JOC Article

Adducts of Thianthrene- and Phenoxathiin Cation Radical Tetrafluoroborates to 1-Alkynes. Structures and Formation of 1-(5-Thianthreniumyl)- and 1-(10-Phenoxathiiniumyl)alkynes on Alumina Leading to α-Ketoylides and α-Ketols

Paramashivappa Rangappa,[†] Henry J. Shine,*[,†] John N. Marx,[†] Teyeb Ould-Ely,[‡] Anna T. Kelly,[‡] and Kenton H. Whitmire[‡]

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, and Department of Chemistry, Rice University, Houston, Texas 77005

henry.shine@ttu.edu

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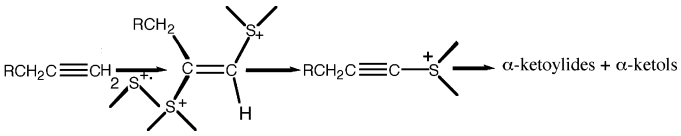

Thianthrene cation radical tetrafluoroborate ($Th^{\bullet+}BF_4^-$) added to the terminal alkynes 1-pentyne, 1-hexyne, 1-heptyne, 1-octyne, 1-nonyne, and 1-decyne to form *trans*-1,2-bis(5-thianthreniumyl)-alkene tetrafluoroborates (**1**−**6**). Similarly, addition of phenoxathiin cation radical tetrafluoroborate ($PO^{\bullet+}BF_4^-$) to the same alkynes gave 1,2-bis(10-phenoxathiiniumyl)alkene tetrafluoroborates (**7**−**12**). The trans configuration of two of the adducts (**1** and **4**) was shown with X-ray crystallography. When solutions of **1**−**6** in chloroform were stirred with activated alumina, cis elimination of a proton and thianthrene (Th) occurred with the formation of 1-(5-thianthreniumyl)alkyne tetrafluoroborates (**1a**−**6a**). Similar treatment of **8**−**12** caused elimination of a proton and phenoxathiin (PO) with formation of 1-(10-phenoxathiiniumyl)alkene tetrafluoroborates (**8a**−**12a**). Stirring of **1a**−**6a** with alumina for short periods of time caused their conversion into 5-[(α-keto)alkyl]thianthrenium ylides (**1b**−**6b**) and α-ketols, $RC(O)CH_2OH$ (**1c**−**6c**).

Introduction

Recently, we have reported that addition of thianthrene- and phenoxathiin cation radical tetrafluoroborates ($Th^{\bullet+}BF_4^-$ and $PO^{\bullet+}BF_4^-$) to symmetrical alkynes gave trans bisadducts.[1] When these adducts were treated with alumina in chloroform or acetonitrile solution, complete loss of the heterocycle (Th or PO) occurred. Cumulenes were formed and subsequently were converted in situ into α-diketones, α-hydroxyalkynes, and α-acetamidoalkynes. In continuation of our work with alkynes we have found that addition of $Th^{\bullet+}$ and $PO^{\bullet+}$ to terminal alkynes gives 1,2-bisadducts, also with trans configurations. The chemistry of the 1,2-bisadducts on alumina is quite dissimilar to that of symmetrical alkyne adducts. We report here the formation and configuration of the 1,2-bisadducts and their reactions on alumina.

SCHEME 1

R =	propyl,	butyl,	pentyl,	hexyl,	heptyl,	octyl
compound =	**1 ; 7**	**2 ; 8**	**3 ; 9**	**4 ;10**	**5 ;11**	**6 ;12**

Results and Discussion

Structure of Adducts 1−12. Reaction of $Th^{\bullet+}BF_4^-$ and $PO^{\bullet+}$ BF_4^- with all alkynes readily gave 1,2-bisaducts (**1**−**12**, Scheme 1). In all of these reactions only a bisadduct was formed; no evidence for monoadduct[2,3] formation was found. Crystals of **1** and **4** were grown successfully for X-ray crystallography, which confirmed their trans configuration. Only the ORTEP diagram of **4**

[†] Texas Tech University.
[‡] Rice University.

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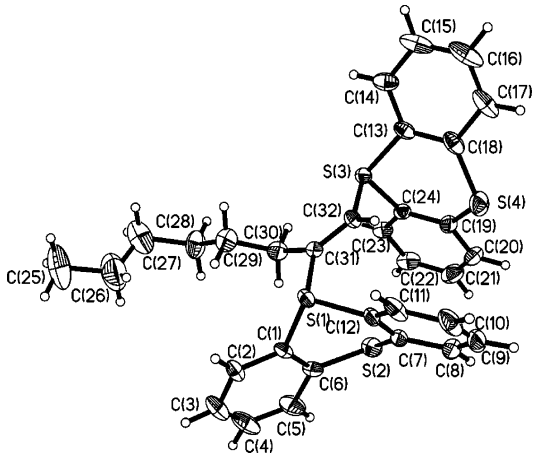


FIGURE 1. ORTEP diagram for 1,2-bis(5-thianthreniumyl)-1-octene ditetrafluroborate (**4**). The counterions and solvent of crystallization are omitted.

TABLE 1. ^{13}C NMR Data[a] for 1−6

	chemical shifts (ppm)					
assignment	**1**	**2**	**3**	**4**	**5**	**6**
C_2	148.5	148.7	148.7	148.7	148.7	148.7
Th$^+$quat	138.2	138.2	138.2	138.2	138.2	138.2
Th$^+$CH	137.1	137.1	137.1	137.1	137.1	137.1
Th$^+$CH	137.0	137.0	137.0	137.0	137.0	137.0
Th$^+$quat	136.9	136.9	136.9	136.9	136.9	136.9
Th$^+$CH	136.6	136.5	136.5	136.5	136.5	136.5
Th$^+$CH	134.9	134.9	134.9	134.9	134.9	134.9
Th$^+$CH	131.9	131.9	131.9	131.9	131.9	131.9
Th$^+$CH	131.7	131.7	131.7	131.7	131.7	131.7
Th$^+$CH	131.5	131.5	131.5	131.5	131.5	131.5
Th$^+$CH	131.4	131.4	131.4	131.4	131.4	131.4
C_1	121.2	121.2	121.2	121.2	121.2	121.2
Th$^+$quat	119.6	119.7	119.7	119.7	119.7	119.7
Th$^+$quat	116.6	116.7	116.7	116.7	116.7	116.7
	33.2	31.5	31.7	31.8	32.2	32.4
	22.0	30.2	31.7	31.7	31.8	31.8
	13.6	22.9	28.0	29.2	29.5	29.7
		13.5	22.7	28.2	29.2	29.6
			14.1	23.1	28.3	29.5
				14.2	23.2	28.3
					14.3	23.3
						14.4

[a] The last peak in each column is for the terminal CH_3 group. All other unassigned peaks are for CH_2 groups.

is shown (Figure 1). The ORTEP diagram of **1** is to be found in Supporting Information.

