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Decomposition of Alkene Adducts of Thianthrene Cation Radical in Nitrile Solvents. Formation of Alkyl-2-oxazolines and a New Class of Four-Component Products: 5-[(1-Alkoxyalkylidene)ammonio]alkylthianthrenium Diperchlorates

Henry J. Shine,*,† Bing-Jun Zhao,† John N. Marx,† Teyeb Ould-Ely,‡ 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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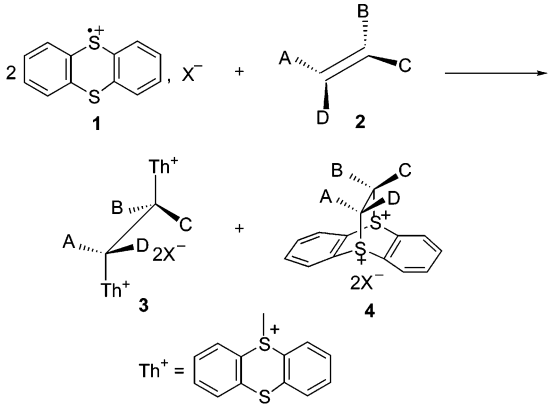
The monoadducts (**4a**−**d**) of thianthrene cation radical perchlorate (**1a**) and isobutene, 2-methylbutene, 2-methyl-2-butene, and 2-methylpentene decompose spontaneously in acetonitrile (MeCN) solution, with the formation of thianthrene (Th). Decomposition of **4a** (1,2-(5,10-thianthreniumdiyl)-2-methylpropane diperchlorate) and **4a′**, the corresponding dihexafluorophosphate, was studied in depth and extensively with ^{1}H and ^{13}C NMR spectroscopy. Decomposition of **4a** was found to involve the solvent itself as well as water in the solvent, remaining from incomplete drying, and gave, apart from Th, successively, the perchlorate salts of 2,4,4-trimethyl-2-oxazoline (**6**) and 2-amino-2-methylpropyl acetate (**7**). These salts, **6-HClO$_4$** and **7-HClO$_4$**, respectively, were prepared and used in understanding the reactions of **4a** as well as the relationships among **6**, **7**, and 2-(acetylamino)-2-methyl propanol (**8**) in acidified MeCN solution. Decompositions of **4a**−**d** in MeCN and other nitriles (RCN) containing an added alcohol (R′OH) led to new products, 5-[(1-alkoxyalkylidene)ammonio]alkylthianthrenium diperchlorates (**5a**−**u**). These compounds were identified with ^{1}H and ^{13}C NMR spectroscopy and, in part, with X-ray crystallography and elemental analysis. The mechanisms of formation of **5**−**7** are discussed.

Introduction

Salts of thianthrene cation radical (Th$^{\bullet+}$X$^-$, **1**), X$^-$ = ClO_4^-, PF_6^-, BF_4^-, SbF_6^-, add to cycloalkenes and alkenes (**2**) to form bis- (**3**) and monoadducts (**4**). The additions are stereospecific, in which, as far as alkenes are concerned, the geometry of the alkene is retained.[1−3] This is illustrated with Scheme 1. The addition reactions are carried out in dry acetonitrile (MeCN) solution, from which the adducts are precipitated with ether.

When we began our work on addition of **1a** (X$^-$ = ClO_4^-) to isobutene, we used isobutene that, unknown to us, was contaminated in its cylinder with methanol. Consequently, reaction with **1a** led not only to a monoadduct (**4a**) but also, serendipitously, to a second product that was shown with X-ray crystallography and elemental analysis to be a new compound, 5-[2-[(1-methoxyethylidene)ammonio]-2-methylpropyl]thianthrenium diperchlorate (**5a**). As far as we know, this class of compounds has not been reported before. Identification of **5a** led us to an extensive study of reactions of **1a** with alkenes in nitrile solvents (RCN) containing small amounts of a deliberately added alcohol (R′OH). We found that suc-

SCHEME 1



	A	B	C	D	X
4a	Me	H	H	Me	ClO_4
4a′	Me	H	H	Me	PF_6
4b	Me	H	H	Et	ClO_4
4c	Me	Me	H	Me	ClO_4
4d	Me	H	H	Pr	ClO_4

† Texas Tech University.
‡ Rice University.

