ had disappeared, whereupon 0.10 mL of 4 M aqueous K_2CO_3 solution was injected and the volume was made up to 25 mL with acetonitrile. GC analyses were carried out on columns B and C. Following GC analysis, 5 mL of water was added and the solution was extracted with dichloromethane. The remaining procedure for analysis on column A was as described above. A portion of the dichloromethane solution was also used for isolation of the benzoxazole **5a–e** by TLC. The benzoxazole was identified by GC-MS, ^1H NMR, and elemental analysis (**5b,d,e**). Each reaction was carried out twice, and the averaged results are given in Table II.

The melting points and solvents for crystallization of the benzoxazoles were as follows: **5a**, 62–63 °C (hexane), lit.[12] mp 55–56 °C; **5b**, 45–46 °C (pentane); **5d**, 60–62 °C (pentane); **5e**, 102–104 °C (sublimed); **5c** was an oil.

Reaction of $Th^{\bullet+}ClO_4^-$ with 2-*tert*-Butyl-4,6-dimethylphenol (9). Because **9** is a liquid, the procedure was changed. The $Th^{\bullet+}ClO_4^-$ (250 mg, 0.80 mmol) was placed under 10 mL of acetonitrile in the septum-capped, 25-mL volumetric flask. A solution of 71 mg (0.40 mmol) of **9** in 10 mL of acetonitrile was added by syringe. The mixture was stirred for 3 h, by which time the color of $Th^{\bullet+}$ had disappeared, and was worked up as described. The products obtained were *N*-*tert*-butylacetamide (**8a**, 0.026 mmol, 6.5%), isobutene (0.10 mmol, 25%), 2,4-dimethylphenol (**13**, 0.023 mmol, 5.8%), 4-*tert*-butyl-2,5,7-trimethylbenzoxazole (**11**, 0.056 mmol, 14%), Th (0.74 mmol, 92.5%), and ThO (0.036 mmol, 4.5%). Compound **11** was sublimed and had mp 72–73 °C. ^1H NMR ($CDCl_3$), δ: 6.96 (s, 1 H), 2.65 (s, 3 H), 2.47 (s, 3 H), 2.35 (s, 3 H), 1.45 (s, 9 H). GC-MS, *m/e* (relative intensity): 217 (M^+, 26.1), 202 (100), 174 (10.3), 133 (15.8), 115 (11.5), 91 (17.7), 77 (12.1), 65 (10.4), 42 (15.9). Elemental analysis was satisfactory (Table IV, supplementary material).

Reaction of $Th^{\bullet+}ClO_4^-$ with 2,4-Di-*tert*-butylphenol (17). $Th^{\bullet+}ClO_4^-$ (250 mg, 0.80 mmol) and **17** (84 mg, 0.40 mmol) were used in the usual way. It was found that the retention times on column A for Th and the product 4-acetamino-2-*tert*-butylphenol (**19**) were the same, ruling out direct assay by that means. Therefore, the solution of the residue that was obtained from the workup of the reaction mixture was divided into two portions. One portion was used for assay of **8a** on column A. The second portion was used for TLC with ether as eluent. This allowed for separation and removal from the plate of **19** and the second product, the quinonoid **18**, formally 5-(3,5-di-*tert*-butyl-6-oxo-2,4-cyclohexadien-1-ylidene)-5,5-dihydrothianthrene. However, Th, ThO, and unreacted **17** eluted together. They were removed from the plate as a mixture and were assayed by GC on column A. The quantitative results were as follows: Th (0.59 mmol, 73.8%), ThO (0.009 mmol, 1.1%), **17** (9.07, 18.3% recovered), **18** (0.042 mmol, 10.5% based on **17**, mp 123–128 °C), and **19** (0.20 mmol, 50%, mp 145–146 °C after crystallization from aqueous methanol). The ^1H NMR spectrum of **19** was coincident with that of authentic **19** (see below).

18. ^1H NMR ($CDCl_3/CD_3CN$, 1:6): δ, 8.06 (dd, J = 7.19, 1.93 Hz, 2 H), 7.80 (dd, J = 7.50, 1.58 Hz, 2 H), 7.61 (m, 4 H), 7.23 (d, J = 2.44 Hz, 1 H), 6.24 (d, J = 2.58 Hz, 1 H), 1.29 (s, 9 H), 1.08 (s, 9 H).

Conversion of 18 into 5-(3,5-Di-*tert*-butyl-2-hydroxyphenyl)thianthreniumyl Perchlorate (23). A solution of 10 mg (0.024 mmol) of **18** in 10 mL of dichloromethane was acidified with $HClO_4$. Workup gave 8 mg (0.015 mmol, 63%) of **23**, mp 176 °C dec. ^1H NMR (CD_3CN): δ, 8.24 (td, J = 7.72, 1.62 Hz, 2 H), 7.96 (dd, J = 7.71, 1.77 Hz, 2 H), 7.85 (td, J = 7.08, 1.59

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Hz, 2 H), 7.76 (td, J = 7.50, 1.67 Hz, 2 H), 7.59 (d, J = 2.12 Hz, 1 H), 6.48 (d, J = 2.26 Hz, 1 H), 1.34 (s, 9 H), 1.10 (s, 9 H); the OH signal was not seen.

