Reactions of Pinacols with One-Electron Oxidants

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Oxidation of the tetraarylpinacols $(Ar_2COH)_2$, **1a**−**e**, in which Ar = C_6H_5 (**1a**), 4-ClC_6H_4 (**1b**), 4-MeC_6H_4 (**1c**), 4-$MeOC_6H_4$ (**1d**) and 4-$Me_2NC_6H_4$ (**1e**), by thianthrene cation radical ($Th^{\bullet+}$) in CH_3CN and in CH_2Cl_2 led quantitatively to the corresponding diaryl ketones $Ar_2C{=}O$ (**2a**−**e**), provided a sufficient amount of base, 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), was present to prevent presumed acid-catalyzed rearrangement. In the case of **1e**, continued oxidation of **2e** was also observed. Oxidation of **1a** by $(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$ and $(4\text{-}BrC_6H_4)_3N^{\bullet+}SbF_6^-$ ($Ar_3N^{\bullet+}$) occurred analogously. Evidence for the catalytic, cation-radical rearrangement of **1a** by $Ar_3N^{\bullet+}$ (reported in earlier literature) and by $Th^{\bullet+}$ could not be found. Quantitative oxidation of **1a** to **2a** and of **1d** to **2d** was obtained also with $NOBF_4$, again provided that sufficient DTBMP was present to prevent acid-catalyzed rearrangement. Catalytic, oxidative rearrangement of **1d** at room temperature and (as reported in earlier literature) at −5 °C was not observed. Oxidation was also observed of 2,3-diphenyl-2,3-butanediol (**3**) to acetophenone (**9**) and of 1,1-dimethyl-2,2-diphenylethanediol (**4**) to **2a** and acetone by $Th^{\bullet+}$. Oxidation of 2,3-dimethyl-2,3-butanediol (**5**) by $Th^{\bullet+}$ was not observed. Instead, even in the presence of DTBMP, pinacolone (**10**) and tetramethyloxirane (**11**) were formed, through, it is proposed, a mechanism involving complexation with $Th^{\bullet+}$.

Introduction

The oxidation of aromatic pinacols [$(Ar_2COH)_2$, **1**] to diaryl ketones ($Ar_2C{=}O$, **2**) by one-electron transfer oxidants has been the subject of a number of reports in recent years.[1−5] Prominent among these reports are those of Kochi, in which the extremely short lifetimes of $\mathbf{1}^{\bullet+}$ to scission have been recorded,[1] and of Penn, which describe the rates of electron transfer for and the characteristics of oxidation of a number of **1** by iron tris(phenanthroline) complexes and by dichlorodicyanobenzoquinone (DDQ).[2] Penn and co-workers have shown, particularly, that unless precaution with the addition of a sufficient excess of organic base is taken, the acid liberated in the oxidation (eq 1) will catalyze the typical rearrangement of the pinacols.[2b,c]

$$(Ar_2COH)_2 - 2e^- \rightarrow 2Ar_2C{=}O + 2H^+ \qquad (1)$$

Studies have been made in these laboratories, recently, of the reactions of alcohols and diols with the thianthrene cation radical ($Th^{\bullet+}ClO_4^-$).[6,7] It was recognized in those studies that the presence of base (2,6-di-*tert*-butyl-4-methylpyridine, DTBMP) was essential to prevent acid-catalyzed reactions. Accordingly, all reactions were carried out with equimolar amounts of $Th^{\bullet+}ClO_4^-$ and DTBMP. It appears now that this recipe may have contained an insufficient amount of base, so that reactions attributed to oxygen-transfer to $Th^{\bullet+}$ may have been, instead, initiated in part by acid catalysis. In particular, reactions of some pinacols with $Th^{\bullet+}ClO_4^-$ were studied in which both rearrangements and oxidations were found, and the cause of the rearrangements observed then appears now to be uncertain.[7] New work has now been carried out on reactions of $Th^{\bullet+}ClO_4^-$ and (to some extent) $Th^{\bullet+}BF_4^-$ with the pinacols **1a** (Ar = C_6H_5), **1b** (Ar = 4-ClC_6H_4), **1c** (Ar = 4-MeC_6H_4), **1d** (Ar = 4-$MeOC_6H_4$), and **1e** (Ar = 4-$Me_2NC_6H_4$). Similar work has been carried out on reactions of $Th^{\bullet+}$ with 2,3-diphenyl-2,3-butanediol (**3**), 1,1-dimethyl-2,2-diphenylethanediol (**4**), and 2,3-dimethyl-2,3-butanediol (**5**). These works are the subject of this report.

Work somewhat analogous to ours has been reported by Lopez and co-workers[8] and by Arce de Sanabia and Carrión,[9] that also raises the issue of oxidation versus rearrangement. For example, reaction of benzopinacol (**1a**) with catalytic amounts (10 mol %) of tris(4-bromophenyl)aminium ($Ar_3N^{\bullet+}$) or tris(2,4-dibromophenyl)aminium ($Ar'_3N^{\bullet+}$) hexachloroantimoate in CH_2Cl_2 is reported to have caused the quantitative rearrangement of **1a** to phenyl triphenylmethyl ketone (**6a**). The rearrangement was found to be retarded but not inhibited by the presence of 10 mol % of 2,6-di-*tert*-butylpyridine (DTBP). When reaction of **1a** with $Ar'_3N^{\bullet+}$ (50 mol %) was carried out in CH_3CN, both **2a** (70%) and **6a** (30%) were formed, a result said to appear to be at variance with observations by Penn and co-workers[2c] in that it was thought that both **2a** and **6a** might arise from $\mathbf{1a}^{\bullet+}$.[8]