We deduce that the other adducts have the same configuration on the basis of the uniformity and consistency in their NMR data. For clarity of presentation pertinent NMR data are given in tabular form. The ^{13}C data for **1**−**6** (Table 1) and **7**−**12** (Table 2) show uniformly eight aromatic CH, four aromatic quaternary C atoms, the CH and quaternary C of the alkene, and the relevant CH_2 and CH_3 carbons

The aromatic ^{1}H NMR spectra of **1**−**12** were made complex by overlapping multiplets. The spectra were, for the most part, consistent in their complexity within each series and were in agreement with the structures of the adducts. The ^{1}H NMR data have not been presented in tabular form. Satisfactory elemental analyses were obtained for **2**, **4**, **5**, **6** and **8**.

Reactions of 1−12 on Alumina. When solutions of adducts were stirred with alumina, one-half of the Th$^+$ (or PO$^+$) units were eliminated. This behavior differs from that of adducts of symmetrical alkynes from which all of the heterocycle was eliminated.[1] Eliminations from **1**−**6** gave the terminally substituted alkynes **1a**−**6a**, and **8**−**12** gave **8a**−**12a**. It is evident from the structures of **1**−**12** that cis elimination occurred in the formation of **1a**−**12a** (Scheme 2).

TABLE 2. ^{13}C NMR Data[a] for 7−12

	chemical shifts (ppm)					
assignment	**7**	**8**	**9**	**10**	**11**	**12**
PO$^+$quat	153.6	153.6	153.6	153.6	153.6	153.6
PO$^+$quat	153.5	153.5	153.5	153.5	153.5	153.5
C_2	153.3	153.4	153.4	153.4	153.4	153.4
PO$^+$CH	139.3	139.3	139.4	139.4	139.4	139.3
PO$^+$CH	138.8	138.8	138.8	138.8	138.9	138.8
PO$^+$CH	133.4	133.4	133.4	133.4	133.4	133.4
PO$^+$CH	132.4	132.4	132.4	132.4	132.4	132.4
C_1	130.3	130.4	130.6	130.6	130.1	130.6
PO$^+$CH	128.8	128.8	128.6	128.8	128.8	128.8
PO$^+$CH	128.5	128.5	128.5	128.5	128.5	128.5
PO$^+$CH	121.83	121.83	121.84	121.84	121.87	121.83
PO$^+$CH	121.76	121.77	121.79	121.79	121.83	121.80
PO$^+$quat	104.4	104.4	104.5	104.5	104.5	105.0
PO$^+$quat	102.1	102.1	102.0	102.0	102.0	102.0
	32.9	31.9	32.1	31.7	32.2	32.4
	23.7	31.0	31.3	31.4	31.4	31.4
	14.1	23.3	29.7	30.0	30.1	30.0
		13.5	22.7	29.7	30.0	29.9
			14.1	23.0	29.2	29.7
				14.2	23.2	29.5
					14.4	23.3
						14.4

[a] The last peak in each column is for the terminal CH_3 group. All other unassigned peaks are for CH_2 groups.

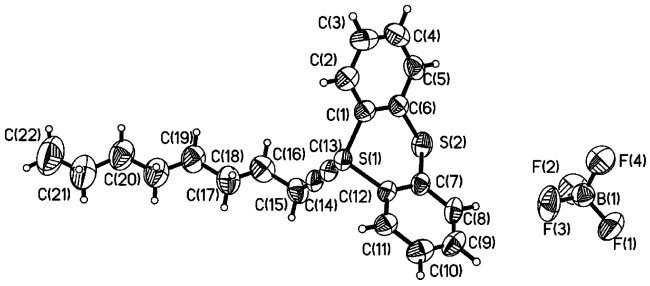
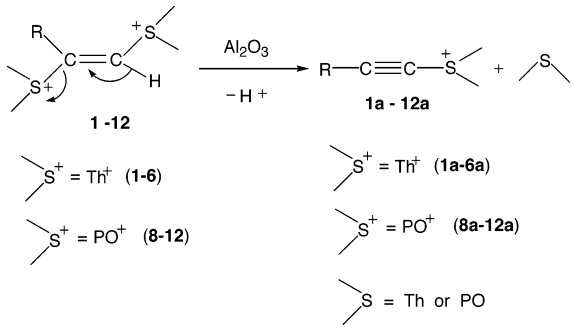


FIGURE 2. ORTEP diagram for 1-(5-thianthreniumyl)-1-decyne tetrafluroborate (**6a**).

SCHEME 2



The structure of **6a** was confirmed with X-ray crystallography (Figure 2). The structures of the remaining products were deduced with detailed NMR studies, pertinent data of which are given in tabular form. The aromatic ^{1}H data for **1a**−**6a** (Table 3) and **8a**−**12a** (Table

TABLE 3. ^{1}H NMR Data for Aromatic Protons in 1a−6a

	chemical shifts (ppm) and coupling (Hz)					
multiplicity	**1a**	**2a**	**3a**[a]	**4a**	**5a**	**6a**
dd, 2H	8.48 (8.3, 1.3)	8.48 (8.0, 1.0)	8.49 (8.0)	8.48 (8.0, 1.0)	8.49 (8.0, 1.0)	8.46 (8.0, 1.0)
dd, 2H	7.89 (7.8, 1.3)	7.90 (8.0, 1.0)	7.89 (7.5)	7.90 (8.0, 1.0)	7.90 (7.5, 1.3)	7.90 (8.0, 1.0)
td, 2H	7.75 (7.7, 1.2)	7.76 (7.8, 1.3)	7.75 (7.5)	7.76 (7.7, 1.2)	7.76 (7.7, 1.3)	7.77 (7.8, 1.5)
td, 2H	7.67 (7.5, 1.0)[b]	7.68 (7.8, 1.3)	7.68 (7.5)	7.68 (7.5, 0.5)	7.68 (7.9, 1.2)	7.67 (7.8, 1.0)

[a] Resolved as only d and t. [b] Central peak of td is seen as overlapped dd.

TABLE 4. ^{1}H NMR Data for Aromatic Protons in 8a−12a

	chemical shifts (ppm) and coupling (Hz)				
multiplicity	**8a**	**9a**	**10a**	**11a**	**12a**
dd, 2H	8.23 (8.0, 1.5)	8.23 (8.0, 1.0)	8.23 (8.0, 1.5)	8.27 (8.0, 1.5)	8.23 (8.0, 1.5)
td, 2H	7.86 (7.3, 1.3)	7.86 (8.0, 1.3)	7.86 (8.0, 1.5)	7.84 (7.3, 1.3)[a]	7.86 (7.8, 1.5)
dd, 2H	7.63 (8.5, 1.0)	7.64 (8.5, 1.0)	7.64 (8.3, 0.8)	7.61 (8.3, 1.3)	7.63 (8.5, 1.0)
td, 2H	7.55 (7.3, 1.0)[a]	7.55 (8.0, 1.3)	7.55 (7.8, 1.0)	7.58 (7.0, 1.0)[a]	7.55 (7.8, 1.5)

[a] Central peak of td is seen as overlapped dd.