Preparation of Authentic 19 and of Its Isomer 2-Acetamino-4-*tert*-butylphenol (20). Compound **19** is recorded as having mp 168–169 °C,[13] differing from our mp 145–146 °C. Therefore, preparation of **19** was carried out as described in that patent. Sulfanilic acid (870 mg, 5.0 mmol) was dissolved in a hot solution of 270 mg (2.5 mmol) of Na_2CO_3 in 5 mL of water. To this solution, after it had cooled, was added a solution of 380 mg (5.0 mmol) of $NaNO_2$ in 1 mL of water. The resulting solution was poured into a mixture of 1.3 g (13 mmol) of concd HCl and 6 g of crushed ice. The suspension of the diazonium salt that had been formed was poured into a solution of 750 mg (5.0 mmol) of 2-*tert*-butylphenol (**1h**) and 1.1 g (28 mmol) of NaOH in 6 mL of water to which had been added 4 g of crushed ice. A dark red solution formed that was stirred at 5 °C for 30 min and then warmed to 75 °C. To the warm solution was added 2.8 g (16 mmol) of sodium hydrosulfite in small amounts. The temperature of the solution rose to 80 °C and the solution became pale yellow. A dark green oil settled out and solidified when cooled to 10 °C. The solid was removed, washed with a dilute sodium hydrosulfite solution, and dissolved in 3 mL of acetic acid containing 600 mg of acetic anhydride. This solution was warmed for 1 h on a steam bath and then poured into 20 mL of water. The precipitated solid was collected, dried under vacuum, and crystallized from aqueous methanol, giving 520 mg (2.5 mmol, 50%) of **19**, mp 146–147 °C. ^{1}H NMR ($CDCl_3/CD_3CN$, 5:1): δ, 7.71 (br s, 1 H), 7.29 (dd, J = 8.46, 2.60 Hz, 1 H), 7.21 (d, J = 2.52 Hz, 1 H), 6.66 (d, J = 8.42 Hz, 1 H), 6.39 (s, 1 H), 2.09 (s, 3 H), 1.36 (s, 9 H).

Anal. Calcd for $C_{12}H_{17}O_2N$: C, 69.6; H, 8.21; N, 6.76. Found: C, 69.3; H, 8.49; N, 6.66.

20. A solution of 100 mg (0.61 mmol) of 2-amino-4-*tert*-butylphenol (Aldrich) in 2 mL of acetic acid containing 540 mg (5.3 mmol) of acetic anhydride was heated for 30 min under reflux. The solution was cooled and poured onto crushed ice. The precipitate was collected and dried under vacuum, giving 950 mg (0.46 mmol, 75%) of 2-acetamino-4-*tert*-butylphenol (**20**), mp 167–168 °C; lit.[14] mp 170 °C. ^{1}H NMR ($CDCl_3/CD_3CN$, 5:1): δ, 8.91 (s, 1 H), 8.32 (br s, 1 H), 7.13 (dd, J = 8.30, 2.33 Hz, 1 H), 7.09 (d, J = 2.02 Hz, 1 H), 6.90 (d, J = 8.28 Hz, 1 H), 2.23 (s, 3 H), 1.28 (s, 9 H).

Reaction of $Th^{\bullet+}ClO_4^-$ with 4-*tert*-Butylphenol (14). (A) 2:1 Ratio. The amounts of reactants were 60 mg (0.40 mmol) of **14** and 250 mg (0.80 mmol) of $Th^{\bullet+}ClO_4^-$. Precipitation gave 160 mg (0.344 mmol, 86% based on **14**) of 5-(5-*tert*-butyl-2-hydroxyphenyl)thianthreniumyl perchlorate (**15**), mp 214–215 °C, having acceptable elemental analysis (Table IV). GC analysis of the filtrate on column A gave 82 mg (0.38 mmol, 47.5%) of Th and 2.1 mg (0.014 mmol, 3.5%) of unused **14**.

15. ^{1}H NMR (CD_3CN): δ, 8.24 (dd, J = 7.73, 1.57 Hz, 2 H), 7.96 (dd, J = 7.68, 1.62 Hz, 2 H), 7.86 (td, J = 7.61, 1.55 Hz, 2 H), 7.76 (td, J = 7.54, 1.67 Hz, 2 H), 7.58 (dd, J = 8.62, 2.32 Hz, 1 H), 7.07 (d, J = 8.62 Hz, 1 H), 6.58 (d, J = 2.20 Hz, 1 H).