In the work of Arce de Sanabia and Carrión,[9] a catalytic amount of $NOBF_4$ (20 mol %) was found to cause quantitative rearrangement of **1d** to **6d** in CH_3CN at −5

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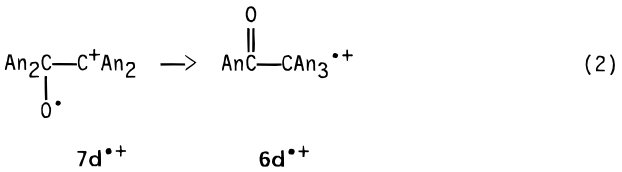
Table 1. Products (mmol) of Reactions of Benzopinacol (1a)

	reactants, mmol × 10^2				products,[c] mmol × 10^2					
run	**1a**	$Th^{\bullet+}X^-$ or other	DTBMP[a]	solvent[b]	**2a**	**6a**	**8a**	Th	ThO	product balance[d]
1	10	40[e]	40	A	20			30	9.3	0.96
2	9.9	40[e]	40	B	20			30	11	1.05
3	60	40[e]	60	A	15	tr		26	12	1.07
4	40	40[e]	61	B	30			35	4.7	0.99
5	60	40[e]		A	8.2	55		24	14	0.82
6	40	41[e]		B	1.7	37	tr	22	20	0.85
7	20	2.4[e]		B	tr	18	tr	1.7	0.6	
8	20	21[f]	30	A	15			18	2.7	0.98
9	10	24[f]		A	3.5	8.1	tr	14	9.2	0.73
10	40	40[f]	21	B	7.5	33	tr	23	16	1.07
11	20	33[g]		A		20				
12	40	40[h]		B	*i*					
13	75	7.5[j]	15	B	4.8	tr	tr			
14	75	7.5[j]		B		73				
15	75	7.5[k]	15	B	5.3	tr				
16	75	7.5[k]		B	tr	73				
17	40	21.5[l]	42	A	*i*	tr	tr			
18	40	20.4[m]	10	A		39				

[a] 2,6-Di-*tert*-butyl-4-methylpyridine. [b] A = CH_3CN, B = CH_2Cl_2. [c] In runs 3, 4, 8, 10, 13, 15, and 17, **2a** (benzophenone) was separated by TLC and assayed by GC. In runs 12 and 17, **1a** was unchanged. In other runs, **1a** was consumed completely. DTBMP, when used, was recovered (GC assay) almost completely. [d] Ratio mmol of **2a**/(mmol of Th − mmol of ThO). [e] $X^- = ClO_4^-$. [f] $X^- = BF_4^-$. [g] $HClO_4$. [h] $Bu_4N^+ClO_4^-$. [i] All of the **1a** was converted into **2a** on the GC column, but only **1a** (no **2a**) was found with TLC. [j] $(BrC_6H_4)_3N^{\bullet+}SbCl_6^-$. [k] $(BrC_6H_4)_3N^{\bullet+}SbF_6^-$. [l] $DTBMPH^+ClO_4^-$, which was added in increments over a period of time. See procedure B in the Experimental Section. [m] $DTBMPH^+ClO_4^-$, which was added in one increment. See procedure A in the Experimental Section.

°C, and the result was not changed by the presence of 32 mol % of DTBP. Consequently, a catalytic chain process was proposed in which $\mathbf{1d}^{\bullet+}$ was formed by reaction of **1d** with $NOBF_4$, and lost a molecule of H_2O, to give the cation radical ($\mathbf{7d}^{\bullet+}$) that next rearranged to $\mathbf{6d}^{\bullet+}$ (eq 2, An = *p*-anisyl). The chain of electron transfer



(2)

was continued by oxidation of **1d** by $\mathbf{6d}^{\bullet+}$.[9] The same behavior was reported for **1e**. This report attracted our interest, since we had found, and we report here, that both $Th^{\bullet+}ClO_4^-$ and $Th^{\bullet+}BF_4^-$ oxidized **1d** cleanly to **2d**. $Th^{\bullet+}BF_4^-$ is prepared by the oxidation of thianthrene (Th) with $NOBF_4$,[10] so that we were surprised that $NOBF_4$ had not also oxidized **1d** to **2d** cleanly. Further, the half-life of $\mathbf{1d}^{\bullet+}$ is reported by Kochi and co-workers to be 66 ps, so that the likelihood that $\mathbf{1d}^{\bullet+}$ could competitively and exclusively have time to lose a molecule of water and become $\mathbf{7d}^{\bullet+}$ in the chain rearrangement process seemed questionable.

We report here, then, the reactions of **1a** with $Ar_3N^{\bullet+}SbCl_6^-$ and with $Ar_3N^{\bullet+}SbF_6^-$, and of **1a** and **1d** with $NOBF_4$, in the absence and presence of DTBMP. Most reactions were carried out at room temperature (25 °C) but some with $NOBF_4$ were at −5 °C.

Results and Discussion

Reactions of Benzopinacol (1a). The results of these reactions are summarized in Tables 1 and 3. We will discuss the results in Table 1 first, and their emphasis is on the reactions of **1a** with cation radicals $Th^{\bullet+}$ and $Ar_3N^{\bullet+}$ in the presence and absence of the base DTBMP. The data in Table 1 are derived also from reactions in which either **1a** or the cation radical was used in excess, and we must first clarify the consequences of that difference. The products of reaction were identified and assayed by gas chromatography (GC). **1a** (and its analogs, considered later) decomposed on the GC column that was used, to **2a**. Therefore, when **1a** was used in excess, the formation of **2a** from reaction with a cation radical could not be assessed by direct GC measurement. Instead, the **2a** was first isolated with quantitative thin layer chromatography (TLC) and next assayed with GC. When an excess of cation radical was used, none of **1a** remained for decomposition on the column, and, therefore, direct GC measurements of **2a** could be made. In some cases of excessive amounts of **1a** (e.g., runs 5 and 6 in absence of DTBMP), the **1a** also reacted completely, mainly to **6a**, as shown by TLC, and, again, direct GC analysis could be carried out.