TABLE 5. ^{13}C NMR Data for Aromatic and Yne Carbon Atoms in 1a−6a

	chemical shifts (ppm)					
assignment	**1a**	**2a**	**3a**	**4a**	**5a**	**6a**
Th$^+$quat	136.2	136.2	136.1	136.1	136.1	136.1
Th$^+$CH	134.5	134.5	134.5	134.5	134.5	134.6
Th$^+$CH	133.5	133.5	133.6	133.4	133.5	133.4
Th$^+$CH	130.2	130.2	130.2	130.2	130.2	130.2
Th$^+$CH	130.1	130.1	130.1	130.1	130.1	130.1
Th$^+$quat	121.0	121.0	120.1	121.0	121.0	121.0
yne	107.4	107.6	107.5	107.6	107.6	107.6
yne	54.6	54.4	54.5	54.4	54.6	54.4

TABLE 6. ^{13}C NMR Data for Aromatic and Yne Carbon Atoms in 8a−12a

	chemical shifts (ppm)				
assignment	**8a**	**9a**	**10a**	**11a**	**12a**
PO$^+$quat	152.6	152.6	152.6	152.6	152.6
PO$^+$CH	136.9	136.9	136.9	136.8	136.9
PO$^+$CH	131.4	131.4	131.3	131.7	131.4
PO$^+$CH	127.4	127.4	127.4	127.5	127.4
PO$^+$CH	120.4	120.3	120.4	120.2	120.3
PO$^+$quat	107.5	107.5	107.5	107.8	107.5
yne	110.7	110.7	110.7	110.6	110.7
yne	59.9	59.9	59.9	60.0	59.9

4) show uniformity throughout each series. The occurrence of two dd (from 1,9- and 4,6-protons) and two td (from 2,8- and 3,7-protons) in each series attests to the symmetry of the sulfonium heterocycle in each compound. This is confirmed with the ^{13}C data for the Th$^+$ (Table 5) and PO$^+$ (Table 6) rings, there being in each set of data only four CH and two quaternary carbon atoms. The difference in the sequences of the ^{1}H dd and td multiplets in the Th$^+$ and PO$^+$ series (Tables 3 and 4) has been explained earlier.[1] Satisfactory elemental analyses were obtained for **1a**, **3a**, and **5a**.

Reactions of 1a−6a on Alumina. Formation of α-Ketoylides and α-Ketols. A. Formation of α-Ketoylides. When a chloroform solution of a 1-(5-thianthreniumyl)alkyne itself was stirred with alumina for short periods of time, two products were formed: an α-ketoylide and an α-ketol. This behavior was studied with five of the terminally substituted alkynes: **1a**, **2a**, and **4a**−**6a**. The ylide (**1b**, **2b**, **4b**−**6b**), the major product, was isolated in each case. Each ylide was found with NMR spectroscopy to be a mixture of two components in an approximate ratio of 5:1, deduced to be the (*Z*)- and (*E*)-isomers. Many of the NMR signals from pairs of isomers, particularly those with shorter carbon chains (**1b**, **2b**), were sufficiently well separated to enable their distinction. An example is given with **2b** in Table 7. The major isomer is assigned the (*Z*)-configuration. The data show that the aromatic signals of the (*Z*)-assigned isomer are upfield of those of the (*E*)-assigned isomer. The reverse is true of the alkyl chain signals. Our reasoning for these assignments is that in the (*E*)-isomer the alkyl chain is shielded by the aromatic π-system and thus resonates upfield. At the same time, the ylide's singlet proton is shielded by the nearness of the enolate oxygen atom and also resonates upfield. In the (*Z*)-isomer the aromatic protons are shielded by the enolate oxygen and thus resonate upfield.

TABLE 7. ^{1}H NMR Data for Isomers of 2b

	chemical shifts (ppm) and coupling (Hz)	
multiplicity	(*Z*)-**2b**	(*E*)-**2b**
d	7.75 (7.5)[a]	7.92 (8.0, 1.0)[b]
dd	7.63 (7.3, 1.3)	7.67 (7.5, 1.5)
td	7.48 (7.6, 1.3)	7.54 (7.6, 1.2)
td	7.43 (7.5, 1.5)	7.48 (7.5, 1.3)
s	3.97	3.95
t	2.50 (7.8)	2.47 (7.5)
quint	1.79 (7.6)[c]	1.66 (7.6)[c]
sext	1.44 (7.5)	1.34 (7.6)
t	0.99 (7.3)	0.86 (7.3)

[a] The major signal was d. [b] The minor signal was dd. [c] Treated as a quintet. In each multiplet the three central signals were further split with shoulders suggestive of triplets.

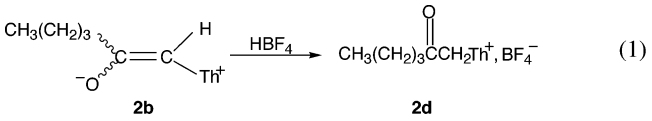
The consistency in the ^{1}H NMR data for the major (*Z*)-isomers of the four remaining ylides is shown in Table 8. Notably, the furthest downfield signal, which should be a dd in each compound, was broadened into a d; the reason is being sought. It was possible to assign the ^{13}C signals for all carbon atoms in each of the five ylides, and the data are listed in Table 9.

Although the two isomers of each ylide were seen clearly in the NMR spectra, they could not be detected separately by GC. Two ylides (**2b** and **4b**) were characterized with direct-insertion mass spectrometry. Satisfac-

TABLE 8. ^{1}H NMR Data for the Aromatic Protons of the (*Z*)-isomers

multiplicity	chemical shifts (ppm) and coupling (Hz)			
	1b	**4b**	**5b**	**6b**
d, 2H	7.75 (7..5)	7.68 (8.0)	7.76 (7.5)	7.82 (7.5)
dd, 2H	7.62 (7.3, 1.3)	7.56 (7.5, 1.5)	7.63 (7.8, 1.3)	7.56 (7.3, 1.3)
td, 2H	7.46 (7.8, 1.5)	7.40 (7.5, 1.5)	7.47 (7.5, 1.5)	7.40 (7.5, 1.5)
td, 2H	7.42 (7.5, 1.5)	7.36 (7.5, 1.3)	7.43 (7.5, 1.5)	7.36 (7.5, 1.5)

tory elemental analysis was obtained for **2b**. Confirmation of the nature of **2b** was also obtained by protonation with HBF_4-etherate, which converted **2b** into 5-[(2-keto)-hexyl]thianthrenium tetrafluoroborate (**2d**), eq 1. The



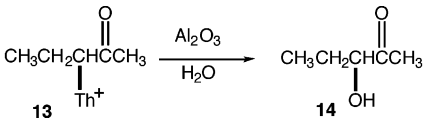
(1)

formation of 5-[(*β*-keto)alkyl]thianthrenium perchlorates by reactions of ketones with $Th^{\bullet+}ClO_4^-$ was reported from this laboratory about 30 years ago.[4–6] Reactions were deduced then and later[7] to occur by addition of $Th^{\bullet+}$ to the enolic form of the ketone. In those cases, reactions with methyl ketones, MeC(O)R, in which the group R had an enolizable H atom, e.g., 2-butanone, occurred necessarily at that enolizable position rather than at the methyl group. That means that formation of **2d**, for example, would not be possible by reaction of 2-hexanone with $Th^{\bullet+}$ BF_4^-. Consequently, the preparation of **2d** via **2a** and **2b** is unique.

