JOC Article

Adducts of Thianthrene- and Phenoxathiin Cation Radical Salts with Symmetrical Alkynes. Structure and Formation of Cumulenes on Alumina Leading to α-Diketones, α-Hydroxyalkynes, and α-Acetamidoalkynes

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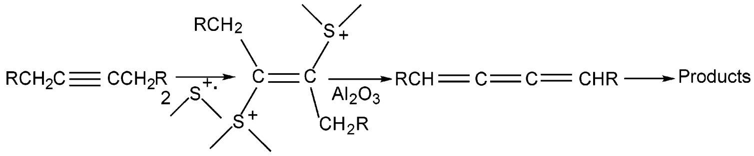
Received January 31, 2005



Thianthrene cation radical tetrafluoroborate ($Th^{\bullet+}BF_4^-$) added to 2-butyne, 3-hexyne, 4-octyne, and 5-decyne in MeCN to form trans bisadducts $R(Th^+)C{=}C(Th^+)R$, where R = Me, Et, Pr, Bu (**7a**−**d**). Phenoxathiin cation radical tetrafluoroborate ($PO^{\bullet+}BF_4^-$) added similarly to the last three alkynes to form adducts $R(PO^+)C{=}C(PO^+)R$, **8b**−**d**. Cyclic monoadducts were not found. The trans structures of **7** and **8** were deduced with X-ray crystallography (**7c**) and NMR spectroscopy. When solutions of adducts in $CHCl_3$ and MeCN were deposited on activated alumina, elimination of thianthrene (Th) and phenoxathiin (PO) occurred almost quantitatively. Detailed studies with (**7b**−**d**) indicated that a cumulene (**15**) was formed by the elimination of Th and that **15** was subsequently converted into small amounts of other products. In $CHCl_3$, these products were the respective alkyne, thianthrene 5-oxide, an α-diketone (**11**), an α-hydroxyalkyne (**12**), and hydrogen. The same products were formed in MeCN along with an α-acetamidoalkyne (**13**). The formation of **15** and products derived from it is explained and was confirmed by preparation and reactions of 2,3,4-hexatriene.

Introduction

Some years ago, the addition of thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) and phenoxathiin cation radical perchlorate ($PO^{\bullet+}ClO_4^-$) to some alkynes was reported from this laboratory.[1] Adducts were characterized with 100 MHz ^1H NMR spectroscopy and elemental analysis, and the data indicated that alkene disulfonium perchlorates had been formed, of which those with symmetrical alkynes are shown here (**1**, **2**). At that time, the configuration (cis or trans) of addition to the triple bond was not determined, and no further work was carried out on the adducts. In more recent times, we have reported extensively on the stereospecific addition of $Th^{\bullet+}$ and $PO^{\bullet+}$ salts to alkenes and cycloalkenes and on the chemistry of those adducts.[2−4] With alkenes and cycloalkenes, $Th^{\bullet+}$ gave both cyclic monoadducts (**3**) and acyclic bisadducts (**4a**). On the other hand, $PO^{\bullet+}$ salts gave only bisadducts (**4b**). Each class of adducts underwent elimination reactions when their solutions were deposited on a bed of activated alumina, with the formation of salts of (5-thianthreniumyl)- and (10-phenoxathiiniumyl)alkenes (**5a** and **5b**, respectively). These findings prompted us to return to additions to alkynes. We were interested, particularly, in finding if cyclic monoadducts (**6**) of $Th^{\bullet+}X^-$ could be found and in establishing the configuration of acyclic bisadducts. Moreover, we were interested in discovering what type of reactions would occur on alumina.

We now report the addition of $Th^{\bullet+}BF_4^-$ to 2-butyne, 3-hexyne, 4-octyne, and 5-decyne and the addition of $PO^{\bullet+}BF_4^-$ to the last three of these alkynes. We report

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† Texas Tech University.

‡ Rice University.

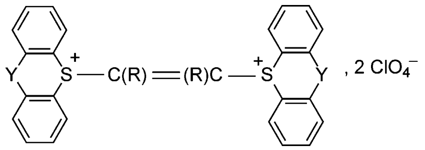
(1) Shine, H. J.; Bandlish, B. K.; Mani, S. R.; Padilla, A. G. *J. Org. Chem.* **1979**, *44*, 915−917.

(2) Qian, D.-Q.; Shine, H. J.; Guzman-Jimenez, I. Y.; Whitmire, K. H. *J. Org. Chem.* **2002**, *67*, 4030−4039.

(3) Shine, H. J.; Zhao, B.; Qian, D.-Q.; Marx, J. N.; Guzman-Jimenez, I. Y.; Thurston, J. H.; Ould-Ely, T.; Whitmire, K. H. *J. Org. Chem.* **2003**, *68*, 8910−8917.

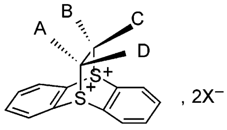
(4) Shine, H. J.; Zhao, B. J.; Marx, J. N.; Ould-Ely, T.; Whitmire, K. H. *J. Org. Chem.* **2004**, *69*, 9255−9261.

10.1021/jo050198b CCC: $30.25



1 a-c, Y = S ; R = (**a**) H, (**b**) Me, (**c**) Ph

2 a, Y = O ; R = Ph



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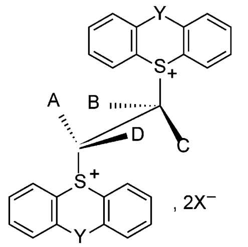
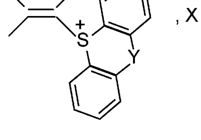
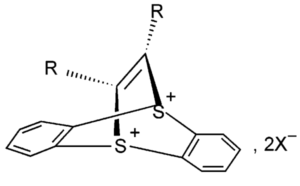


4a, Y = S
4b, Y = O



5a, Y = S
5b, Y = O



6

also the novel products of reaction of the bisadducts of these alkynes when they are deposited on alumina.