Reaction of **1a** with $Th^{\bullet+}$ in the presence of sufficient DTBMP led only to benzophenone (**2a**). This is seen in runs 1−4 ($Th^{\bullet+}ClO_4^-$ in CH_3CN and CH_2Cl_2) and run 8 ($Th^{\bullet+}BF_4^-$ in CH_3CN). If DTBMP was not used (runs 5, 6, and 9) or if an insufficient amount of DTBMP was used (run 10), all of **1a** was consumed and converted mainly into rearrangement product, phenyl triphenylmethyl ketone (**6a**). These results are analogous to those reported by Penn and co-workers in the reactions of **1a** with tris(phenanthroline)iron complexes [Fe(III)L_3], for example,[2b] and in reactions of **1d** with Fe(III)L_3 and DDQ.[2a] The quantitative conversion of **1a** into **6a** by $HClO_4$ is shown in run 11, while the inertness of **1a** to oxidation by ClO_4^- is reported in run 12. It is evident, then, that unless enough base (DTBMP in Table 1) was present, acid generated either by hydrolysis of $Th^{\bullet+}$ by water[11] in the solvent or in the early stage of oxidation of **1a** was the probable cause of rearrangement of **1a**. Penn and co-workers have reported that 2,6-di-*tert*-butylpyridinium ion caused rearrangement of **1d**,[2a] and we found, analogously, that $DTBMPH^+ClO_4^-$ caused rearrangement of **1a** unless an excess of DTBMP was also present (compare run 17 with run 18). We found, also,

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Table 2. Products of Reactions of Pinacols 1b-e, 3, and 4

	reactants, mmol × 10^2				products,[c] mmol × 10^2				
run	pinacol	$Th^{\bullet+}X^-$ or other	DTBMP[a]	solvent[b]	ketone	pinacol, recovd	Th	ThO	product balance[d]
1	**1b**, 10	40[e]	40	A	**2b**, 20		30	11	1.05
2	**1c**, 9.7	40[e]	40	A	**2c**, 19		29	10	1.00
3	**1d**, 10	40[e]	50	B	**2d**, 20		30	10	1.00
4	**1e**, 10	40[e]	50	B	**2e**, 12[f]		37	tr[f]	
5	**1e**, 10	40[e]	50	A	**2e**, 11[f]		40	tr[f]	
6	**3**, 60	41[e]	60	A	**9**, 35	44	37	3.1	1.03
7	**3**, 41	40[e]	62	A	**9**, 30	23	34	4.4	1.01
8	**3**, 40	40[g]	60	A	**9**, 26	26	32	9.0	1.13
9	**3**, 40	40[g]	60	B	**9**, 17	30	29	12	1.00
10	**3**, 40	41[h]	21	A		40			
11	**3**, 20	21[i]	30	A	**9**, tr	17			
12	**3**, 21	19[j]	20	A	**9**, tr	21			
13	**4**, 40	40[g]	60	A	**2a**, 8.5	30	28	9.9	0.94

[a] 2,6-Di-*tert*-butyl-4-methylpyridine. [b] A = CH_3CN, B = CH_2Cl_2. [c] Assayed by GC in all runs except run 13 in which **2a** was separated by TLC before GC assay. In run 1, column was OV-17; in all other runs, OV-101. [d] Ratio of mmol of ketone/(mmol of Th − mmol of ThO) in runs 1−3 and 6−9. In run 13, acetone was found by GC but not assayed; the ratio, therefore, is (2 × mmol of **2a**)/(mmol of Th − mmol of ThO). [e] $X^- = ClO_4^-$. [f] **2e** was found to be oxidized also by $Th^{\bullet+}ClO_4^-$ (see Experimental Section); hence all $Th^{\bullet+}$ was converted into Th. [g] $X^- = BF_4^-$. [h] $Bu_4N^+ClO_4^-$. [i] $Bu_4N^+BF_4^-$. [j] $DTBMPH^+ClO_4^-$.

that even if DTBMP was present and in excess of the amount of $DTBMPH^+ClO_4^-$, small amounts of rearrangement to **6a** and **8a**, as well as decomposition to **2a** occurred upon injection onto the GC column. If $DTBMPH^+$ was neutralized with aqueous K_2CO_3 before injection onto the column, the formation of **6a** and **8a** on the column diminished and almost quantitative formation of **2a** occurred. The data in runs 17 and 18 in Table 1 were, in fact, obtained by GC after neutralizing the $DTBMPH^+$ with aqueous K_2CO_3. The distinction between these runs is that in run 17, having an excess of DTBMP, **1a** remained in the neutralized solution and decomposed to **2a** thermally on the column. In contrast, in run 18, having insufficient DTBMP, **1a** was converted by acid catalysts entirely into **6a** before neutralization and no **1a** remained in the neutralized solution for decomposition on the column. Runs 7 and 13−16 are concerned with "catalytic" amounts of oxidants and are related to the report of Lopez and co-workers.[8] The use of 12 mol % of $Th^{\bullet+}BF_4^-$ (run 7) and 10 mol % of $Ar_3N^{\bullet+}$ (runs 14 and 16) without DTBMP caused quantitative rearrangement of **1a** to **6a**. In the presence of sufficient DTBMP, however, conversion into **6a** was prevented and was replaced largely by oxidation (**2a**), runs 13 and 15. Thus, our results show that catalytic amounts (10 mol %) of one-electron oxidant caused rearrangement (**6a**) only if base was not present. In the presence of base (20 mol %, runs 13 and 15) rearrangement was suppressed and oxidation (**2a**) prevailed. The results suggest that rearrangement was acid-catalyzed rather than originating from a catalytic, cation-radical reaction, induced by $Ar_3N^{\bullet+}$.[8]