Ketosulfonium ylides[8] have been described as being isolable compounds for about 40 years.[9] Their cis/trans enolate isomers were recognized quite early in that period, and Trost[10] suggested as early as 1967 that steric and electrostatic factors favored a (*Z*)- over an (*E*)-isomer. Our work with terminal alkyne adducts has led us unexpectedly through an unconventional route into this area of organic chemistry.

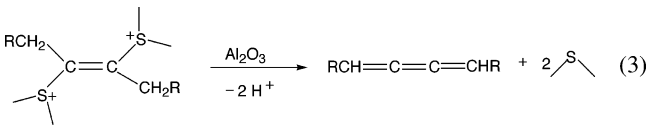
B. Formation of α-Ketols. The presence of a small amount of an α-ketol (**1c**, **4c**, and **6c**) was detected with NMR spectroscopy as a minor product in the isolated crude mixture of products of reaction in three cases (**1a**, **4a**, and **6a**). α-Ketol **6c** was isolated and its structure was confirmed by comparison of its ^{1}H and ^{13}C NMR spectra with those of an authentic sample prepared by the oxidation of 1,2-decanediol.[11] The other two α-ketols could not be isolated separately. Their structures were deduced, however, from comparisons of their NMR spectra discernible in the mixture with the corresponding ylide. That was more easily achieved with their ^{13}C spectra than with their ^{1}H spectra, most of whose signals were overlapped with signals from the ylide. The only ^{1}H signals that could be attributed with confidence to the α-ketol in a mixture were those from the terminal methylene group, $-CH_2OH$, in the region of 4.2 ppm, and the terminal methyl group in the region of 0.9 ppm, well-separated from the ylide's methyl group signal in the region of 1.0 ppm. The ^{13}C NMR data agreed well with those of authentic **4c** prepared by the oxidation of 1,2-octane diol[12] and reported data of **1c**.[13]

We attribute the formation of ylides and α-ketols to hydration reactions of **1a**–**6a** on the alumina (Schemes 3 and 4). The major hydration reaction (releasing a proton) on the basic surface of the alumina led directly to the ylide (Scheme 3). A small amount of the ylide became protonated to give a *β*-ketosulfonium ion, which underwent displacement of Th to give the α-ketol (Scheme 4). That only a small part of the ylide was protonated may be attributed to the neutralizing, basic nature of the alumina. The possibility of displacing Th from a 5-(ketoalkyl)thianthrenium ion on alumina was confirmed with the use of 5-[(2-keto)-3-pentyl]thianthrenium tetrafluoroborate (**13**), from which 3-hydroxy-2-pentanone (**14**) was obtained, eq 2.



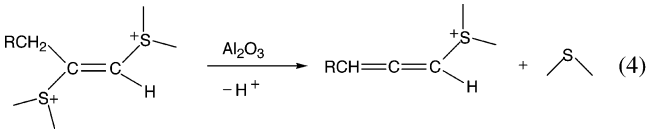
(2)

Two Classes of Adducts. Adducts of symmetrical alkynes[1] and of the present terminal alkynes each have the trans configuration. They differ in their reactions on alumina in ways that are now clear. Symmetrical adducts can readily undergo E2-type eliminations to give cumulenes (eq 3), which continue on to give the observed



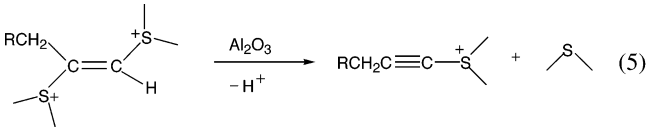
(3)

products.[1] Terminal alkynes can in principle undergo elimination to give 1-(sulfoniumyl)allenes (eq 4), but the



(4)

preferred elimination involves the more acidic terminal proton (eq 5). Once that has happened, removal of the



(5)

remaining sulfonium group (Th^+ or PO^+ in the present cases) can only occur by an unlikely substitution reaction at the alkynyl carbon atom; it cannot happen by elimina-

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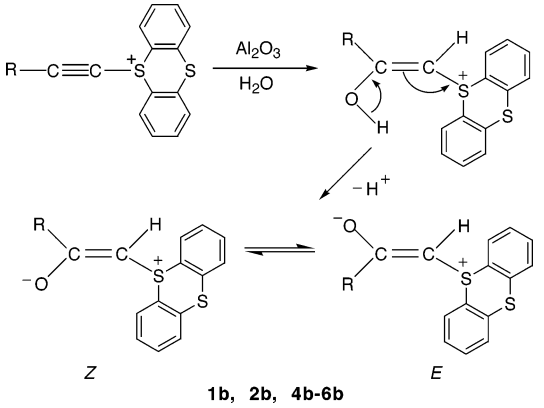
TABLE 9. ^{13}C NMR Data[a] for (*Z*)- and (*E*)-Isomers 1b−6b

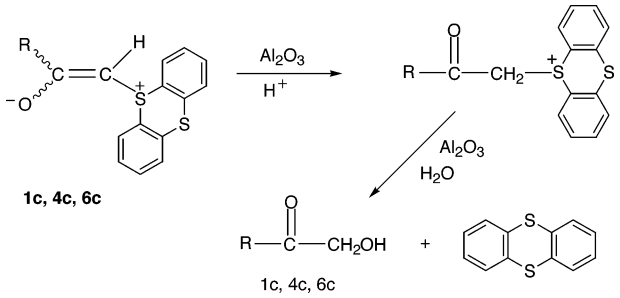
	chemical shifts (ppm)									
	1b		**2b**		**4b**		**5b**		**6b**	
	(*Z*)	(*E*)	(*Z*)	(*E*)	(*Z*)	(*E*)	(*Z*)	(*E*)	(*Z*)	(*E*)
CO	193.0	194.5	193.2	194.8	193.1	194.8	193.1	194.8	193.2	194.8
T h$^+$quat	132.5	134.8	132.6	134.9	132.6	134.8	132.6	134.8	132.6	134.9
T h$^+$CH	131.9	131.7	131.9	131.8	131.9	131.8	132.0	131.8	132.0	131.8
T h$^+$CH	130.1	130.5	130.1	130.5	130.1	130.4	130.1	130.4	130.1	130.5
T h$^+$CH	129.4	129.7	129.5	129.7	129.5	129.7	129.5	129.7	129.5	129.7
T h$^+$CH	128.4	128.9	128.4	129.0	128.4	128.9	128.4	128.9	128.4	128.9
T h$^+$quat	125.8	125.6	125.8	125.7	125.8	125.7	125.9	125.7	125.9	125.7
	49.9	*b*	49.7	*b*	49.7	*b*	49.8	*b*	49.7	*b*
	43.8	38.2	41.6	36.0	41.8	36.2	41.8	36.2	41.9	36.2
	20.6	20.9	29.5	29.8	31.8	31.7	31.9	31.7	31.9	31.8
	14.3	14.1	22.9	22.8	29.5	29.3	29.8	29.6	29.9	29.6
			14.0	13.9	27.3	27.6	29.3	29.1	29.6	29.4
					22.6	22.5	27.4	27.7	29.4	29.2
					14.1	14.0	22.1	22.6	27.4	27.6
							14.1	14.0	22.7	22.6
									14.1	14.0

[a] The last peak listed in each column is for the terminal CH_3. All other unassigned data are for CH_2 groups. [b] Signal too small to be seen.