Results and Discussion

Structure of Adducts. We have found no evidence of the formation of cyclic monoadducts such as **6**. Only bisadducts **7a**−**d** and **8b**−**d** were formed. As noted earlier,[1] these reactions were very slow in comparison with additions to alkenes, taking many hours to go to completion. The adducts have the trans configuration.

This is shown in Figure 1, the ORTEP diagram for **7c**. We deduce that the other adducts have the same configuration on the basis of the conformity of their NMR data. These are shown in tabular form for clarity of presentation (Tables 1−4). The ^{1}H and ^{13}C signals in the series **7a**−**d** (Tables 1 and 2) have a uniformity that suggests that all adducts have the same symmetry, the symmetry shown in the ORTEP diagram of **7c**. In the ^{1}H NMR spectra, this symmetry results in two sets of dd for the 1,9- and 4,6- protons and two sets of td for the 2,8- and 3,7- protons of the two equivalent thianthrenium groups (Table 1). The ^{13}C data show a similar uniformity for the aromatic and double-bond signals. The uniformity in chemical shifts is striking. That there are only two quaternary and four CH carbon atom signals attests to the equivalence of the two thianthrenium groups and to the similarity in structures throughout the series.

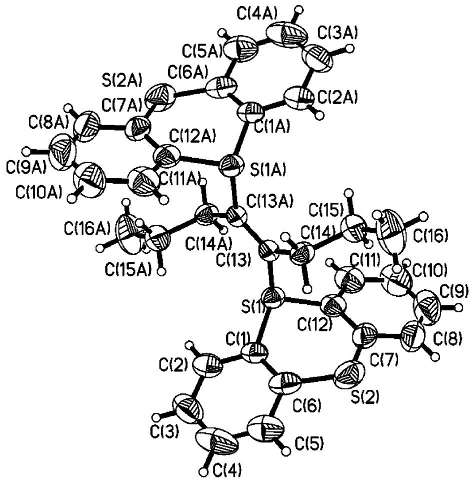


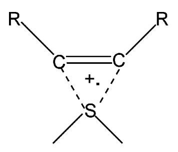
FIGURE 1. ORTEP diagram for 4,5-bis(5-thianthreniumyl)-4-octene ditetrafluoroborate (**7c**). The counterions and solvent of crystallization are omitted.

Uniformity of the ^{1}H and ^{13}C portions of the aromatic and double-bond signals is again seen in the adducts of PO$^{\bullet+}$ (Tables 3 and 4). Among the ^{1}H signals from these adducts, the two td seen in the thianthrenium spectra are not seen in the phenoxathiinium spectra. The complete center-peak overlap that occurs in the coupling of the 2,8- and 3,7- protons with their neighbors in the thianthrenium rings no longer occurs in the phenoxathiinium rings. Instead, incomplete overlap occurs and appears as two overlapping d. Consequently, the signals from these rings appear as six dd.

A notable difference between the ^{1}H spectra of series **7** and series **8** is that the furthest downfield signals in the **8** series come from either the 2,8- or 3,7- protons rather than, as seen in the **7** series, the 1,9- or 4,6- protons. We have made assignment of the aromatic ^{1}H and ^{13}C NMR signals with the help of HMQC and HMBC and with the assumption that in **7a**−**d** and **8b**−**d** the furthest downfield ^{1}H signals will be those from protons at which charge delocalization occurs. An example of the results for **7b** and **8b** is shown in Figure 2.

In both series, the far-downfield ^{13}C signal from the double-bond C atoms, established with HMBC, is notable and is enhanced in the **8** series by the electronegativity of the oxygen atom in each PO$^+$ group.

We were unable to grow crystals of **8b**−**d** suitable for X-ray crystallography. Therefore, we relied on elemental analyses for their composition and on the analogy of their NMR spectra with those of **7a**−**d** for the diagnosis of their trans configuration. Trans configurations require that an intermediate is formed by the addition of the first cation radical to the triple bond, whose structure will control the trans approach of the second cation radical. That intermediate may be a thiirenium ion radical (**9**) or an open distonic radical ion of preferred configuration (**10**).



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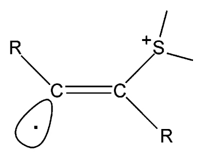

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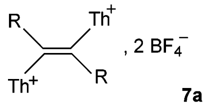
Reactions on Alumina. When solutions of **7b**−**d** and **8b**−**d** in MeCN and CHCl$_3$ were placed on alumina, Th and PO, respectively, were formed almost quantitatively. This behavior was strikingly different from that of bisadducts (**4**) of alkenes, in which only half of the adducts' sulfonium groups is eliminated, eq 1. Most of

TABLE 1. Aromatic[a] ^{1}H NMR Data for 7a−d



7a, R = Me ; **7b,** R = Et ; **7c,** R = Pr ; **7d,** R = Bu

multiplicity	chemical shifts (ppm) and coupling (Hz)			
	7a	**7b**	**7c**	**7d**
dd, 4H	8.18 (8.5, 1.5)	8.17 (8.3, 1.3)	8.16 (8.0, 1.0)	8.19 (8.0, 1.0)
dd, 4H	7.92 (8.0, 1.5)	7.95 (8.0, 1.5)	7.99 (8.0, 1.0)	7.98 (8.0, 1.0)
td, 4H	7.85 (7.5, 1.2)	7.87 (7.8, 1.0)	7.88 (7.9, 1.2)	7.90 (7.8, 1.0)
td, 4H	7.71 (7.5, 1.3)	7.72 (7.8, 1.5)	7.73 (7.8, 1.5)	7.75 (7.8, 1.3)

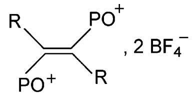
[a] Data for other H atoms are in the Experimental Section.