The last column in Table 1 expresses the quantitative nature of the oxidations of **1a** into **2a**, best seen in runs 1−4, 8, and 10. Oxidation of **1a** by $Th^{\bullet+}$ (eq 3) gives 2

$$\mathbf{1a} + 2\ Th^{\bullet+} \rightarrow 2\ \mathbf{2a} + 2\ Th + 2\ H^+ \qquad (3)$$

equiv of thianthrene (Th). Reaction of $Th^{\bullet+}$ with water, either present in the dried solvent or added in workup as 2 M K_2CO_3, gives equal amounts of Th and thianthrene 5-oxide (ThO),[11] eq 4. The ratio **2a**/(Th−ThO)

$$2Th^{\bullet+} + H_2O \rightarrow Th + ThO + 2\ H^+ \qquad (4)$$

expresses, therefore, the stoichiometric result of eq 3, and ideally should be 1.0.

Table 3. Products of Reactions of 1a and 1d with $NOBF_4$ in CH_3CN[a]

	temp,	time,	reactants, mmol × 10^2			product,[b]
run	°C	h	**1**	$NOBF_4$	DTBMP[c]	mmol × 10^2
1	25	24	**a**, 40	40	60	**2a**, 14.5
2	25	24	**a**, 10	40	60	**2a**, 18.5
3	25	24	**a**, 40	8		**6a**, 39.5
4	25	24	**d**, 40	40	60	**2d**, 19
5	25	24	**d**, 10	41	60	**2d**, 17
6	25	24	**d**, 40	8		**6d**, 40
7	25	24	**d**, 100	21	32	**2d**, 17
8	−5	6	**d**, 40	8	12	**2d**, tr[d]
9	−5	6	**d**, 40	8		**6d**[e]
10	25	2	**d**, 40	*f*		**6d**, 40

[a] 25 mL. [b] Because **1a** and **1d** decomposed to **2a** and **2d**, respectively, on the GC column, **2a** and **2d** were separated first by TLC in runs 1, 4, 7, and 8 and next assayed (runs 1, 4, 7) by GC. In runs 2 and 5, only a trace of **1** remained (TLC) in the presence of excess of $NOBF_4$, so assay of **2** was made by GC directly. [c] 2,6-Di-*tert*-butyl-4-methylpyridine. [d] Most of the **1d** remained unchanged. [e] The major product, by TLC. Small amounts of **1d** and **2d** were found, also. [f] One drop of 70% $HClO_4$; no $NOBF_4$.

Reactions of Tetraarylpinacols (1b-e) with $Th^{\bullet+}ClO_4^-$. An excess of $Th^{\bullet+}ClO_4^-$ was used in order to obviate TLC separation of products. Oxidations of **1b−d** to **2b−d** took place cleanly. The data, including the ratios **2**/(Th-ThO), are given in Table 2. **1e** engendered more extensive oxidation than anticipated. Thus, only approximately 50% of the expected **2e** was obtained. All of the $Th^{\bullet+}$ that was used was reduced to Th (runs 4 and 5). The data suggest that **2e** itself was oxidized by 2 equiv of $Th^{\bullet+}$, and this was confirmed with control experiments (see Experimental Section). Further investigation of the product(s) of oxidation of **2e** was not made.

Reactions of 1a and 1d with $NOBF_4$. Reactions of these pinacols with $NOBF_4$ in the presence of a sufficient amount of DTBMP ended only in oxidation to **2a** and **2d**, respectively (runs 1, 2, 4, and 5, Table 3). Whether or not TLC separation of **2** was necessary depended on the amount of **1** used, as explained earlier for **1a**. Run 3 with **1a** and run 6 with **1d** are analogs, but at room temperature, of experiments with **1d** and 20 mol % of $NOBF_4$ at −5 °C reported by Arce de Sanabia and Carrión,[9] while run 9 at −5 °C replicates their experiment with **1d**. In each case, as reported for **1d**,[9] rearrangement was quantitative. Run 7, at room temperature, and run 8 at −5 °C with **1d** correspond with the reported use of 20

Table 4. Products of Reactions of Tetraphenyloxirane (8a) with $Th^{\bullet+}ClO_4^-$ in CH_3CN[a]

	reactants, mmol × 10^2			products,[b] mmol × 10^2			
run	**8a**	$Th^{\bullet+}ClO_4^-$	DTBMP	**6a**	recovd **8a**	Th	ThO
1	10	40	40		10	20	20
2	20	20		20		10	9.8

[a] 25 mL. [b] Assayed by GC, OV-101 column.