SCHEME 3



SCHEME 4



tion. Thus, the products **1a**−**12a** are obtained in the present work.

Experimental Section

Solvent acetonitrile was dried by distillation from P_2O_5. Diethyl ether was dried over sodium. Alkynes were purchased from commercial sources. NMR spectra were recorded in a 500 MHz instrument; coupling constants (*J*) are averaged where necessary. DEPT, HMQC, HMBC, and COSY were used in aiding identification of new compounds. Gas chromatography (GC) was carried out with an OV-101 column. X-ray crystallographic data were recorded as described earlier.[1] Activated basic alumina was from the Aluminum Company of America.

Preparation of Adducts 1−12. An example is given with **1**. Thianthrene (1.00 g, 4.62 mmol) and $NOBF_4$ (0.610 g, 5.22 mmol) were placed side by side in an argon-flushed 500 mL round-bottom flask equipped with magnetic stirrer, rubber septa, and argon bubbler. Then, 25 mL of acetonitrile was injected through a septum. The solution, which turned blue immediately, was stirred for 45 min, after which 0.69 g (10.1 mmol) of 1-pentyne was added through a septum. Stirring was continued for 60 h, during which the color of the solution faded to pale yellow. Dry ether (250 mL) was added, causing the precipitation of a cream-colored solid; filtration and washing with ether gave 850 mg (1.26 mmol, 48%) of **1**, mp 229−230 °C (dec). Single crystals were grown successfully for X-ray crystallography. All other products were made with this procedure; % yield and mp °C (dec): **2**, 53, 213−214; **3**, 51, 217−218; **4**, 63, 220−222; **5**, 50, 215−216; **6**, 56, 200−201; **7**, 82, 192−193; **8**, 76, 186−188; **9**, 76, 182−183; **10**, 66, 177−178; **11**, 54, 149−150; **12**, 29, 130−132.

Elemental Analyses. 2. Calcd for $C_{30}H_{26}S_4B_2F_8$: C, 52.3; H, 3.8; F, 22.1; S, 18.6. Found: C, 52.2; H, 3.7; F, 21.6; S, 18.5. **4**. Calcd for $C_{32}H_{30}S_4B_2F_8$: C, 53.6; H, 4.2; S, 17.9; F, 21.2. Found. C, 53.5; H, 4.2; S, 18.0; F, 20.7. **5**. Calcd for $C_{33}H_{32}S_4B_2F_8$: C, 54.6; H, 4.4; F 20.8; S, 17.3. Found: C, 54.5; H, 4.3; F, 20.4; S, 17.3. **6**. Calcd for $C_{34}H_{34}S_4B_2F_8$: C, 54.9; H, 4.6; F 20.4; S, 17.2. Found: C, 55.2; H, 4.8; F, 20.3; S, 16.9. **8**. Calcd for $C_{30}H_{26}SOB_2F_8$: C, 54.9; H, 4.0; S, 9.8; F, 23.2. Found: C, 54.7; H, 3.8; S, 9.2; F, 23.

^{1}H NMR (500 MHz, CD_3CN). Only ^{1}H data δ (*J*) are given below; *J* data are averaged. ^{13}C NMR data are listed in Tables 1 and 2. **1**: 8.21 (8.0, 0.5), bd dd, 2H; 8.16 (7.8), bd d, 2H; 7.92 (8.0, 1.0), dd, 2H; 7.90−7.88, m, 4H; 7.78−7.41, m, 2H; 7.85 (7.8, 1.5), td, 2H; 7.72 (8.0, 1.5), dd, 1H overlapping 7.71 (8.0, 1.5), dd, 1H; 6.36, s, 1H; 2.48 (7. 8), t, 2H; 1.48 (7.5) sext, 2H; 0.93 (7.3), t, 3H. **2**: 8.22 (8.3), bd d, 2H; 8.16 (8.0), bd d, 2H; 7.92 (8.0, 1.0), dd, 2H; 7.89, m, 4H; 7.85 (7.8, 1.2), td, 2H; 7.77−7.74, m, 2H; 7.71 (7.6, 1.2), td, 2H; 6.34, s, 1H; 2.50 (7.5), t, 2H; 1.35−1.28, m, 4H; 0.84 (6.8), t, 3H. **3**: 8.21 (8.0), bd d, 2H; 8.16 (8.0, 1.0), dd, 2H; 7.92 (8.3, 1.3), dd, 2H; 7.89, m, 4H; 7.85 (7.6, 1.2), td, 2H; 7.78−7.74, m, 2H; 7.71 (7.8, 0.8), td, 2H; 6.33, s, 1H; 2.51 (8.0), t, 2H; 1.34−1.30, m, 2H; 1.27−1.26, m, 4H; 0.86 (7.0), t, 3H. **4**: 8.21 (8.0, 1.0), bd dd, 2H; 8.15 (8.0), bd d, 2H; 7.92 (8.0, 1.5), dd, 2H; 7.89, m, 4H; 7.85 (7.8, 1.5), td, 2H; 7.77−7.40, m, 2H; 7.71 (7.8, 1.0), td, 2H; 6.33, s, 1H; 2.51 (7.3), t, 2H; 1.34−1.30, m, 2H; 1.29−1.23, m, 4H; 1.20−1.16, m, 2H; 0.89 (7.3), t, 3H. **5**: 8.21 (8.5), bd d, 2H; 8.15 (8.0, 1.0), bd dd, 2H; 7.92 (8.0, 1.0), dd, 2H; 7.89, m, 4H; 7.85 (7.8, 1.3), td, 2H; 7.78−7.74, m, 2H; 7.71 (7.8, 0.8), td, 2H; 6.33, s, 1H; 2.51 (7.8), t, 2H; 1.93−1.33, m, 10H; 0.91 (7.3), t, 3H. **6**: 8.21 (8.0), bd d, 2H; 8.15 (8.0, 1.0), dd, 2H; 7.92 (8.0,1.0), dd, 2H; 7.90−7.88, m, 4H; 7.85 (8.0, 1.5), td, 2H; 7.77−7.74, m,