TABLE 2. ^{13}C NMR Data for 7a−d

assignment	chemical shifts (ppm)			
	7a	**7b**	**7c**	**7d**
C=C	142.2	148.3	146.8	147.2
Th$^+$quat	138.6	138.7	138.6	139.4
Th$^+$ CH	136.6	136.7	136.7	137.3
Th$^+$ CH	136.4	136.1	136.0	136.7
Th$^+$ CH	132.0	132.2	132.2	132.9
Th$^+$ CH	131.0	131.5	131.5	133.2
Th$^+$quat	119.1	118.0	a	119.2
	23.2[b]	29.2[c]	36.9[c]	35.8[c]
		14.4[b]	34.4[c]	33.0[c]
			13.9[b]	23.7[c]
				14.0[b]

[a] Covered by solvent CD_3CN. [b] CH_3 group. [c] CH_2 group.

TABLE 3. Aromatic[a] ^{1}H NMR Data for 8b−d

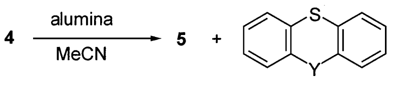


8b, R = Et ; **8c,** R = Pr ; **8d** , R = Bu

multiplicity	chemical shifts (ppm) and coupling (Hz)		
	8b	**8c**	**8d**
dd, 2H[b]	8.04 (7.5, 1.5)	8.02 (7.3, 1.3)	8.023 (7.0, 1.3)
dd, 2H[b]	8.02 (7.5, 1.3)	8.01 (7.5, 1.5)	8.016 (7.0, 1.3)
dd, 4H	7.83 (8.0, 1.5)	7.79 (8.0, 1.5)	7.78 (8.5, 1.3)
dd, 4H	7.74 (8.0, 1.3)	7.73 (8.3, 1.3)	7.72 (8.5, 1.0)
dd, 2H[b]	7.61 (7.5, 1.0)	7.58 (7.5, 1.0)	7.59 (7.0, 1.0)
dd, 2H[b]	7.59 (7.0, 1.3)	7.57 (7.0, 1.0)	7.58 (7.5, 1.0)

[a] Data for other H atoms are in the Experimental Section. [b] Total integration was for 4H but has been divided for two signals clearly overlapped in the central portion.

our explorations of the reactions of the alkyne adducts were carried out with **7b−d**.



(1)

Each of these adducts gave small amounts of five products in addition to the large amount of Th when solutions in $CHCl_3$ were used. The products were thianthrene 5-oxide (ThO), the respective alkyne, an α-diketone (**11**), an α-hydroxyalkyne (**12**), and H_2. They were identified with GC, NMR, and comparison with authentic compounds, some of which (**11b**,**c** and **12b**,**c**) were prepared for that purpose. The surprising product, H_2, was identified with GC and assayed by measuring the increase its formation caused in the headspace pressure of a sealed reaction flask; a calibrated sensor was used for the assays. Reaction on alumina under MeCN gave not only the products listed but yet another, an α-acetamidoalkyne (**13**). The α-acetamidoalkynes (**13a−c**) were isolated and identified with NMR and mass spectrometry (MS, **13c**) and high-resolution mass spectrometry (HRMS, **13a**,**b**).

TABLE 4. ^{13}C NMR Data for 8b−d

assignment	chemical shifts (ppm)		
	8b	**8c**	**8d**
PO$^+$quat	153.2	153.2	153.2
C=C	151.5	150.3	150.3
PO$^+$ CH	139.5	139.6	139.6
PO$^+$ CH	133.2	133.1	133.1
PO$^+$ CH	128.8	128.8	128.8
PO$^+$ CH	122.1	122.1	122.1
PO$^+$quat	100.1	100.1	100.1
	26.1[a]	34.0[a]	35.1[a]
	16.3[b]	27.0[a]	32.1[a]
		14.5[b]	23.6[a]
			13.3[b]

[a] CH_2 group. [b] CH_3 group.

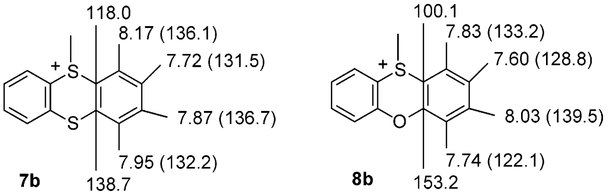
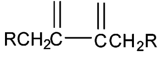


FIGURE 2. ^{1}H and ^{13}C NMR assignments for **7b** and **8b**.



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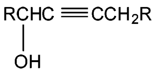

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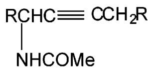
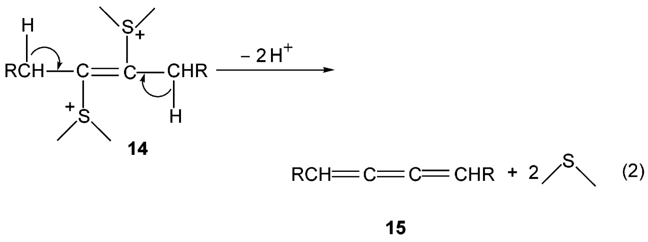


13

R: **a** = Me ; **b** = Et ; **c** = Pr

Closely equimolar amounts of alkyne and ThO were obtained. **7c** in $CHCl_3$ gave 0.14 mmol of 4-octyne and 0.15 mmol of ThO, while in MeCN it gave 0.065 and 0.068 mmol of these products. Approximately equimolar amounts of diketone and H_2 were also obtained. Measurements were made with **7c** and **7d**, and the increase in pressure caused by the H_2 was compared to the increase calculated if the molar amount of H_2 was equal to that of the diketone. The results were 84% (**7c**) and 91% (**7d**) of the anticipated increase.

