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RESEARCH ARTICLE

Reactions of thianthrene cation radical with acyclic α, ω-diols: Formation of monoadducts and bisadducts. Intramolecular cyclization of monoadducts to cyclic ethers

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Reactions of thianthrene cation radical tetrafluoroborate ($Th^{\bullet+}BF_4^-$) with α, ω-diols, $HO(CH_2)_nOH$ (**4b–g**, $n = 5$, 6, 8–10, 12), at the molar ratio $Th^{\bullet+}$:**4** 2/1 in MeCN containing 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) led to formation of bisadducts, α, ω-di(5-thianthreniumoxy)alkane ditetrafluoroborates (**7b–g**). Reactions with **4b,c** gave also the cyclic ethers **6b,c** by intramolecular cyclization. Preparation of the bisadduct (**7a**) from 1,4-butanediol (**4a**) was achieved only in the absence of DTBMP, in low yield. The major product was tetrahydrofuran (THF, **6a**). Reactions of $Th^{\bullet+}BF_4^-$ with **4b–g** in the molar ratio 1/6, carried out in MeCN without DTBMP, led to the formation of monoadducts, α-hydroxy-ω-(5-thianthreniumoxy)alkane tetrafluoroborates (**5b–g**). Reactions with **4b,c** led again also to cyclic ethers **6b,c**. Cyclization of adducts to ethers (**6b,c**) was confirmed with the isolated monoadducts (**5b,c**). Attempts to prepare a monoadduct (**5a**) from **4a** were unsuccessful; only THF (**6a**) was obtained. **5b–g** and **7a–g** were characterized with ^1H and ^{13}C NMR spectroscopy. Reactions of **7b,c** with basic alumina resulted in formation of **4b,c** rather than in elimination of thianthrene oxide and formation of linear dienes.

Keywords: Thianthrene cation radical; α, ω-Diols; Cyclic ethers

1. Introduction

Reactions of thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) with alcohols were first reported by Shine and Yueh in the early 1990s [1–3]. It was recognized then that 5-alkoxythianthrenium salts (**1**) were being formed, but it was not until later that such salts were isolated, characterized and studied in detail by Zhao and Shine [4–6]. In the same decade, Shine and coworkers found that pinacols (**2**) were oxidized quantitatively by $Th^{\bullet+}$ to the corresponding ketones (**3**, equation (1)), provided that enough 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) was present to prevent acid-catalyzed pinacol rearrangement [7].

In contrast, little attention had been given to reactions of α, ω-diols, $HO(CH_2)_nOH$. Reactions of $Th^{\bullet+}ClO_4^-$ with 1,4-, 1,5-, and 1,6-alkanediols (**4**, $n = 4$–6) had, in fact, been carried out by Yueh, but in such a way as to produce only cyclic ethers (**6**) [2, 8]. It was accepted

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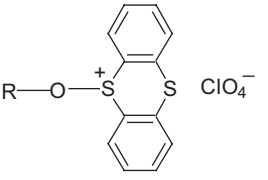

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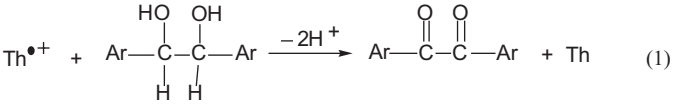


2 **3**

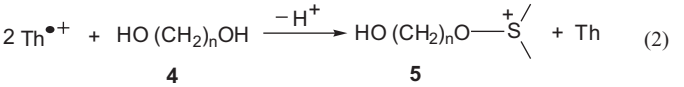
(1)

that an α-hydroxy-ω-(5-thianthreniumoxy)alkane salt (**5**) had probably been formed, but had cyclized to give **6** and thianthrene 5-oxide (ThO, scheme 1). In the present study, we have made a systematic investigation of the reactions of a number of **4** (n = 4–6, 8–10, 12) with $Th^{\bullet+}BF_4^-$. We have been able to isolate the tetrafluoroborates of the corresponding **5**, which we call monoadducts, and also the ditetrafluoroborates of the α, ω-di(5-thianthreniumoxy)alkanes (**7**), which we call bisadducts. We have found that only some of **5** (n = 4–6) undergo cyclization (scheme 1). We have studied also the reactions of **7b,c** with basic alumina and now contrast them with earlier reported reactions of adducts of alkenes and alkynes.