2H; 7.71 (7.6, 1.2), td, 2H; 6.33, s, 1H; 2.51 (7.8), t, 2H; 1.34−1.16, m, 12H; 0.91 (7.3), t, 3H. **7**: 7.96−7.90, m, 6H; 7.86 (8.0, 1.5), dd, 2H; 7.67 (8.5, 1.5), dd, 2H; 7.60 (8.5, 1.0), dd, 2H; 7.58−7.54, m, 4H; 6.87, s, 1H; 2.72−2.69, m, 2H; 1.34 (7.4), sext, 2H; 0.91 (7.3), t, 3H. **8**: 7.96−7.91, m, 6H; 7.87 (8.0, 1.5), dd, 2H; 7.67 (8.5, 1.0), dd, 2H; 7.60 (8.8, 1.3), dd, 2H; 7.56−7.55, m, 4H; 6.93, s, 1H; 2.74−2.70, m, 2H; 1.31 (7.1), sext, 2H; 1.24−1.18, m, 2H; 0.82 (7.3), t, 3H. **9**: 7.99−7.95, m, 4H; 7.92 (8.3, 1.3), dd, 2H; 7.89 (8.0, 1.5), dd, 2H; 7.70 (8.0, 1.0), dd, 2H; 7.63 (7.0, 1.0), dd, 2H; 7.61−7.57, m, 4H; 6.98, s, 1H; 2.75−2.72, m, 2H; 1.28−1.21, m, 6H; 0.86 (7.0), t, 3H. **10**: 7.99−7.95, m, 4H; 7.92 (8.3, 1.3), dd, 2H; 7.88 (8.0, 1.5), dd, 2H; 7.70 (8.5, 1.0), dd, 2H; 7.63, (8.0, 1.0), dd, 2H; 7.61−7.57, m, 4H; 6.99, s, 1H; 2.75−2.71, m, 2H; 1.29−1.22, m, 6H; 1.21−1.16, m, 2H; 0.91(7.3), t, 3H. **11**: 7.97−7.92, m, 4H; 7.90 (8.0, 1.5), dt, 2H; 7.86 (8.5, 1.3), dt, 2H; 7.68 (8.3, 1.3), dd, 2H; 7.60 (8.5, 1.3), dd, 2H; 7.58−7.54, m, 4H; 6.98 (2.0), d, 1H; 2.72−2.69, m, 2H; 1.31−1.17, m, 10H; 0.91 (7.3), t, 3H. **12**: 7.97−7.92, m, 4H; 7.90 (8.0, 1.0), dd, 2H; 7.86 (8.0, 1.5), dd, 2H; 7.68 (7.5), bd d, 2H; 7.60 (8.5), bd d, 2H; 7.58−7.54, m, 4H; 6.98, s, 1H; 2.72−2.69, m, 2H; 1.34−1.29, m, 2H; 1.28−1.12, m, 10H; 0.91 (7.0), t, 3H.

Preparation of 1a−6a and 8a−12a. An example is given with 1-(5-thianthreniumyl)-1-pentyne tetrafluroborate (**1a**). In a 100 mL flask were placed 850 mg (1.26 mmol) of **1**, 3.4 g of alumina, and 15 mL of chloroform. The suspension was stirred for 2 h at room temperature and filtered. The alumina was washed with 25 mL of chloroform, and the combined chloroform solution was concentrated under reduced pressure to small volume, to which was added 75 mL of ether precooled in ice. The precipitate was separated by filtration, washed with ether, and dried under vacuum to give 350 mg (0.945 mmol, 75%) of **1a**, mp 128−130 °C (dec). GC analysis of the etherate filtrate gave 1.19 mmol (95%) of Th. Similar reactions were carried with **2**−**6** and **8**−**12**; % yield, mp °C (dec), and %Th or PO: **2a**, 83, 122−123, 94; **3a**, 75, 69−70, 95; **4a**, 71, 96−97, 98; **5a**, 78, 125−126, 95; **6a**, 75, 91−92, 96; **8a**, 63, 98−99, 96; **9a**, 53, 86−88, 97; **10a**, 60, 115−116, 96; **11a**, 39, 98−99, 92; **12a**, 68, 83−84, 93.

Elemental Analyses. 1a. Calcd for $C_{17}H_{15}S_2BF_4$: C, 55.2; H, 4.08; S, 17.3. Found: C, 55.3; H, 4.07; S, 17.6. **3a**. Calcd for $C_{19}H_{19}S_2BF_4$: C, 57.3; H, 4.8; S, 16.1. Found: C, 57.0; H, 5.1; S, 15.9. **5a**. Calcd for $C_{21}H_{23}S_2BF_4$: C, 59.2; H, 5.40; S, 15.0. Found: C, 59.2; H, 5.45; S, 15.2.

NMR Data (500 MHz, $CDCl_3$) for 1a−6a, 8a−12a. The aromatic portions of the ^{1}H data are listed in the Tables 3 and 4. The ^{13}C data for aromatic and yne carbon atoms are listed in the Tables 5 and 6. The remaining ^{1}H, δ (*J*) and ^{13}C data are given below. *J* values are averaged. **1a**. ^{1}H: 2.34 (7.0), t, 2H; 1.54 (7.2), sext, 2H; 0.88 (7.3), t, 3H. ^{13}C: 21.9 (CH_2), 20.4 (CH_2), 13.3 (CH_3). **2a**. ^{1}H: 2.37 (7.0), t, 2H; 1.50 (7.4), quint, 2H; 1.28 (7.4), sext, 2H; 0.84 (7.3), t, 3H. ^{13}C: 28.7(CH_2), 21.9 (CH_2), 19.7 (CH_2), 13.2 (CH_3). **3a**. ^{1}H: 2.36 (7.0), t, 2H; 1.51 (7.0), quint, 2H; 1.23, m, 4H; 0.83 (6.8), t, 3H. ^{13}C: 30.8 (CH_2), 26.4, (CH_2), 21.8 (CH_2), 20.0 (CH_2), 13.7 (CH_3). **4a**. ^{1}H: 2.37 (7.3), t, 2H; 1.50 (7.3), quint, 2H; 1.21, m, 6H; 0.83 (7.0), t, 3H. ^{13}C: 30.8 (CH_2), 28.3 (CH_2), 26.6 (CH_2), 22.2 (CH_2), 20.0 (CH_2), 13.9 (CH_3). **5a**. ^{1}H: 2.36 (7.0), t, 2H; 1.50 (7.3), quint, 2H; 1.21, m, 8H; 0.85 (7.0), t, 3H. ^{13}C: 31.4 (CH_2), 28.6 (CH_2), 28.3 (CH_2), 26.7 (CH_2), 22.4 (CH_2), 20.0 (CH_2), 14.0 (CH_3). **6a**. ^{1}H: 2.36 (7.3), t, 2H; 1.50 (7.3), quint, 2H; 1.94−1.25, m, 10 H; 0.87 (7.3), t, 3H. ^{13}C: 31.6 (CH_2), 28.9 (CH_2), 28.7 (CH_2), 28.6 (CH_2), 26.7 (CH_2), 22.5 (CH_2), 20.0 (CH_2), 14.0 (CH_3). **8a**. ^{1}H: 2.37 (7.3), t, 2H; 1.48 (7.5), quint, 2H; 1.25, (7.7), sext, 2H; 0.82 (7.5), t, 3H. ^{13}C: 28.6 (CH_2), 21.8 (CH_2), 19.8 (CH_2), 13.2 (CH_3). **9a**. ^{1}H: 2.36 (7.3), t, 2H; 1.49 (7.3), quint, 2H; 1.20, m, 4H; 0.81 (6.8), t, 3H. ^{13}C: 30.7 (CH_2), 26.3 (CH_2), 21.7 (CH_2), 20.0 (CH_2), 13.7 (CH_3). **10a**. ^{1}H: 2.36 (7.3), t, 2H; 1.48 (7.0), quint, 2H; 1.19, m, 6H; 0.82 (6.8), t, 3H. ^{13}C: 30.8 (CH_2), 28.2 (CH_2), 26.6 (CH_2), 22.2 (CH_2), 20.0 (CH_2), 13.8 (CH_3). **11a**. ^{1}H: 2.36 (7.3), t, 2H; 1.49 (7.1), quint, 2H; 1.22, m, 8H; 0.85 (7.0), t, 3H. ^{13}C: 31.4 (CH_2), 28.6, (CH_2), 28.3 (CH_2), 26.6 (CH_2), 22.4 (CH_2), 20.0 (CH_2), 14.0 (CH_3). **12a**. ^{1}H: 2.36 (7.3), t, 2H; 1.48 (7.3), quint, 2H; 1.23, m, 10H; 0.86, (7.3), t, 3H. ^{13}C: 31.6 (CH_2), 28.9, (CH_2), 28.6 (2 CH_2), 26.6 (CH_2), 22.5 (CH_2), 20.0 (CH_2), 14.0 (CH_3).