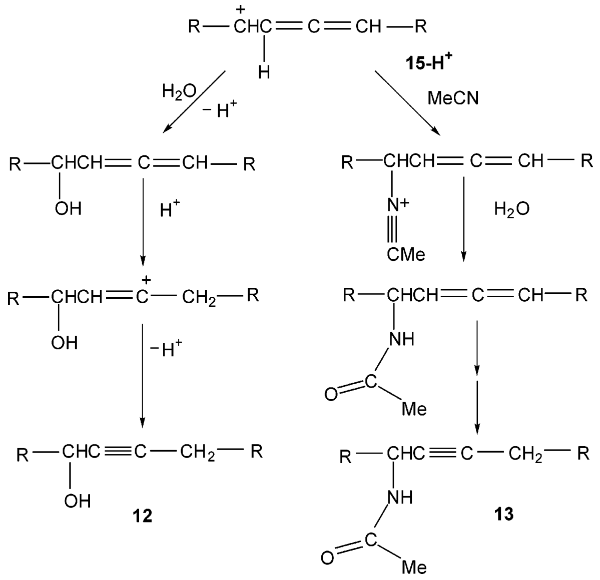
The source of these products from **7b**–**d**, except for ThO and alkyne, appears to be a cumulene (**15**) formed by elimination of Th from the adducts on the alumina surface (eq 2, in which the adduct is represented as **14**).

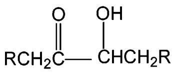


R = **a**, Me ; **b**, Et ; **c**, Pr

Protonation of **15** and reaction with a nucleophile such as water in the system or solvent MeCN will lead to **12** and **13** (Scheme 1). With respect to the diketone (**11**), we thought initially that its most likely source would be an α-hydroxyketone; for example, 6-hydroxydecane-5-one (**16**) would be the source of **11c**. However, **16** was prepared[5] and found to be oxidized to **11c** on alumina under $CHCl_3$ only very slowly, far too slowly to be the source of **11c** in the reactions of **7d**. Having found that H_2 was formed in the alumina reactions in amounts close to those of **11**, we have chosen to relate the two.

SCHEME 1



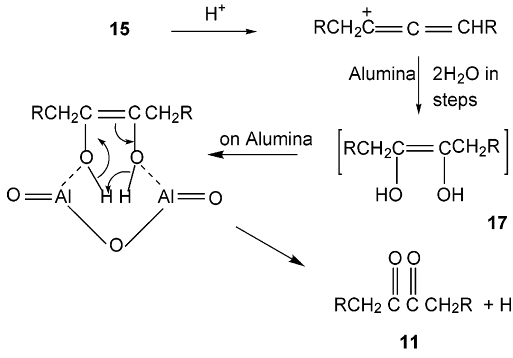


$RCH_2C(=O)-CH(OH)CH_2R$

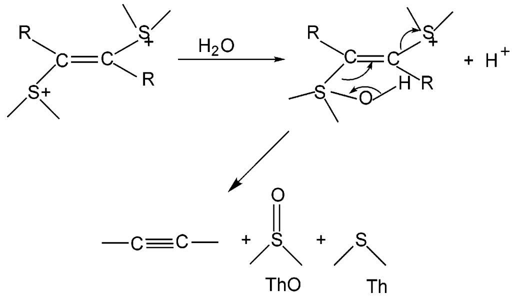
16 , R = Pr

This poses a mechanistic challenge for which we propose that an enediol (**17**) is formed and stabilized on the alumina surface to be oxidized thereon (Scheme 2).

SCHEME 2

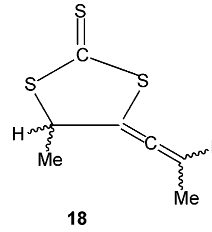


SCHEME 3

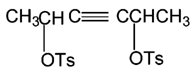


We have no further experimental evidence for this speculation. Insofar as the formation of ThO and an alkyne is concerned, we propose the sequence of reactions in Scheme 3, this being the sequence that is not connected with cumulene formation.

Little is to be found in the literature on the chemistry of cumulenes. Some are reported to be unstable to polymerization and in the air.[6] Preparations of several have been reported; among them is 2,3,4-hexatriene, prepared by the desulfurization of 4-propenylidene-5-methyl-1,3-dithiolane-2-thione (**18**).[6]



18



$CH_3CH(OTs)C\equiv CCH(OTs)CH_3$

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Therefore, we prepared **18** from the ditosylate (**19**) as a mixture of its syn and anti isomers and carried out desulfurization with Raney nickel as described. Rather than isolate the labile 2,3,4-hexatriene, we distilled it directly at low pressure from the preparation vessel onto alumina under $CDCl_3$. Both **11a** and **12a** were formed and were characterized with NMR spectroscopy without isolation. The spectra agreed with those of authentic **11a** and **12a**, providing support for our proposals for the source of products from reactions of the adducts on alumina.