2. Results and discussion

2.1 *Preparation of adducts*

Whether a mono- (**5**) or bisadduct (**7**) was formed depended on the molar ratio of reactants. The stoichiometry of monoadduct formation is shown in equation (2). But, when that stoichiometry was used, formation of **7** occurred, in moderate yields. Successful preparations of **5** were achieved when a large excess of **4** was used, that is, in a molar ratio of 1/6.

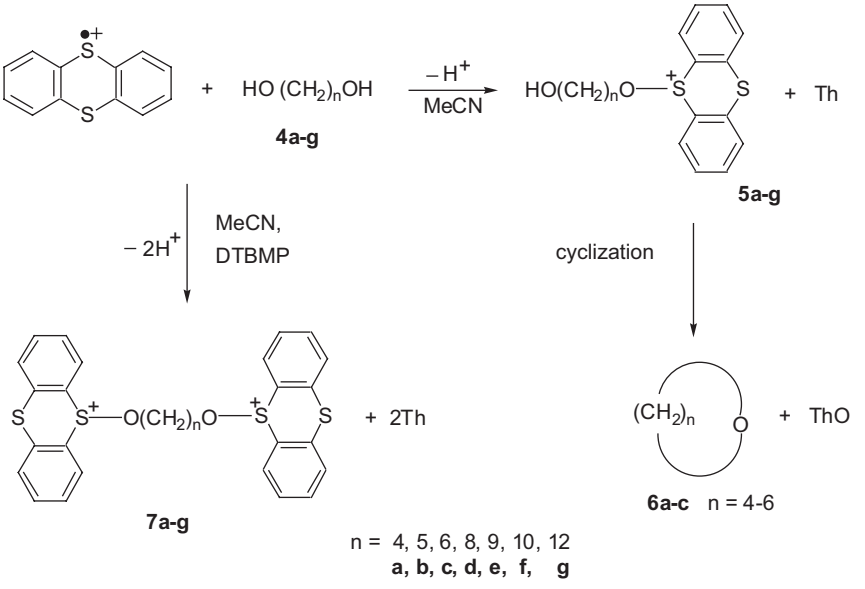


4 **5**

(2)

2.2 *Formation of bisadducts (7a–g)*

Reactions of $Th^{\bullet+}BF_4^-$ with **4b–g** in the presence of DTBMP were fast. The adducts **7b–g** were obtained as mixtures with the tetrafluoroborate of protonated DTBMP, which was removed from **7b–g** by washing with water. When **4b,c** were used, a cyclic ether (tetrahydropyran, **6b**; oxepane, **6c**) was also formed, attesting to the coincidental formation and cyclization of a monoadduct (scheme 1). Cyclic ethers were not formed in reactions of **4d–g**. Reaction of 1,4-butanediol (**4a**) under the same conditions gave only THF (**6a**) and none of **7a**. Successful preparation of **7a** was achieved in a 2/1 ratio reaction, but in the absence of DTBMP. Even so, only 7% of the $Th^{\bullet+}BF_4^-$ ended as **7a**; the greater part (85%) produced THF (scheme 1).



SCHEME 1

2.3 *Formation of monoadducts (5b–g)*

Isolation of monoadduct tetrafluoroborates was not successful in reactions containing DTBMP; attempts to remove the salt of DTBMP by washing with water caused the hydrolysis of **5**. Therefore, reactions were carried out in the absence of DTBMP and led successfully to **5b–g** (scheme 1). Cyclic ethers (**6b,c**) were obtained in addition to **5b,c** from reactions of **4b,c**. Attempts to prepare **5a** from **4a** were unsuccessful; only THF (**6a**, 87%) was obtained. All of the monoadduct tetrafluoroborates were oils except **5b** (mp 72 °C). The oils resisted all attempts at crystallization. Nevertheless, their NMR spectra were consistent with their structure.

The control of forming two types of adduct was demonstrated by converting **5d,g** into **7d,g** by reaction with an excess of $Th^{\bullet+}BF_4^-$.

2.4 *NMR spectra of 5b–g and 7a–g*

The aromatic ^1H and the ^{13}C data of each set of adducts are tabulated for clarity of presentation in tables 1–4. We present the data for bisadducts (**7a–g**) first because their identities are

Table 1. ^1H NMR data for aromatic protons in **7a–g**.