mol % of $NOBF_4$ and 32 mol % of base,[9] but whereas the earlier authors obtained **6d** in these conditions we obtained only **2d**. Last, run 10 reports the quantitative rearrangement of **1d** at room temperature with a small amount (unmeasured) of $HClO_4$, a result that is similar to that with **1a**, run 11, Table 1. Arce de Sanabia and Carrión found **1d** to be inert to 20 mol % of H_2SO_4 under their conditions of use. The difference between our results with $HClO_4$ and the earlier results with H_2SO_4[9] may have occurred because of the difference in temperatures (25 °C vs −5 °C) that were used. The variations in efficiencies of proton-catalyzed pinacol rearrangements have been noted elsewhere, too.[12] Our results indicate that **1a** and **1d** are oxidized but not rearranged by reaction with $NOBF_4$. Bearing in mind that Th is readily oxidized to $Th^{\bullet+}$ by $NOBF_4$[10] and that $Th^{\bullet+}$ oxidized **1a** and **1d** to **2a** and **2d**, it is not surprising to find that these pinacols are oxidized by $NOBF_4$. The rearrangements that have been reported here (in the absence of base) and earlier appear to be acid catalyzed, the acid being generated, perhaps, by small amounts of oxidation, eq 1.

Reactions of Pinacols 3 and 4. 2,3-Diphenyl-2,3-butanediol (**3**) did not decompose on our OV-101 column so that GC assay of products could be used directly. Oxidations by $Th^{\bullet+}$ in the presence of DTBMP were quantitative (runs 6−9, Table 2). The pinacol was affected little or not at all by $Bu_4N^+ClO_4^-$, $Bu_4N^+BF_4^-$, and $DTBMPH^+ClO_4^-$ in the presence of DTBMP (runs 10−12). Thus 3 behaved similarly to **1a**−**1d**. Pinacol **4** was also oxidized cleanly by $Th^{\bullet+}BF_4^-$ in the presence of DTBMP (run 13, Table 2).

Table 1 shows that small amounts (traces, tr) of tetraphenyloxirane (**8a**) were obtained in some runs alongside small amounts of the rearrangement product **6a**. We were interested to know if **8a** was reactive toward $Th^{\bullet+}$, and found (Table 4) that it was unreactive if base was present. In the absence of base, **8a** was converted into **6a**, presumably by acid catalysis.

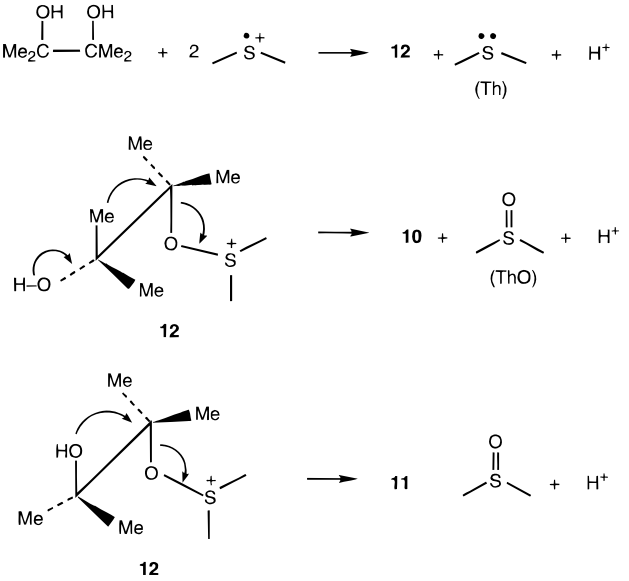
Reactions of 2,3-Dimethyl-2,3-butanediol (5). In the presence of a large amount of DTBMP, **5** reacted with $Th^{\bullet+}$ in dry CH_3CN and dry CH_2Cl_2 to give pinacolone (**10**) and tetramethyloxirane (**11**), Table 5. In CH_2Cl_2 that had been saturated with water, and, again, in the presence of DTBMP, **5** was recovered, and only the products of reaction of $Th^{\bullet+}$ with water, Th and ThO, were found. The results in Table 5 suggest, then, that **10** and **11** (runs 1−3) were not formed by acid catalysis, but by direct reaction with $Th^{\bullet+}$. A proposal for that reaction is shown in Scheme 1. The supposition here is that **5** cannot be oxidized by $Th^{\bullet+}$ and behaves, instead, in the way that we have proposed for alcohols which also have high oxidation potentials. In principle, the sum of the yields of **10** and **11** should equal each of those of Th and ThO, Scheme 1. Because equal amounts of Th and ThO are formed also from reaction of $Th^{\bullet+}$ with water, the yields of Th and ThO in Table 5 should be the same. This is seen in runs 3 and 4 but there are discrepancies in runs 1 and 2. The balance between yields of **10** and **11** and yields of Th and ThO is reasonable in runs 2 and 3, in which CH_2Cl_2 was the solvent, but is not at all close in run 1, with CH_3CN, the reason for which is not known.

Table 5. Products of Reactions of 2,3-Dimethyl-2,3-butanediol (5) with $Th^{\bullet+}ClO_4^-$ and $Th^{\bullet+}BF_4^-$

	reactants, mmol × 10^2				products,[b] mmol × 10^2				
run	**5**	$Th^{\bullet+}X^-$	DTBMP	solvent[a]	recovd **5**	**10**[f]	**11**[g]	Th	ThO
1	63	40[c]	60	A	54	3	3	23	17
2	61	41[c]	61	B	42	2	11	23	19
3	52	40[d]	60	B	39	2	14	21	19
4	61	40[c]	61	B[e]	59			19	20

[a] 10 mL; A = CH_3CN, B = CH_2Cl_2. [b] Assayed by GC on SE-54 capillary column. [c] $X^- = ClO_4^-$. [d] $X^- = BF_4^-$. [e] Saturated with water. [f] Pinacolone. [g] Tetramethyloxirane.