Reaction with KI. In earlier work, we have shown that compounds containing the 5-thianthrenium group react with iodide ion (and other nucleophiles) at both a

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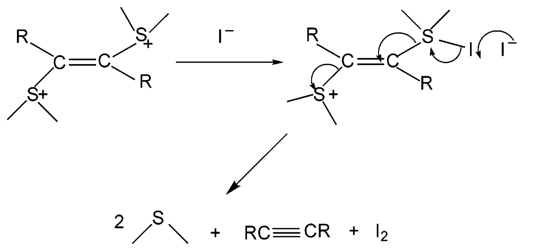
[5] Srinivasan, N. S.; Lee, D. G. *Synthesis* **1979**, *7*, 520–521.

[6] Herges, R.; Hoock, C. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1611–1613.

SCHEME 4



nearby carbon atom and at sulfonium sulfur.[7-9] Each reaction produces Th, but the latter reaction also produces I_2. We were interested in finding which pathway the reaction of an alkyne adduct with iodide ion would follow; reaction of **7c** with KI in MeCN solution was carried out to find if nucleophilic or thiophilic displacement of Th would occur. The reaction gave Th, 4-octyne, and I_2 in a molar ratio of 2:1:1, indicating that thiophilic displacement had occurred (Scheme 4), analogous to the proposed reaction with water (Scheme 3).

Experimental Section

Solvent acetonitrile (MeCN) was dried by distillation from P_2O_5. NMR spectroscopy data were recorded with a 500 MHz instrument; coupling constants (J) are averaged where necessary. DEPT, HMQC, HMBC, and COSY were 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 alkynes, hexane-2,3-dione (**11a**), and 2-hydroxy-3-hexyne (**12a**) were from commercial sources and were used as supplied after characterization with GC and NMR. 3-Hexyne-2,5-diol was obtained as a mixture of *meso*- and *dl*-isomers. Octane-4,5-dione (**11b**) and decane-5,6-dione (**11c**) were prepared by oxidation of the respective alkyne with $KMNO_4$[10] and were characterized with GC and NMR. **11b**, ^1H NMR, $CDCl_3$, δ (J): 2.72 (7.3), t, 4H; 1.62 (7.4), sext, 4H; 0.95 (7.5), t, 6H. ^{13}C NMR, δ: 200.3, 37.9 (CH_2), 16.5 (CH_2), 13.6 (CH_3). **11c**, ^1H NMR, $CDCl_3$, δ (J): 2.74 (7.5), t, 4H; 1.56 (7.4), quint, 4H; 1.34 (7.4), sext, 4H; 0.92 (7.3), t, 6H. ^{13}C NMR, δ: 200.2, 35.8 (CH_2), 25.1 (CH_2), 22.3 (CH_2), 13.6 (CH_3). 3-Hydroxy-4-octyne (**12b**) was prepared by reaction of propanal with lithiated 1-pentyne, and 4-hydroxy-5-decyne (**12c**) was prepared by reaction of butanal with lithiated 1-hexyne.[11] **11c**[12] and **12b**[13] have been reported and characterized with NMR. For our purposes, it was necessary to characterize these compounds with GC and NMR at 500 MHz. **12b**, ^1H NMR, $CDCl_3$, δ (J): 4.31, m, 1H; 2.19 (7.0, 2.0), td, 2H; 1.90, bs, 1H; 1.69, m, 2H; 1.53 (7.3), sext, 2H; 1.00 (7.5), t, 3H; 0.98 (7.5), t, 3H. ^{13}C NMR, δ: 85.4 and 81.2 (yne), 63.9 (CH), 31.2 (CH_2), 22.1 (CH_2), 20.6 (CH_2), 13.4 (CH_3), 9.4 (CH_3). **12c**, ^1H NMR, $CDCl_3$, δ (J): 4.36, m, 1H; 2.21 (7.0, 2.0), td, 2H; 1.65, m, 2H; 1.45, m, 6H; 0.94 (7.5), t, 3H; 0.91 (7.3), t, 3H. ^{13}C NMR, $CDCl_3$, δ: 85.3 and 81.3 (yne), 62.4 (CH), 40.2 (CH_2), 30.7 (CH_2), 21.9 (CH_2), 18.29 (CH_2), 18.27 (CH_2), 13.7 (CH_3), 13.5 (CH_3).

Preparation of Adducts 7a–d and 8b–d. Initially, adducts were prepared by adding the alkyne to a suspension of $Th^{\bullet+}BF_4^-$ or $PO^{\bullet+}BF_4^-$ in MeCN. It was found, however, to be more convenient not to isolate the cation radical salt but to add the alkyne to a solution of the salt made in situ. An example is given with **7a**, the adduct of 2-butyne. Thianthrene (3.0 g, 13.9 mmol) and $NOBF_4$ (1.8 g, 15.5 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 75 mL of dry MeCN was injected through a septum. The mixture was stirred for 45 min, during which bubbling of argon was continuous. The mixture adopted the dark purple color of $Th^{\bullet+}$. Into the stirred mixture was injected 3.0 mL (54 mmol) of 2-butyne. Stirring was continued for 20 h, during which time the color of the solution faded to pale yellow. Dry ether (750 mL) was added, causing the precipitation of **7a**. This was collected and washed with dry ether to give 3.0 g (4.5 mmol, 65%) of **7a**, mp 210–212 °C (dec) after reprecipitation from MeCN. All other adducts were made with this procedure; % yield and mp °C (dec): **7b**, 35, 169–170; **7c**, 17, 140–141; **7d**, 43, 161–162; **8b**, 47, 210–212; **8c**, 54, 195–196; **8d**, 49, 180–182. An adduct (**8a**) of 2-butyne was not prepared.