	Chemical shifts (ppm) and coupling constants (Hz)						
Multiplicity	**7a**	**7b**	**7c**	**7d**[a]	**7e**	**7f**	**7g**[a]
dd, 4H	8.36 (8.0)	8.39 (7.8)	8.39 (8.0)	8.41 (8.0)	8.41 (8.0)	8.42 (8.5)	8.42 (8.0)
dd, 4H	8.05 (8.0)	8.05 (8.3)	8.06 (8.3)	8.06 (8.3)	8.07 (8.0)	8.06 (8.0)	8.06 (8.0)
td, 4H	7.95 (7.8)	7.96 (8.0)	7.96 (7.8)	7.96 (7.8)	7.96 (7.8)	7.96 (7.8)	7.96 (7.8)
td, 4H	7.78 (7.6)	7.80 (7.8)	7.79 (7.8)	7.80 (7.8)	7.80 (7.8)	7.80 (7.8)	7.80 (7.8)

[a]Resolved as only d and t.

Table 2. ^{13}C NMR data for bisadducts **7a–g**.

	Chemical shifts (ppm)						
Assignment	**7a**	**7b**	**7c**	**7d**	**7e**	**7f**	**7g**
Th^+	137.5	137.5	137.5	137.4	137.4	137.4	137.4
Th^+quat	136.7	136.7	136.8	136.8	136.8	136.7	136.8
Th^+	135.8	135.8	135.8	135.8	135.7	135.8	135.8
Th^+	130.3	130.3	130.2	130.2	130.2	130.2	130.2
Th^+	130.3	130.3	130.2	130.2	130.2	130.2	130.2
Th^+quat	120.3	120.4	120.4	120.5	120.5	120.6	120.5
	75.3	75.9	76.4	76.7	76.7	76.8	76.8
	25.8	29.0	29.5	29.7	29.8	29.8	30.01
		21.2	24.8	29.0	29.6	29.7	29.9
				25.3	29.1	29.2	29.8
					25.4	25.5	29.3
							25.5

Note: All other peaks in each column are for CH_2 groups.

supported with elemental analyses (**7b,c,e–g**). The aromatic ^{1}H data (table 1) show consistency in coupling patterns for two equivalent thianthrenium (Th^+) groups, each of which is magnetically symmetrical. The symmetry of the adducts is seen also in the ^{13}C data (table 2), there being six aromatic peaks and complements of methylene-group peaks appropriate to the structures. Comparison of these NMR data with those of **5b–g** (tables 3 and 4) shows again the symmetry of the single Th^+ group, but the anticipated larger number of alkyl ^{13}C peaks consistent with unsymmetrical adducts. Conspicuous in the comparison are the single terminal methylene signals of **7** (ca. 76 ppm) and the two terminal methylene signals of **5** (ca. 76 ppm and 62 ppm). The difference in terminal methylene ^{13}C data is seen also in the alkyl chain ^{1}H spectra (Experimental section); That is, **7** (one triplet, ca. 4 ppm) and **5** (two triplets, ca. 4 ppm and 3.4 ppm). Thus, the NMR data of **5b–g** and **7a–g** are consistent with their structures.

2.5 *Formation of cyclic ethers*

In the earliest work with α, ω-diols in our laboratory, **6a–c** were the only products obtained. Adducts, themselves, were not found. In the present work, these ethers were again obtained, **6a** as the major product from **4a**, and **6b,c** as minor products from **4b,c**. It is evident that the monoadduct **5a**, which we were unable to isolate, must have cyclized rapidly after formation (scheme 1). In contrast, **5b** and **5c** were slower to cyclize. The cyclization was demonstrated directly with the isolated adducts. That is, a sample of **5b** stored in CD_3CN solution at room temperature cyclized completely to **6b** after 30 h; a similar solution of **5c** cyclized to **6c** partially after six days of storage. When heated at 85 °C in CD_3CN, a sample of **5c** cyclized completely

Table 3. ^{1}H NMR data for aromatic protons in **5b–g**.