Scheme 1



The pinacols we have used have high oxidation potentials[2] so that oxidation by $Th^{\bullet+}$, $Ar_3N^{\bullet+}$, and NO^+ (as well as by $Fe(III)L_3$[2]) would not have been expected. Penn[2a,b] has attributed ease of oxidation to interaction of aryl rings in both the 1,1- and 1,2-configuration, and the generality of these oxidations supports that idea. Insofar as **5** is concerned, oxidation is not promoted, and bonding at sulfur (**12**) is an alternative that leads to **10** and **11**.

Experimental Section

Acetonitrile was refluxed over and distilled from P_2O_5 and again from CaH_2, each under N_2; with dichloromethane, only P_2O_5 was used. 2,6-Di-*tert*-butyl-4-methylpyridine (DTBMP), from Aldrich, was dried under vacuum. Thin layer chromatographic (TLC) separations for later quantitative assays (by GC) were made with Analtech Uniplate plates. Quantitative gas chromatographic (GC) assays were made with a Varian Associates Model 3700 instrument attached to a Spectra Physics Model 4270 or 4290 integrator. The columns used were 10% OV-101 on 80-100 mesh Chrom WHP, 4 ft × 1/8 in stainless steel (ss), with injector at 250 °C, detector at 300 °C, and oven temperature held at 50 °C for 2 min and ramped at 10 °C/min to 250 °C; a 10% OV-17 on 80−100 mesh Chrom Q II, 6 ft × 1/8 in. ss, used similarly; and an SE-54 capillary, 30 m × 0.25 mm, with injector and detector temperatures at 250

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°C, and oven temperature held at 36 °C for 7 min and ramped 12 °C/min to 250 °C. Column use is noted in the tables.

Thianthrene (Th), from Fluka, was purified by column chromatography, petroleum ether eluent, and was crystallized from acetone. Thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$, *warning*)[11] and tetrafluoroborate ($Th^{\bullet+}BF_4^-$)[10] were prepared and assayed as described earlier. Tris(4-bromophenyl)aminium hexafluoroantimonate ($TBPA^{\bullet+}SbF_6^-$)[13] and hexachloroantimonate ($TBPA^{\bullet+}SbCl_6^-$)[14] were prepared as described from TBPA.[15] 2,3-Dimethylbutane-2,3-diol (pinacol, **5**) was dried as described.[16] 2,3-Dimethyl-2-butene, benzophenone (**2a**), 4,4′-dichloro- (**2b**), 4,4′-dimethoxy- (**2d**), and 4,4′-bis(dimethylamino)benzophenone (**2e**) were from Aldrich. 4,4′-Dimethylbenzophenone (**2c**) was from TCI America. Benzopinacol (1,1,2,2-tetraphenyl-1,2-ethanediol, **1a**) was prepared by irradiation of **2a** in isopropyl alcohol,[2b] mp 188−190 °C (crystallized from benzene/90−100 °C ligroin); lit.[2b] mp 185−189 °C. **1,1,2,2-Tetrakis(4-chlorophenyl)-1,2-ethanediol** (**1b**) was prepared by reduction of **2b** with $Zn/ZnCl_2$,[17] mp 173−175 °C (crystallized from 90−100 °C ligroin); lit.[18] mp 173−174 °C. **1,1,2,2-Tetrakis(4-methylphenyl)-1,2-ethanediol** (**1c**) was prepared from **2c** as with **1b**, mp 179−181 °C (crystallized from chloroform/ethanol); lit.[2b] mp 174−175 °C. **1,1,2,2-Tetrakis(4-methoxyphenyl)-1,2-ethanediol** (**1d**) was prepared from **2d** as with **1a**, mp 180−182 °C (crystallized from hexane/ethylacetate); lit.[18] mp 183 °C. **1,1,2,2-Tetrakis-[4-(dimethylamino)phenyl]-1,2-ethanediol** (**1e**) was prepared by reduction of **2e** with Mg/I_2,[19] mp 195−197 °C (crystallized from chloroform/ethanol and benzene/ethanol); lit.[19] mp 196−197 °C. ***meso*-2,3-Diphenyl-2,3-butanediol** (**3**), mp 116−117 °C (crystallized from hexane/ethanol) was prepared as described;[20] lit.[20] mp 116.2−117.8 °C; **1,1-dimethyl-2,2-diphenyl-1,2-ethanediol** (**4**) was prepared as described by Parry.[21] The product was not, however, steam distilled to remove bromobenzene and biphenyl. Instead, the ether solution from the Grignard reaction was washed with cold 0.1 M H_2SO_4 and with water several times and was dried over $MgSO_4$. The dried solution was concentrated under reduced pressure, and to the concentrate was added hexane to precipitate crude **4**, the bromobenzene and biphenyl remaining in solution. The **4** was crystallized several times from benzene/petroleum ether, mp 90−90.5 °C. Literature[21] mp 89−89.5 °C. **Phenyl triphenylmethyl ketone** (benzopinacolone, **6a**),[22] mp 185−187 °C (crystallized from benzene/ligroin), lit.[22] mp 179−180 °C; and pinacolone,[23] bp 107−108 °C were prepared as described in the literature. **Tetraphenyloxirane** (**8a**) was prepared by oxidation of tetraphenylethene,[24] which itself was prepared by reduction and rearrangement of **6a**[25] and had mp 211−213 °C (crystallized from ethyl acetate); lit.[24] mp 209.7−210.2 °C. **Tetramethyloxirane** (**11**) was prepared from tetramethylethene as described.[26]