The ^1H NMR data of the aromatic portions of the adduct spectra are listed in Tables 1 and 3. Only the data for the alkenyl chain are given below. The ^{13}C NMR data for the adducts are listed in Tables 2 and 4.

^1H NMR, CD_3CN, δ (J): **7a**, 2.20, s, 6H. **7b**, 2.59 (7.3), q, 4H; 0.78 (7.5), t, 6H. **7c**, 2.41–2.38, m, 4H; 1.93 (7.5), quint, 4H; 0.67 (7.3), t, 6H. **7d**, 2.45–2.42, m, 4H; 1.11–0.99, m, 8H; 0.67 (7.3), t, 6H. **8b**, 2.99 (7.5), q, 4H; 0.86 (7.5), t, 6H. **8c**, 2.85–2.82, m, 4H; 1.13–1.05, m, 4H; 0.82 (7.3), t, 6H. **8d**, 2.88–2.84, m, 4H; 1.25 (7.3), sext, 4H; 1.21 (8.0), quint, 4H; 0.74 (7.3), t, 6H.

Elemental Analyses. 8b, Calcd for $C_{30}H_{26}S_2O_2B_2F_8$: C, 54.9; H, 3.99; S, 9.77; F, 23.2. Found: C, 54.8; H, 3.98; S, 9.45; F, 22.9. **8c**, Calcd for $C_{32}H_{30}S_2O_2B_2F_8$: C, 56.2; H, 4.41; S, 9.37; F, 22.2. Found: C, 56.2; H, 4.47; S, 9.45; F, 22.4. **8d**, Calcd for $C_{34}H_{34}S_2O_2B_2F_8$: C, 57.3; H, 4.81; S, 9.00; F, 21.3. Found: C, 57.5; H, 4.49; S, 8.36; F, 20.9.

Preparation of 3-Hexyne-2,5-ditosylate (19). To a solution of 25 g (130 mmol) of *p*-tosyl chloride in 400 mL of ether was added a solution of 5.9 g (51 mmol) of 3-hexyne-2,5-diol in 25 mL of ether. The stirred mixture was cooled to −15 °C, and 28 g (500 mmol) of powdered KOH was added in small portions while maintaining the temperature below −5 °C. The mixture was stirred 2 h at 0–5 °C and poured into cold water. The ether layer was separated, and the aqueous layer was extracted with 250 mL of CH_2Cl_2. The combined organic layers were washed with water, dried (Na_2SO_4), and concentrated to give 12.5 g (30 mmol, 58%) of **19**. ^1H NMR, $CDCl_3$ δ (J): 7.75 (8.5), d, and 7.74 (8.0), d, 4H; 7.34, d, 4H; 5.00 (6.2), q, and 4.98 (7.0), q, 2H; 2.453, s, and 2.447, s, 6H; 1.345 (6.5), d, and 1.342 (6.5), d, 6H. ^{13}C NMR, $CDCl_3$, δ: 145.03, 144.99, 133.76, 133.72, 129.73, 129.71, 127.96, 127.90, 83.50, 83.35, 67.08, 67.07, 22.02, 21.92, 21.59.

Preparation of 4-Propylidene-5-methyl-1,3-dithiolane-2-thione (18). Reaction between 1.0 g (2.4 mmol) of **19** and 1.5 g (8.1 mmol) of freshly prepared K_2CS_3 in 100 mL of CH_2Cl_2 containing 5 mg (0.02 mmol) of 18-crown-6 was carried out as described.[6] An excess of K_2CS_3 was used because reactions did not go to completion in our hands when following the literature. Sonication was continued for 36 h, after which thin-layer chromatography (TLC) showed that about 20% of **19** remained. The mixture was filtered; the filtrate was placed in a foil-wrapped flask, and the solvent was removed under reduced pressure to leave a yellow oily residue. This was dissolved in a small amount of CH_2Cl_2 and loaded onto a foil-wrapped silica gel column under a nitrogen atmosphere. Elution with hexane in a nitrogen-filled glovebox gave 110 mg (0.59 mmol, 25%) of a yellow oil, a mixture of *syn*- and *anti*-dithiolanes (**18**) as shown with NMR spectroscopy. ^1H NMR revealed not only coupling between each methyl group and its adjacent proton but also long-range coupling between the two single protons in both syn and anti isomers of the dithiolanes. The ^{13}C NMR spectra showed the presence of the two isomers,

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and the data agreed well with those of Herges and Hoock.[6] From integration of the unoverlapped methyl-group signals at 1.82 and 1.81 ppm and from averaging of ^{13}C peak heights, the two isomers were found to be present in a ratio of 55:45, but we are unable to name the dominant isomer. **18**, ^{1}H NMR, $CDCl_3$, δ (J): 5.75 (7.3, 3.3), qd, and 5.71 (7.3, 3.5), qd, 1H; 4.99 (3.5), a multiplet of nine peaks representing two unresolved overlapping qd, 1H; 1.82 (7.5), d, and 1.81 (7.0), d, 3H; 1.67 (6.5), d, and 1.66 (6.5), d, 3H. ^{13}C NMR, methyl groups only, δ: 14.5, 13.4. Other ^{13}C data were as reported.[6]