Reaction of 1a, 2a, and 4a−6a on Alumina. Isolation of α-Ketothianthrene Ylides. Method A. A mixture of 0.450 g (1.22 mmol) of **1a** and 50 mL of chloroform was stirred with 11 g of alumina for 1 h at room temperature. The combined chloroform filtrate and washing (20 mL) was concentrated to a small volume to which was added 5 mL of cold acetonitrile to precipitate Th. The filtered MeCN solution was concentrated under reduced pressure, and the residue was triturated three times with warm hexane. The hexane solution (75 mL) was concentrated to 10 mL, which at room temperature overnight deposited 45 mg (0.166 mmol, 13%) of crystalline **1b**, mp 129−130 °C. The product was shown with NMR spectroscopy to contain two components. Similar treatment of **2a** gave **2b**, 19%, mp 109−110 °C; **5a** gave **5b**, 7%, 99−100 °C.

Method B. The same procedure was applied to **4a** and **6a**, to obtain the residue from concentrating the MeCN solution of product. Thereafter, the residue was dissolved in a small amount of chloroform and loaded onto a column of activated alumina. Elution with hexane containing 2% of ethyl acetate removed Th. Elution with hexane containing 10% ethyl acetate gave the ylide, which was recrystallized from hexane. In this way was obtained **4b**, 10%, mp 104−105 °C, and **6b**, 10%, mp 78−79 °C.

NMR Spectra (500 MHz, $CDCl_3$) for 1b, 2b, and 4b−6b. ^{1}H and ^{13}C spectra showed the presence of two components, the (*E*)- (minor), and (*Z*)- (major) isomers. In the ^{1}H spectra, the downfield aromatic signals were well separated as dd. In the upfield region there was some overlapping of two sets of td. Nevertheless, in the upfield aromatic region the two major td of the (*Z*)-isomer were clearly characterized. Therefore it was possible to tabulate (Table 8) the major aromatic signals of the five ylides. All of the minor isomer's aromatic signals were downfield from the corresponding major isomer's signals. Among the alkyl ^{1}H signals it was possible to differentiate the signals from the two CH (ylide) protons and the two terminal CH_3 groups. Some other signals, particularly in the smaller chains of **1b**, **2b**, were also reasonably well separated.

The aromatic ^{1}H proton data δ (*J*) of (*E*)-isomers and all other nontabulated data for **1b** and **4b**−**6b** are given below. All ^{1}H signals from the isomer **2b** were sufficiently well discernible that they are listed in Table 7 to show their downfield-upfield relationship. The ^{13}C signals of the two isomers were clearly assignable based on peak height. They are tabulated, for clear presentation, in Table 9. Two features of each ^{1}H and ^{13}C spectrum were noted. The most downfield aromatic ^{1}H signals in each (*Z*)-isomer were broadened into a doublet instead of dd. The carbonyl carbon peak of each (*Z*)-isomer was also broadened.

(*Z*)-**1b**: 4.0, s, 1H; 2.48 (7.8), t, 2H; 1.83 (7.5), sext, 2H.; 1.08 (7.3), t, 3H. (*E*)-**1b**: 7.90 (8.0, 1.5), dd, 2H; 7.66 (7,8, 1.3), dd, 2H; 7.53 (7.6, 1.3), td, 2H; 7.47, m, 2H overlapped with (*Z*)-**1b**; 3.97, s, 1H; 2.45 (8.0), t, 2H, partly overlapped with (*Z*)-**1b**; 1.70 (7.5), sext, 2H; 0.92 (7.5), t, 3H. (*Z*)-**4b**: 3.90, s, 1H; 2.43 (7.3), t, 2H; 1.73 (7.6), quint, 2H; 1.42−1.37, m, 2H; 1.32−1.28, m, 4H; 0.86 (7.3), t, 3H. (*E*)-**4b**: 7.85 (8.0, 1.5), dd, 2H; 7.60 (7.8, 1.3), dd, 2H; 7.47 (7.6, 1.3), td, 2H; 7.42, m, 2H overlapped with (*Z*)-**4b**; 3.89, s, 1H; 2.40 (7.5), t, 2H, partly overlapped with (*Z*)-**4b**; 1.60 (7.4), quint, 2H; 0.73 (7.3), t, 3H; other peaks were poorly defined. (*Z*)-**5b**: 3.97, s, 1H; 2.50 (7.5), t, 2H; 1.80 (7.5), quint, 2H; 1.49−1.43, m, 2H; 1.41−1.36, m, 2H; 1.34−1.31, m, 4H; 0.91 (7.0), t, 3H. (*E*)-**5b**: 7.92 (8.0, 1.5), dd, 2H; 7.67 (7.8, 1.3), dd, 2H; 7.55 (7.6, 1.2), td, 2H; 7.49, m, 2H overlapped with (*Z*)-**5b**; 3.96, s, 1H; 2.47 (8.0), t, 2H overlapped with (*Z*)-**5b**; 0.80 (7.0), t, 3H; other multiplets were poorly defined. (*Z*)-**6b**: 3.90, s, 1H; 2.43 (7.8), t, 2H; 1.73 (7.5), quint, 2H; 1.41−137, m, 2H; 1.34−1.19, m, 8H; 0.83 (6.8), t, 3H. (*E*)-**6b**: 7.85 (8.0, 1.0), dd, 2H; 7.60 (7.5, 1.0), dd, 2H; 7.48

(7.5, 1.2), td, 2H; 7.42, m, 2H overlapped with (*Z*)-**6b**; 3.89, s, 1H; 2.40 (7.5), t, 2H; 0.75 (7.3), t, 3H; other peaks were poorly defined.