Reactions of Benzopinacol (1a). A typical procedure (e.g., run 3, Table I) for reaction with $Th^{\bullet+}ClO_4^-$ is given. The procedure was followed with some modification where needed with other reactants listed in the tables. **1a** (220 mg, 0.60 mmol), $Th^{\bullet+}ClO_4^-$ (126 mg, 0.40 mmol), and DTBMP (123 mg, 0.60 mmol) were placed in a 25 mL volumetric flask, containing a stirrer magnet bar, and the flask was purged with dry N_2 after capping with a septum. Dry CH_3CN was introduced to the mark by syringe, and the mixture was stirred for 3 h, by which time the color of $Th^{\bullet+}$ has disappeared and the solution was pale yellow. Next, 0.2 mL of aqueous 2 M K_2CO_3 was injected into the flask and stirring was continued for 1 h. GC analysis (OV-101), after adding naphthalene as internal standard, showed Th, ThO, and only **2a** as products, and that no **1a** remained. The Th and ThO were assayed (GC). A 10 mL portion of the solution was concentrated under vacuum to small volume, and this was streaked on a preparative TLC plate. Development with hexane/ethyl acetate (15:1) showed that both **1a** and **2a** were present. The band containing **2a** was removed, and the **2a** was extracted with CH_2Cl_2 for GC analysis, with naphthalene as an internal standard. The result is listed in Table 1. When an excess of oxidant was used in the presence of DTBMP, none of the pinacol remained (as shown by TLC spotting) for later decomposition into **2a** on the GC column (e.g., runs 1 and 2, Table 1). Therefore, GC analysis was carried out without intervention of TLC separation. When an oxidant was used in the absence of DTBMP (e.g., runs 5−7, 9, Table 1) much of the pinacol underwent acid-catalyzed reaction and little or none remained (TLC spotting) for later decomposition on the column. Therefore, GC analysis was again carried out without prior use of TLC separation. Reactions with other solid oxidants and with other pinacols were carried out in much the same way. When $HClO_4$ was used with **1a** (run 11, Table 1), 0.08 mL of 70% $HClO_4$ was injected into the volumetric flask after the solvent had been added. Monitoring by GC showed the formation of 91% of **6a** after 10 min, 96% after 1 h, and complete conversion into **6a** after 24 h. When $(BrC_6H_4)_3N^{\bullet+}$ was used as oxidant, workup with 0.5 mL (instead of 0.2 mL) of 2 M K_2CO_3 was used. Initially, reactant solutions were stirred overnight (24 h), e.g., runs 1, 2, 5, 9, 10 of Table 1. Later, shorter times (1−6 h) of stirring before workup were used, as judged by the disappearance of cation radical color. Solutions were stirred for approximately 1 h after adding aqueous K_2CO_3 and before GC analysis was carried out. Most reactions were repeated two or three times, and the results tabulated are averages.

Reaction of Benzopinacol (1a) with $DTBMPH^+ClO_4^-$. A: A solution of 147 mg (0.402 mmol) of **1a**, 20.5 mg (0.100 mmol) of DTBMP, and 62.3 mg (0.204 mmol) of $DTBMPH^+ClO_4^-$ in 25 mL of CH_3CN was stirred for 50 min. GC analysis gave 0.015 mmol of **2a**, 0.346 mmol of **6a**, and 0.040 mmol of **8a**. After a total of 4 h the solution was neutralized with 0.2 M K_2CO_3. GC analysis gave 0.387 mmol of **6a** (96%); **2a** and **8a** were not found.

B: A solution of 147 mg (0.402 mmol) of **1a** in 25 mL of CH_3CN, containing naphthalene as an internal standard, was kept for 40 min, and an aliquot was injected onto the OV-101 column. Almost all of the **1a** was converted into **2a** (0.776 mmol, 97%). Small amounts of **6a** (0.008 mmol) and **8a** (0.007 mmol) were obtained, too. The analysis was repeated after 3 h with a similar result. Then, 85 mg (0.415 mmol) of DTBMP was added to the solution and GC analysis was repeated, giving 92% of **2a**, 0.006 mmol of **6a**, and 0.007 mmol of **8a**. To the solution was next added four increments of 15−16 mg (approximately 0.05 mmol) of $DTBMPH^+ClO_4^-$ over a period of 72 h and after each addition GC analysis was carried out. The amount of **2a** decreased with each incremental addition (to 0.640 mmol, 80%) while the amounts of **6a** and **8a** increased to, finally, 0.034 mmol (8.5%) and 0.064 mmol (16%), respectively. After 75 h, 0.2 mL of 2 M K_2CO_3 was added to the solution, and GC analysis gave 0.820 mmol (102%) of **2a**, with 0.003 mmol of **6a** and 0.004 mmol of **8a**. The summation of additions of $DTBMPH^+ClO_4^-$ and the analysis after workup with K_2CO_3 is given as run 17, Table 1.

Reactions of Tetraphenyloxirane (8a) with $Th^{\bullet+}ClO_4^-$. **8a** (70 mg, 0.20 mmol) and $Th^{\bullet+}ClO_4^-$ (63 mg, 0.20 mmol) were placed with 25 mL of CH_3CN in a septum-capped volumetric flask as described. After 30 min, 0.2 mL of 2 M K_2CO_3 solution

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was added which discharged the color of $Th^{\bullet+}$ immediately. One hour later GC analysis showed quantitative conversion into **6a**. The result in Table 4, run 2, is an average of three experiments. The reaction was repeated with 10 mmol of **8a**, 40 mmol of $Th^{\bullet+}ClO_4^-$, and 40 mmol of DTBMP. Stirring was continued for 24 h, by which time the color of $Th^{\bullet+}$ had disappeared. One hour after addition of 0.2 mL of 2 M K_2CO_3, GC analysis showed none of **6a**; only **8a** remained, run 1, Table 4 (two experiments). When this reaction was repeated but with a lesser amount of DTBMP, periodic GC monitoring showed the gradual conversion of **8a** into **6a**, while the color of $Th^{\bullet+}$ persisted. The conversion into **6a** was complete after 5 h.