Conversion of 18 into 11a and 12a via 2,3,4-Hexatriene. A mixture of dithiolanes **18** was prepared from 4.0 g (9.47 mmol) of **19** and 3.0 g (16 mmol) of K_2CS_3 as described. The reaction gave 2.3 g of crude **18**, which was subjected to desulfurization with 2.0 g of Raney nickel in 10 mL of DMF. The product of desulfurization, 2,3,4-hexatriene,[6] was not isolated but along with some DMF was distilled off under vacuum into a receiver containing 5 mL of $CDCl_3$, 4.0 g of alumina, and 0.1 mL of HBF_4. That mixture was stirred for 1 h, and a sample was withdrawn for NMR spectroscopy. The NMR spectrum showed signals characteristic of **11a** and **12a** but shifted downfield by the presence of so much DMF in the solution. The observed spectra agreed well with those of a mixture of authentic **11a** and **12a** in d_7-DMF. The observed NMR spectra were as follows: **11a**, ^{1}H NMR, δ (J): 2.72 (7.2), q, 4H; 0.99 (7.3), t, 6H. ^{13}C NMR, δ: 200.2, 29.3 (CH_2), 6.8 (CH_3). **12a**, ^{1}H NMR, δ (J): 4.38 (6.5, 1.8), qt, 1H; 2.13 (7.5, 2.0), qd, 2H; 1.30 (6.5), d, 3H; 1.05 (7.5), t, 3H. ^{13}C NMR, δ: 84.2 and 82.8 (yne), 57.4 (CH), 25.0 (CH_2), 14.0 (CH_3), 12.3 (CH_3). Authentic compounds had the following NMR spectra: **11a**, ^{1}H NMR, d_7-DMF, δ (J): 2.76 (7.2), q, 4H; 0.99 (7.3), t, 6H. ^{13}C NMR, δ: 200.5, 29.5, 7.0. **12a**, ^{1}H NMR, d_7-DMF, δ (J): 5.30 (5.5), d, 1H (OH); 4.40, m, 1H; 2.18 (7.5, 1.6), qd, 2H; 1.30 (7.0), d, 3H; 1.06 (7.5), t, 3H. ^{13}C NMR, δ: 84.4, 83.8, 57.6, 25.4, 14.3, 12.4.

Detection and Assay of Hydrogen. Formation of H_2 in reactions of adducts with alumina under $CHCl_3$ was detected with GC, using a stainless steel column, 9 ft × 1/8 in, packed with 5 Å molecular sieves, isothermally at 35 °C, and with a thermal conductivity detector. Assay of H_2 was made by measuring the increase in pressure caused by H_2 formation in a sealed vessel, using a silicon pressure sensor, electrometer-617, MPX2050 series. The sensor was attached to the reaction vessel via the vessel's septum and was calibrated before use at six pressures between 1 and 6 psi. Qualitative detection of H_2 was obtained with **7c** and **7d**. Reaction of each adduct (1.4 mmol) with 10 g of alumina under 40 mL of $CHCl_3$ was allowed to run for 2 h in a 50 mL flask sealed with a septum. Samples of 100 μL were drawn from the headspace and were found to contain H_2, O_2, and N_2, identified with their retention times of 0.5, 1.5, and 5.0 min, respectively. Control experiments showed that without the addition of an adduct, the headspace registered only O_2 and N_2 in the GC. Quantitative measurements were made with the pressure sensor. The amount (mmol) of H_2 expected to be formed in a reaction was equated to the amount of diketone that had been formed and measured in separate experiments. The anticipated increase in headspace pressure caused by that amount of H_2 was then calculated from the ideal gas equation and compared with the increase measured with the sensor. Thus, from **7c** (1.4 mmol), 0.12 mmol of **11b** had been obtained. The anticipated equivalent of H_2 in increased pressure was 1.59 psi, whereas the measured increase was 1.34 psi (84%). Analogous experiments with **7d** resulted in 91% of the anticipated amount of H_2.

Reaction of 7d with Alumina under MeCN. Formation of 11c, 12c, and 13c. A solution of 1.5 g (2.01 mmol) of **7d** in 50 mL of MeCN was placed in a 250 mL flask containing 40 g of alumina. The mixture was stirred at room temperature for 6 h and was filtered through fritted glass. The alumina was washed with 50 mL of ether. A further 400 mL of ether was added to the filtrate, and the precipitate of unreacted **7d** was removed. The filtrate was concentrated under reduced pressure to give a residue to which was added 10 mL of cold MeCN. Undissolved Th was removed by filtration. To the filtrate was added 10 mL of 1% $NaHCO_3$ solution, and the aqueous solution was extracted with 50 mL of ether. The ether layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure to give an oil. The oil was loaded onto a silica gel column with a small amount of $CHCl_3$. Elution with hexane containing 1−5% ethyl acetate gave 9 mg (0.005 mmol, 0.26%) of **11c** as an oil, 17 mg (0.110 mmol, 5.5%) of **12c** as an oil, and 23 mg (0.117 mmol, 5.8%) of **13c**, mp 31−32 °C. Products **11c** and **12c** were identified by comparison of their GC and NMR data with those of the prepared authentic compounds; **12c** was also identified with mass spectrometry (MS). Product **13c** was identified with NMR and MS. Authentic **13c** was not prepared. **13c**, ^{1}H NMR, $CDCl_3$, δ (J): 5.63 (6.5), d, 1H; 4.63 (8.0, 6.0, 2.0), tdt, 1H; 2.10 (7.0, 2.0), td, 2H; 1.91, s, 3H; 1.59−1.45, m, 2H; 1.43−1.28, m, 6H; 0.86 (7.5), t, 3H; 0.84 (7.3), t, 3H. ^{13}C NMR, δ : 168.8 (C=O), 83.3 and 79.2 (yne), 41.6 (CH), 38.4 (CH_2), 30.7 (CH_2), 23.3 (CH_3), 21.9 (CH_2), 18.9 (CH_2), 18.3 (CH_2), 13.6 (CH_3), 13.5 (CH_3). MS: 196 (M + 1; 100), 114 (M − 81; 13), 57 (M − 138; 9), 43 (M − 152; 39).