A solution of 100 mg (0.216 mmol) of **15** was treated with aqueous Na_2CO_3 to give 60 mg (0.17 mmol, 77%) of the quinonoid 5-(3-*tert*-butyl-6-oxo-2,4-cyclohexadien-1-ylidene)-5,5-dihydrothianthrene (**26**), mp 152–154 °C (from CH_3CN). ^{1}H NMR ($CDCl_3$): δ, 8.04 (m, 2 H), 7.67 (m, 6 H), 7.32 (dd, J = 8.78, 2.36 Hz, 1 H), 6.72 (d, J = 8.84 Hz, 1 H), 6.53 (d, J = 2.34 Hz, 1 H), 1.17 (s, 9 H).

(B) 4:1 Ratio. Reactants were 30 mg (0.20 mmol) of **14** and 250 mg (0.80 mmol) of $Th^{\bullet+}ClO_4^-$. Products by GC were Th (74 mg, 0.34 mmol, 43%) and ThO (9.2 mg, 0.040 mmol, 5.0%). Precipitation gave 120 mg (0.177 mmol, 89%) of the quinonoidal monoperchlorate salt (**16**), mp 220–225 °C.

A solution of 20 mg (0.03 mmol) of **16** in 10 mL of dry CH_3CN was acidified with $HClO_4$. Addition of 50 mL of ether and overnight refrigeration of the mixture led to the precipitation of 18 mg (0.023 mmol, 77%) of the bis(thianthreniumyl) diperchlorate **22**, mp 124–130 °C. ^{1}H NMR (CD_3CN): δ, 8.21 (dd, J = 7.78, 1.37 Hz, 4 H), 7.94 (dd, J = 7.66, 1.64 Hz, 4 H), 7.86 (td, J = 7.53, 1.51 Hz, 4 H), 7.75 (td, J = 7.46, 1.69 Hz, 4 H), 6.76 (s, 2 H), 0.90 (s, 9 H); the OH signal was not seen.

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Registry No. **1a**, 128-39-2; **1b**, 576-26-1; **1c**, 2078-54-8; **1d**, 87-65-0; **1e**, 608-33-3; **1f**, 28177-48-2; **1g**, 108-95-2; **1h**, 88-18-6; **1i**, 1745-81-9; **2a**, 134189-29-0; **2b**, 134189-25-6; **2c**, 134189-27-8; **2d**, 139656-61-4; **2e**, 139656-63-6; **2f**, 139656-65-8; **2g**, 51608-83-4; **2h**, 51608-87-8; **2i**, 139656-67-0; **3**, 139656-78-3; **4a**, 732-26-3; **4b**, 489-01-0; **4c**, 128-37-0; **5a**, 64130-73-0; **5b**, 139656-56-7; **5c**, 139656-57-8; **5d**, 139656-58-9; **5e**, 139656-59-0; **6**, 719-22-2; **7b**, 2409-55-4; **8a**, 762-84-5; **8b**, 1118-32-7; **8c**, 107-58-4; **9**, 1879-09-0; **11**, 139656-52-3; **13**, 105-67-9; **14**, 98-54-4; **15**, 134189-31-4; **16**, 139656-54-5; **17**, 96-76-4; **18**, 139656-55-6; **19**, 4151-47-7; **20**, 17791-62-7; **23**, 134189-33-6; **24a**, 139656-68-1; **24b**, 139656-69-2; **24c**, 139656-70-5; **24d**, 139656-71-6; **24e**, 139656-72-7; **24f**, 139656-73-8; **24g**, 139656-74-9; **24h**, 139656-75-0; **24i**, 139656-76-1; $Th^{\bullet+}$ ClO_4^-, 35787-71-4; Th, 92-85-3; ThO, 2362-50-7; *t*-BuOH, 71-36-3; $Me_2C{=}CH_2$, 115-11-7; MeCN, 75-05-8; EtCN, 107-12-0; $CH_2{=}CHCN$, 107-13-1.

Supplementary Material Available: Absorption spectroscopic data and melting points for compounds **2a–i** and **24a–i** in Table III and elemental analyses of compounds **2h,i**, **5b,d,e**, **11**, **15**, **16**, and **24a–f** in Table IV (2 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of the Radical-Induced Deiodination of Aryl Iodides by Methoxide Ions[1]

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Kinetic study of the deiodination of *m*-chloroiodobenzene (to chlorobenzene and iodide ion), as effected by sodium or potassium methoxide in methanol, with initiation by thermolysis of azobisisobutyronitrile (AIBN), reveals kinetic orders 1.0 in aryl iodide and 0.5 in AIBN. The reaction is 0.86 order in potassium methoxide, but the dependence of rate on sodium methoxide concentration is less easily stated. Nitrobenzene inhibits the reaction. At high inhibitor concentrations, the kinetic order in nitrobenzene approaches −1 and concomitantly the kinetic order in AIBN approaches unity. These and related features of kinetic behavior fail to disqualify the radical chain mechanism with electron-transfer steps that has been proposed for this reaction.

In recent years several types of radical chain mechanisms involving electron-transfer steps have been recognized.[3] One general type involves abstraction of a hydrogen atom from an anion by a reactive radical, generating as a by-

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