Mass Spectroscopy of Ylides. 2b: 315 (M + 1; 100), 229 (M − 113; 5), 216 (M − 98; 60), 184 (M − 130; 10). **4b**: 343 (M + 1; 30), 325 (M − 17; 90); 229 (M − 113; 45), 216 (M − 126; 100), 183 (M − 159; 35).

Elemental Analyses. 2b. Calcd for $C_{18}H_{18}S_2O$: C, 68.7; H, 5.76; S, 20.4 Found: C, 68.3, H, 5.47, S, 20.2.

Reactions of 1-(5-Thianthreniumyl)alkynes on Alumina. A. Isolation of 6c from 6a. A solution of 200 mg (0.454 mmol) of **6a** in 20 mL of chloroform was stirred with 4 g of alumina for 3 h. After filtration and washing the alumina with chloroform the combined chloroform solutions was reduced to small volume and loaded onto a silica gel column. Th was eluted with hexane. Continued elution with hexane/ethyl acetate 9/1 gave a small amount of product containing some Th. Preparative TLC on silica gel plates gave 4.5 mg of yellow oil, shown with NMR spectroscopy to be 1-hydroxy-2-decanone (**6c**). ^{1}H NMR, δ (*J*): 4.23 (3.0), d, 2H; 3.11, b s, (OH), 2.41 (7.5), t, 2H; 1.63 (7.5), quint, 2H; 1.29−1.26, m, 10H; 0.88 (7.0), t, 3H. ^{13}C: 209.9 (C=O), 68.1 (−CH_2OH), 38.4 (−CH_2C=O), 31.8 (CH_2), 29.23 (CH_2), 29.19 (CH_2), 29.06 (CH_2), 23.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3). **6c** was prepared by oxidation of 1,2-decanediol[11] and had ^{1}H and ^{13}C NMR spectra agreeing with the spectra of isolated **6c**.

B. Identification of 1c and 4c. Attempts to isolate **1c** and **4c** were unsuccessful. Each was identified by NMR spectroscopy in a mixture with the corresponding ylide, however. Thus, as described in the isolation of **4b**, part of the residue obtained from concentrating the MeCN solution was dissolved in $CDCl_3$. The NMR spectrum showed the dominant presence of **4b** and smaller peaks assignable to **4c**. In the ^{1}H spectrum these peaks were at 4.2 ppm (-CH_2OH) and 0.86 (J = 6.8) ppm (CH_3). The remaining ^{1}H signals were merged with those of **4b**. ^{13}C: 68.0, 38.4, 31.4, 28.9, 23.5, 22.3,13.9. The assigned signals were in agreement with those of **4c** prepared by oxidation of 1,2-octanediol.[12] Similar treatment of **1a** gave ^{1}H and ^{13}C NMR evidence for the presence of **1c**. ^{1}H: 4.21; 0.93 (7.3). ^{13}C: 68.1, 40.1, 17.0, and 13.7. The ^{13}C data agreed with those reported by Matsumoto et al.; ^{1}H NMR data were not reported.[13]

Conversion of 2b into 2d. To a solution of 10.5 mg (0.033 mmol) of **2b** in 2 mL of chloroform was added 4 μg (0.029 mmol) of HBF_4. A white precipitate formed and was recovered, giving 8.5 mg (0.027 mmol, 82%) of **2d**, mp 178−180 °C (dec). ^{1}H NMR, $CDCl_3$, δ (*J*): 8.15 (8.0, 1.0), dd, 2H; 7.92 (8.0, 1.0), dd, 2H; 7.79 (7.5, 1.5), td, 2H; 7.68 (7.6, 1.3), td, 2H; 4.84, s, 2H; 2.42 (7.5), t, 2H; 1.43 (7.5), quint, 2H; 1.20 (7.5), sext, 2H; 0.82 (7.5), t, 3H. ^{13}C: 207.7 (−C=O), 137.7 (quat), 135.5 (CH), 135.4 (CH), 131.2 (CH), 130.5 (CH), 118.0 (quat), 52.0 (CH_2), 41.5 (CH_2), 25.7 (CH_2), 22.5 (CH_2, 13.9 (CH_3).

Preparation of 5-[(2-Keto)-3-pentyl]thianthrenium Tetrafluroborate (13). A solution of $Th^{\bullet+}BF_4^-$ in 10 mL of MeCN was prepared in situ from 250 mg (1.16 mmol) of Th and 150 mg (1.28 mmol) of $NOBF_4$. To the stirred solution was added 150 mg (1.74 mmol) of 2-pentanone. The blue color of the solution faded to pale yellow during 1 h. Ether was added, causing the precipitation of 165 mg (0.42 mmol, 36%) of **13**. ^{1}H NMR, $CDCl_3$, δ (*J*): 8.16 (7.8, 1.3), dd 1H; 8.09 (8.0, 1.0), dd, 1H; 7.97 (8.3, 1.3), dd, 1H; 7.90 (7.8, 1.3), dd,1H; 7.85 (7.3, 1.0), td, 1H; 7.76 (7.7, 1.3), td, 1H; 7.71 (7.7, 1.2), td, 1H; 7.67 (7.8, 1.3), td, 1H; 5.673 (5.0) and 5.665 (5.0), overlapping d, 1H; 2.23−2.16, m, 1H; 2.15, s, 3H; 1.43−1.39, m, 1H; 0.94 (7.5), t, 3H. ^{13}C: 203.5 (−C=O), 138.5 (quat), 137.6 (quat), 136.5 (CH), 136.0 (CH), 135.8 (CH), 135.3 (CH), 131.6 (CH), 131.4 (CH), 130.9 (CH), 130.4 (CH), 118.3 (quat), 115.8 (quat), 67.4 CH), 28.5 (CH_2), 21.6 (CH_2), 9.0 (CH_3).

Conversion of 13 into 3-Hydroxy-2-pentanone (14). A solution of 30 mg (0.077 mmol) of **13** in 2 mL of $CDCl_3$ containing 5 μL of added water was stirred with 600 mg of alumina for 3 h. NMR spectroscopy showed that Th had been formed. The remaining signals were deduced to be those of **14**. Water was added deliberately in this control experiment, rather than relying on adventicious water in solvent, to ensure complete and quicker reaction. ^{1}H NMR, δ (*J*): 4.18 (6.5, 4.4), dt, 1H; 3.47 (5.0), d, (OH); 2.20, s, 3H; 1.96−1.88, m, 1H; 1.68−1.60, m, 1H; 0.95 (7.5), t, 3H. ^{13}C: 209.9 (−C=O), 77.6 (CH), 26.5 (CH_2), 25.2 (CH_3), 8.2 (CH_3).

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Supporting Information Available: X-ray crystallographic information data for compounds **1**, **4**, and **6a** in CIF format and ORTEP diagram (Figure S1) for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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