	Chemical shifts (ppm) and coupling constants (Hz)					
Multiplicity	**5b**[a]	**5c**[a]	**5d**	**5e**	**5f**	**5g**[a]
dd, 2H	8.42 (8.0)	8.43 (7.5)	8.42 (8.3)	8.43 (7.8)	8.43 (8.0)	8.43 (8.0)
dd, 2H	8.07 (8.0)	8.06 (8.0)	8.07 (8.3)	8.06 (8.0)	8.06 (7.0)	8.05 (8.0)
td, 2H	7.96 (7.5)	7.96 (7.8)	7.97 (7.8)	7.96 (7.8)	7.96 (7.5)	7.95 (7.3)
td, 2H	7.80 (7.5)	7.80 (7.5)	7.80 (7.5)	7.80 (7.0)	7.80 (7.5)	7.80 (7.8)

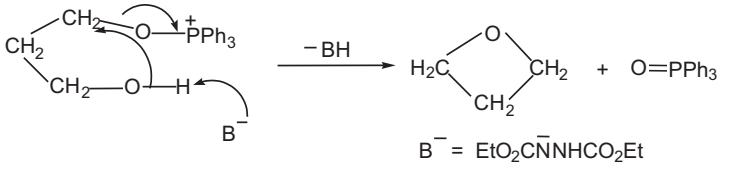
[a]Resolved as only d and t.

Table 4. ^{13}C NMR data for monoadducts **5b–g**.

	Chemical shifts (ppm)					
Assignment	**5b**	**5c**	**5d**	**5e**	**5f**	**5g**
Th^+	137.4	137.4	137.4	137.4	137.4	137.4
Th^+quat	136.8	136.7	136.8	136.7	136.7	136.7
Th^+	135.8	135.8	135.8	135.8	135.8	135.8
Th^+	130.3	130.2	130.25	130.23	130.2	130.22
Th^+	130.2	130.2	130.24	130.21	130.2	130.19
Th^+quat	120.5	120.5	120.5	120.6	120.6	120.6
	76.3	76.7	76.7	76.8	76.8	76.8
	62.0	62.3	62.5	62.6	62.6	62.6
	32.4	33.0	33.4	33.4	33.5	33.5
	29.7	29.8	29.8	29.9	30.0	30.3
	22.1	25.7	29.7	29.9	29.9	30.2
		25.4	29.3	29.8	29.8	30.2
			26.4	29.2	29.8	30.0
			25.5	26.5	29.2	29.9
				25.5	26.5	29.8
					25.5	29.3
						26.6
						25.5

Note: All other peaks in each column are for CH_2 groups.

to **6c** within 1 h. More precise rate data were not pursued. None of the other adducts (**6d–g**) could be made to cyclize, whether by storage at room temperature or by heating at 85 °C. On long heating at 85 °C in CD_3CN solution some of the larger chain length monoadducts decomposed, but we have not pursued their fate. Our observations of these cyclizations are in accord with the limited amount of information in the literature on the formation of larger cyclic alkyl ethers. The Mitsunobu reaction with α, ω-diols has been used successfully to prepare **6a–c** and also oxetane [9, 10], but the preparation of **6e** failed [10]. Apparently, cyclization of diol derivatives is inhibited by unfavorable entropy factors encountered in analogous reactions [11]. It is interesting to note the analogy between the cyclization step shown for the Mitsunobu reaction (scheme 2) [9] and the thianthreniumoxy reaction (scheme 1). The synthesis of larger cyclic ethers (C_{12} and C_{15}) was achieved with reductive desulfurization of thionolactones by organotin hydrides coupled with Ph_2SiH_2 [12] or Et_3B [13].

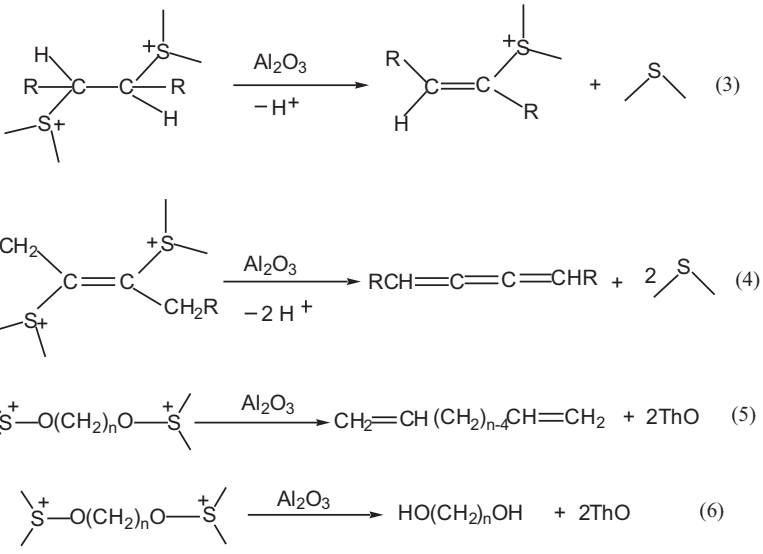


SCHEME 2

2.6 *Reactions of bisadducts (7b,c) on alumina*

Bisadducts of alkenes undergo elimination to give alkene thianthrenium salts (equation (3)) on activated basic alumina in acetonitrile [14, 15] and bisadducts of symmetrical alkynes undergo eliminations to give cumulene (equation (4)) [16]. Bisadducts of α, ω-diols, in principle, should