Reaction of 7d with Alumina under $CHCl_3$. Formation of 11c and 12c. Because adducts **7** and **8** are insoluble in $CHCl_3$, the alumina was added to a stirred suspension of 500 mg (0.67 mmol) of **7d** in 150 mL of $CHCl_3$. Workup and column chromatography gave 27 mg (0.158 mmol, 16%) of **11c** and 21 mg (0.136 mmol, 20%) of **12c**. The products were identified with GC and NMR.

Reaction of 7c with Alumina under MeCN. Formation of 11b, 12b, and 13b. Reaction was carried out as described for **7d**, with 800 mg (1.12 mmol) of **7c**. Prior to separation of products with column chromatography, the crude residue was analyzed with GC, which gave 0.065 mmol (6%) of 4-octyne, 0.12 mmol (11%) of **11b**, 0.098 mmol (9%) of **12b**, 0.17 mmol (15%) of **13b**, 1.87 mmol (84%) of Th, and 0.068 mmol (3%) of ThO. **11b** (0.046 mmol, 4%), **12b** (0.059 mmol, 5%), and **13b** (0.096 mmol, 9%), mp 41−42 °C, were isolated with column chromatography and were characterized with NMR spectroscopy. The NMR spectra of **11b** and **12b** agreed well with those of the prepared authentic compounds. **13b**, ^{1}H NMR, $CDCl_3$, δ (J): 5.61, bs, 1H (NH); 4.65 (8.0, 5.5, 2.3) tdt, 1H; 2.15 (7.0, 2.0), td, 2H; 1.98, s, 3H; 1.65, m, 2H; 1.52 (7.2), sext, 2H; 0.98 (7.3), t, 3H; 0.97 (7.3), t, 3H. ^{13}C NMR, δ: 168.8 (C=O), 83.5 and 79.1 (yne), 43.1 (CH), 29.3 (CH_2), 23.3 (CH_3), 22.1 (CH_2), 20.6 (CH_2), 13.4 (CH_3), 9.9 (CH_3). HRMS (CI) $[M + H]^+$: calcd for $C_{10}H_{18}NO$, 168.138839; found, 168.138838 (error 0.01 ppm).

Reaction of 7c with Alumina under $CHCl_3$. Formation of 11b and 12b. Reaction was carried out as with **7d**, using 500 mg (0.70 mmol) of **7c**, and gave by GC 0.14 mmol (20%) of 4-octyne, 0.17 mmol (24%) of **11b**, 0.12 mmol (17%) of **12b**, 1.04 mmol (74%) of Th, and 0.15 mmol (11%) of ThO. After column chromatography, **11b** (0.075 mmol, 11%) and **12b** (0.10 mmol, 14%) were isolated and characterized with NMR spectroscopy.

Reaction of 7b with Alumina under MeCN. Formation of 11a, 12a, and 13a. Reaction was carried out as described for **7d**. GC analysis of the crude mixture of products gave 3-hexyne (1%), **11a** (1%), **12a** (1%), **13a** (6%), Th (99%), and ThO (0.5%). Only **13a**, mp 39−40 °C, was isolated with column chromatography. **13a**, ^{1}H NMR, $CDCl_3$, δ (J): 5.66, bs, 1H; 4.76 (7.5, 6.8, 2.3), qdt, 1H; 2.18 (7.5, 2.0), qd, 2H; 1.97, s, 3H; 1.36 (7.0), d, 3H; 1.12 (7.5), t, 3H. ^{13}C NMR, δ : 168.7 (C=O), 84.1 and 79.6 (yne), 37.4 (CH), 23.3 (CH_3), 22.9 (CH_3), 13.8 (CH_3), 12.2 (CH_2). HRMS (CI) $[M + H]^+$: calcd for $C_8H_{14}NO$, 140.107539; found, 140.107508 (error 0.22 ppm).

Reaction of 7b with Alumina under $CHCl_3$ and $CDCl_3$. GC analysis of products from reaction in $CHCl_3$ gave 3-hexyne (2%), **11a** (29%), **12a** (9%), Th (97%), and ThO (1%). The identification of products was made with the use of authentic compounds. Reaction was also carried out with 105 mg (0.152 mmol) of **7b** and 1 g of alumina under 2.5 mL of $CDCl_3$. The formation of **11a** and **12a** was confirmed with their NMR spectra and comparison with the spectra of authentic **11a** and **12a**.

Reaction of 7c with KI. To 0.139 mmol of **7c** in 25 mL of MeCN was added 0.313 mmol of KI. After the solution had been stirred for 45 min, it was diluted with 75 mL of water and titrated with sodium thiosulfate solution. The yield of I_2 was 0.137 mmol (98%). In a similar experiment with 0.209 mmol of **7c**, the aqueous MeCN solution was extracted twice with CH_2Cl_2. The dried (Na_2SO_4) CH_2Cl_2 solution was assayed with GC, giving 0.371 mmol (88%) of Th and 0.186 mmol (89%) of 4-octyne.

Acknowledgment. H.J.S thanks the Welch Foundation for support (Grant D-0028). K.H.W. thanks the Welch Foundation for support (Grant C-0976) and the purchase of the CCD and the National Science Foundation for support (Grant CHE-9983352). We thank Mr. David W. Purkiss (TTU) for the 500-MHz NMR spectroscopy and Dr. Yunxuan Xiao (Rice) for HRMS.

Supporting Information Available: CIF X-ray crystallographic information data for compound **7c**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO050198B