Further control tests showed that when a solution of 26.5 mg (0.076 mmol) of **8a**, 83.2 mg (0.406 mmol) of DTBMP, and 63 mg (0.206 mmol) of $DTBMPH^+ClO_4^-$ in 25 mL of CH_3CN was kept for 2 h and used for GC analysis, 0.68 mmol of **8a** and 0.007 mmol of **6a** were found. Yet, if 0.2 mL of 2 M K_2CO_3 was injected 1 h prior to GC analysis, **8a** (0.076 mmol) was fully recovered.

Reactions of 1a and 1d with $NOBF_4$. A solution of 146 mg (0.40 mmol) of **1a**, 48 mg (0.40 mmol) of $NOBF_4$, and 123 mg (0.60 mmol) of DTBMP in 25 mL of CH_3CN was prepared in the usual way. Within a few minutes the color of the solution became pale green, but was colorless after a few hours. The solution was kept for 24 h, 0.2 mL of 2 M K_2CO_3 was added and an aliquot of 10 mL was concentrated under reduced pressure and subjected to TLC separation. Only **2a** was found and assayed, run 1, Table 3. This reaction took place at room temperature and was performed twice.

A similar reaction was performed (twice) with an excess of $NOBF_4$ (run 2, Table 3). TLC showed that only a trace of **1a** remained and, therefore, GC analysis was carried out without TLC separation. No **6a** and **8a** were found.

In run 3, with no DTBMP (two expts), Table 3, a "catalytic" amount (20 mol %) of $NOBF_4$ was used, the ratio of **1a**/$NOBF_4$ being that used by Arce de Sanabia and Carrión, but here at 25 °C rather than −5 °C.[9] GC monitoring after 2 h showed **6a** and a small amount of **8a**, but after 6 h only **6a** was found. Analysis by GC after 24 h gave a quantitative yield of **6a**.

The same series of experiments was performed with **1d**, runs 4−6, Table 3, with similar results. In run 7, the ratio of reactants is that used by Arce de Sanabia and Carrión, but on a larger scale, and at room temperature rather than at −5 °C. Runs 8 and 9, analogous to 6 and 7, but at −5 °C, were carried out by cooling a solution of **1d** with (run 8) or without (run 9) DTBMP in 20 mL of CH_3CN, and injecting into it 4.2 mL (0.08 mmol) of a precooled, 19 mM solution of $NOBF_4$.

Reactions of 1b-e with $Th^{\bullet+}ClO_4^-$. In each case (runs 1−5, Table 2), the reactants and DTBMP were placed in a 25 mL volumetric flask, containing a stirrer bar, under N_2, and the solvent was added by syringe through the septum. Stirring was continued for 34 h (**1b**), 24 h (**1c**,**e**), 20 h (**1d**), before adding 0.2 mL of 2 M K_2CO_3, after which stirring was continued for 1 h. With **1b**,**c**, the color of $Th^{\bullet+}$ faded only slowly, becoming pale yellow on addition of K_2CO_3. With **1d**, the color of $Th^{\bullet+}$ disappeared within 2 h. With **1e**, the color of the solution became deep blue (CH_2Cl_2) and blue-green (CH_3CN) immediately, and the color persisted until K_2CO_3 was added, whereupon it changed to reddish brown.

Reaction of 2e with $Th^{\bullet+}ClO_4^-$ in CH_3CN. A solution of 54 mg (0.20 mmol) of **2e**, 126 mg (0.40 mmol) of $Th^{\bullet+}ClO_4^-$, and 103 mg (0.50 mmol) of DTBMP was prepared in the usual way. The purple color of the solution ($Th^{\bullet+}$) changed to reddish brown overnight, and this color persisted after adding K_2CO_3 solution. GC analysis gave (average of three experiments) 11.8 mmol of **2e**, 38.4 mmol of Th, and a trace of ThO. The GC trace contained also unidentifiable peaks.

Reactions of 3 and 4. The results of these reactions are listed in Table 2. For the most part, reactions of **3** were carried out in the standard way and in 25 mL of solvent. Reactions with $Th^{\bullet+}$ (runs 6−9) were rapid, the color of $Th^{\bullet+}$ disappearing within minutes. These runs were worked up (K_2CO_3) within 0.5−6.0 h. In run 8, a solution of $Th^{\bullet+}BF_4^-$ in 5 mL of CH_3CN was added slowly, dropwise to a solution of **3** and DTBMP in 20 mL of CH_3CN. In runs 11 and 12 only 10 mL of solvent was used. Stirring in runs 10−12 was continued for several hours before addition of K_2CO_3. GC analysis before addition of K_2CO_3 (run 11) gave 0.154 mmol of **3**, 0.023 mmol of 3,3-diphenylbutanone, and traces of acetophenone (**9**) and oxirane. The result in Table 2 is for GC after addition of K_2CO_3. In reaction of **4** with $Th^{\bullet+}BF_4^-$ (run 13), a solution of $Th^{\bullet+}BF_4^-$ in 10 mL of CH_3CN was added slowly, dropwise, through the septum to the stirred solution of **4** and DTBMP in 15 mL of CH_3CN. Control experiments showed that rapid addition of $Th^{\bullet+}BF_4^-$ solution caused some rearrangement of **4**.

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