undergo elimination to give terminal dienes (equation (5)). But, with the use of **7b,c** in MeCN as examples, hydrolytic cleavage occurred to give respective diol and ThO (equation (6)).



3. Experimental

Solvent acetonitrile (MeCN) was dried by distillation from P_2O_5. NMR spectra were recorded in CD_3CN with a 500 MHz instrument; coupling constants (J) were averaged where necessary. DEPT was used in aiding identification of new compounds. Where the progress of a reaction was followed with NMR a 300 MHz instrument was used. Gas chromatography (GC) was carried out with an OV-101 column. All α, ω-diols and cyclic ethers were from commercial sources and were used as supplied after characterization.

3.1 *Preparation of bisadducts 7b–g*

An example is given with **7c**. $Th^{\bullet+}BF_4^-$ (500 mg, 1.65 mmol), 1,6-hexanediol (96 mg, 0.816 mmol) and DTBMP (340 mg, 1.67 mmol) were placed side by side in a three-necked flask equipped with magnetic stirrer, three-way stopcock, rubber septa, and an argon bubbler. The flask was evacuated and flushed with argon, after which 10 mL of dry MeCN was injected through a septum. The suspension was stirred and the color of the cation radical disappeared within 10–15 min. Stirring was continued for 2 h and 50 mL of ether was added to cause the precipitation of a half-white solid, which was separated by filtration. GC assay of the filtrate gave 0.0528 mmol (6.4%) of **6c**, 0.777 mmol of Th, and 0.192 mmol of ThO. The precipitated solid was a mixture of **7c** and the tetrafluoroborate salt of DTBMP, from which the DTBMP salt was removed by dissolving in 5 mL of dichloromethane and washing with 2 × 25 mL of water. The organic layer was dried over sodium sulfate and concentrated to small volume. Addition of 25 mL of ether gave 213 mg (0.294 mmol, 71%) of **7c**, mp 145–146 °C (dec). Reactions of the other diols were carried out similarly. Reaction with 1,5-pentane diol (**4b**) gave not only **7b** but also **6b** (44%). The bisadducts obtained were, with % yield and mp °C (dec): **7b**, 52, 148–149; **7d**, 70, 134–135; **7e,** 66, 132–133; **7f**, 60, 129–130; **7g**, 44, 127–128.

3.2 *Preparation of 7a*

Attempts to separate **7a** from the salt of DTBMP when the procedure described for preparing **7c** was used ended with the hydrolysis of the **7a**. Therefore the reaction of $Th^{\bullet+}$ BF_4^- (450 mg, 1.49 mmol) with **4a** (69 mg, 0.76 mmol) was carried out in 10 mL of MeCN in the absence of DTBMP and gave 18.5 mg (0.0266 mmol) of **7a** (mp 149–150 °C), representing a conversion of 7% of $Th^{\bullet+}$, and 0.630 mmol of THF, representing a conversion of 85% of $Th^{\bullet+}$.

3.3 *Conversion of mono- (5d,g) into bisadducts (7d,g)*

An example is given with **5d**. $Th^{\bullet+}BF_4^-$ (200 mg, 0.66 mmol), 53 mg (0.118 mmol) of **5d** and 130 mg (0.64 mmol) of DTBMP were placed side by side in a three necked flask with the usual set up. MeCN (5 mL) was injected and stirring was continued for 5 h. The excess of cation radical was destroyed by injecting a small amount of water. Workup as described for preparations of **7** gave 58 mg (0.0706 mmol, 60%) of **7d** whose identity was confirmed with NMR spectroscopy. Similarly, **5g** gave **7g** (71%).

3.4 *Elemental analyses*

7b. Calcd for $C_{29}H_{26}O_2S_4B_2F_8$: C, 49.17; H, 3.69; S, 18.10. Found: C, 49.41; H, 3.50; S, 18.35. **7c**. Calcd for $C_{30}H_{28}O_2S_4B_2F_8$: C, 49.88; H, 3.90; S, 17.75. Found: C, 49.80; H, 3.75; S, 17.73. **7e**. Calcd for: $C_{33}H_{34}O_2S_4B_2F_8$: C, 51.84; H, 4.48; S, 16.77. Found: C, 51.54; H, 4.39; S, 16.46. **7f**. Calcd for $C_{34}H_{36}O_2S_4B_2F_8$: C, 52.45; H, 4.66; S, 16.47. Found: C, 52.50; H, 4.52; S, 16.49. **7g**. $C_{36}H_{40}O_2S_4B_2F_8$: C, 53.60; H, 4.68; S, 15.90. Found: C, 53.61; H, 4.99; S, 16.03.

3.5 *NMR spectra (500 MHz, CD_3CN) for 7a–g*

The aromatic portions of ^1H NMR data are listed in table 1. The ^{13}C NMR data are listed in table 2. The remaining ^1H $\delta(J)$ data for aliphatic portions are as follows. **7a**: 3.84–3.81, bt, 4H; 1.27–1.22, m, 4H. **7b**: 3.88 (6.3), t, 4H; 1.27 (6.9), quint, 4H; 0.80 (7.5), quint, 2H. **7c**: 3.92, (6.3), t, 4H; 1.31 (6.3), m, 4H; 0.82 (7.3), m, 4H. **7d**: 4.00, (6.3), t, 4H; 1.42–1.39, m, 4H; 0.88, bs, 8H. **7e**: 4.01 (6.0), t, 4H; 1.44 (6.5), quint, 4H; 0.93, bs, 10H. **7f**: 4.03 (6.3), t, 4H; 1.49–1.43, m, 4H; 0.98, bs, 12H. **7g**: 4.03 (6.3), t, 4H; 1.47 (6.5), quint, 4H; 1.07, bs, 8H; 1.03, bs, 8H.

3.6 *Preparation of monoadducts 5b–g*

Monoadducts (**5b–g**) were prepared successfully from the diols **4b–g** when a reactant ratio $Th^{\bullet+}$:diol 1/6 was used. With 1,4-butanediol (**4a**) isolation of **5a** was unsuccessful and only tetrahydrofuran (**6a**, 87%) was obtained. An example of monoadduct formation is given with **5c**: 1,6-hexanediol (1.21 g, 10.2 mmol) was placed in a three-necked flask equipped with magnetic stirrer, three-way stopcock, rubber septa, and an argon bubbler. Dry MeCN (5 mL) was injected through a septum and gently heated to dissolve the diol. The solution was cooled to room temperature and 500 mg (1.65 mmol) of $Th^{\bullet+}BF_4^-$ was added to the stirred solution through a solid-addition funnel. The color of the cation radical disappeared in 5–10 min. Addition of 125 mL of ether caused the precipitation of an oily liquid from which the supernatant solution was decanted. The oily liquid was washed with ether by decantation and subjected to high-vacuum pumping to remove ether, leaving in the flask 288 mg (0.685 mmol) of **5c**,

representing 83% conversion of $Th^{\bullet+}$. The collected decanted ether solution was assayed with GC to give 0.059 mmol of **6c**, 0.843 mmol of Th, and 0.07 mmol of ThO. The amounts of **6c** and ThO are approximately the same and are consistent with the cyclization of **5c** to form **6c**. The products in total account for 97% of the $Th^{\bullet+}$ that was used. Similar reactions with other diols gave **5b** (67%) and **6b** (28%), **5d** (94%), **5e** (94%), **5f** (93%) and **5g** (92%).

3.7 *NMR spectra (500 MHz, CD_3CN) for 5b–g*

The aromatic portions of ^1H NMR data are listed in table 3. The ^{13}C NMR data are listed in table 4. The remaining ^1H $\delta(J)$ data for aliphatic portions were as follows. **5b**: 4.04, (7.3), t, 2H; 3.32 (6.3), t, 2H; 1.51 (6.8), quint, 2H; 1.26 (6.8), quint, 2H; 1.09 (6.9), quint, 2H. **5c**: 4.04, (6.3), t, 2H; 3.36 (6.5), t, 2H; 1.49 (6.8), quint, 2H; 1.29 (6.9), quint, 2H; 1.06–1.00, m, 4H. **5d**: 4.04, (6.3), t, 2H; 3.43 (6.5), t, 2H; 1.48 (6.8), quint, 2H; 1.38 (7.0), quint, 2H; 1.20–1.15, m, 2H; 1.14–1.08, m, 2H; 1.06–1.00, m, 4H. **5e**: 4.04, (6.3), t, 2H; 3.46 (6.0), t, 2H; 1.47 (6.6), quint, 2H; 1.42 (6.9), quint, 2H; 1.22 (7.1), quint, 2H; 1.15 (7.0), quint, 2H; 1.09 (7.0), quint, 2H, (slightly overlapped); 1.05–0.98, m. 4H. **5f**: 4.04, (6.0), t, 2H; 3.46 (6.0), t, 2H; 1.49–1.42, m, 4H; 1.27–1.18, m, 4H (overlapped); 1.14–1.09, m, 4H; 1.02–1.00, m, 4H. **5g**: 4.05, (6.3), t, 2H; 3.46 (6.3), t, 2H; 1.49–1.42, m, 4H; 1.30–1.14, m, 8H; 1.14–1.04, m, 4H; 1.01–0.98, bs, 4H.

3.8 *Conversion of monoadducts (5b,c) to cyclic ethers (6b,c)*

Intramolecular cyclization of monoadducts (**5b,c**) to cyclic ethers (**6b,c**) was studied separately. A solution of 12.5 mg (0.030 mmol) of **5b** in 0.75 mL of CD_3CN was placed in a NMR tube and stored at room temperature. NMR spectra were recorded at timed intervals. Complete conversion of **5b** to THP (**6b**) and ThO was seen after 30 h. A similar experiment with **5c** led to partial conversion after 6 days. When sample of the solution (**5c**) was heated at 85 °C complete conversion to oxepane (**6c**) was seen in about 1 h.

3.9 *Reaction of bisadducts (7b,c) on alumina*

A solution of 30 mg (0.042 mmol) of **7b** in 1.5 ml CD_3CN was stirred with 600 mg of activated basic alumina for 3 h. NMR spectroscopy showed that ThO and 1,5-pentanediol had been formed. A similar experiment with **7c** showed for the formation of ThO and 1,6-hexanediol.

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References

[1] H.J. Shine, W. Yueh. *Tetrahedron Lett.*, **33**, 6583 (1992).
[2] H.J. Shine. *Phosphorus, Sulfur and Silicon*, **95–96,** 429 (1994). [Report of a paper presented at the 16th International Symposium on the Organic Chemistry of Sulfur, Merseburg, Germany, 1994.]
[3] H.J. Shine, W. Yueh. *J. Org. Chem.*, **59,** 3553 (1994).
[4] W. Zhao, H.J. Shine. *Tetrahedron Lett.*, **37**, 1749 (1996).
[5] W. Zhao, H.J. Shine, B.R. Whittlesey. *J. Org. Chem.*, **62**, 8693 (1997).
[6] W. Zhao, H.J. Shine. *Can. J. Chem.*, **76**, 695 (1998).
[7] D.S. Han, H.J. Shine. *J. Org. Chem.*, **61**, 3977 (1996).
[8] W. Yueh. PhD Dissertation, Texas Tech University (1993).

[9] J.T. Carlock, M.P. Mark. *Tetrahedron Lett.*, **5,** 5153 (1978).
[10] T. Tsunoda, F. Ozaki, N. Shirakata, Y. Tamaoka, H. Yamamoto, S. Itô. *Tetrahedron Lett*., **37**, 2463 (1996).
[11] G. Illuminati, L. Mandolini. *Acc. Chem. Res*., **14**, 95 (1981).
[12] D.O. Jang, S.H. Song, D.H. Cho. *Tetrahedron*, **55**, 3479 (1999).
[13] D.O. Jang, S.H. Song, *Synlett*, 811 (2000).
[14] D.-Q. Qian, H.J. Shine, I.Y. Guzman-Jimenez, K.H. Whitmire. *J. Org. Chem.*, **67,** 4030 (2002).
[15] H.J. Shine, B.-J. Zhao, D.-Q. Qian, J.N. Marx, I.Y. Guzman-Jimenez, J.H. Thurston, T. Ould-Ely, K.H. Whitmire. *J. Org. Chem.*, **68,** 8910 (2003).
[16] H.J. Shine, P. Rangappa. J.N. Marx, D.C. Shelly, T. Ould-Ely, K.H. Whitmire. *J. Org. Chem.*, **70,** 3877 (2005).