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cessful reactions were limited to branched alkenes containing small alkyl groups, i.e., isobutene, 2-methylbutene, 2-methyl-2-butene, and 2-methylpentene. We found also that isolated monoadducts of these alkenes reacted with R′OH in RCN to give compounds **5**. These results led us in turn to study the spontaneous decomposition of monoadducts in nitrile solvents, illustrated here with the use of **4a** in MeCN. We found that this decomposition gave successively 2,4,4-trimethyl-2-oxazoline (**6**) and 2-amino-2-methylpropyl acetate (**7**), each in its protonated form. This finding caused us to study the reactions of **6** itself in MeCN containing an equivalent amount of $HClO_4$ and also the relationships among **6**, **7**, and 2-(acetylamino)-2-methylpropanol (**8**) that affected our work with **4a**. We now explain how **6** and **7** are formed from **4a** and how their formation is diverted in part into formation of **5** when R′OH is present.

Results

Preparations of 5a−u. Two methods of preparing these compounds were used: the addition of **1a** to an alkene in RCN containing R′OH (method 1) and the decomposition of a monoadduct (**4**) in RCN containing R′OH (method 2). The alkenes (or their monoadducts) that could be used were limited by structure to isobutene, 2-methylbutene, 2-methyl-2-butene, and 2-methylpentene. Other alkenes, such as *cis*-2-butene and *trans*-3-hexene and their monoadducts, 2-ethylbutene and (*E*)- and (*Z*)-3-methyl-2-pentene, failed to give **5**. Instead, the *cis*-2-butene and *trans*-3-hexene had stable adducts, while adduct formation was not obtained with the more branched alkenes. Both methods 1 and 2 gave only small yields of **5**, from 5 to 30%. Method 1 was best used with isobutene and 2-methylbutene. It gave very poor yields with 2-methyl-2-butene, so that products corresponding with this alkene (**5o−t**) were prepared with method 2. The reason for the very poor yields of **5o−t** when using method 1 is not known. 2-Methyl-2-butene was available only as a 2 M solution in tetrahydrofuran (THF). Possibly, therefore, the sequence of reactions that led to compounds **5** was affected by the change in solvent from MeCN to a mixture of MeCN and THF; however, the effect of solvent in general on preparing **5** was not explored.

Methanol, ethanol, propanol, isopropyl alcohol, butanol, and cyclohexanol were used successfully, whereas *tert*-butyl alcohol failed to give **5**. In method 1, the amount of alcohol used had to be small in comparison with the amount of alkene to avoid competitive reaction of the alcohol with **1a**. Therefore, the concentration of methanol in the first-used, contaminated supply of isobutene was measured and approximately that concentration was used in all other reactions. Use of equal amounts of methanol and isobutene in the reaction with **1a** in MeCN gave, in fact, only the known[4] 5-methoxythianthrenium perchlorate.

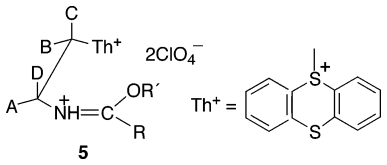
When method 1 was used with ice-cold solutions of reactants, mixtures of **4** and **5** were obtained, from which it was necessary to separate **5** with fractional precipitation from MeCN solution by adding ether. This technique was used for preparing **5e**,**g**,**h**. We found that by stirring a reaction mixture overnight at room temperature, most of the monoadducts decomposed, leaving only the corresponding **5** to be precipitated by adding ether. In that way, tedious fractional precipitation could be avoided. This technique was used for preparing **5a** (run 2),**c**,**d**,**f**,**i**−**n**. In using method 2 for preparing **5o**−**u**, we again continued stirring overnight at room temperature to ensure loss of all of the monoadduct before precipitating the **5**. Method 2 was also used for preparing **5a** (run 1) and **5b**.

For the most part, MeCN was the solvent. Propionitrile (EtCN) was used to prepare **5g**,**n**,**t**, while butyronitrile was used for **5h**.

In all, therefore, 21 members of this new class of compounds were isolated. They are listed in Table 1. All were characterized with ^1H, ^{13}C, and DEPT NMR spectroscopy in a 500 MHz spectrometer. We were able to grow single crystals of 15 compounds (**5a**−**c**,**e**−**g**,**i**−**l**, **n**−**r**) for X-ray crystallography (Figures S1−S15). Two (**5a**,**g**) had satisfactory elemental analyses. Analyses of other **5** products were not sought.

Decomposition of Monoadducts (4) in RCN. Formation of 6-H$^+$ and 7-H$^+$. In the absence of added R′OH, **4a**−**d** decomposed in MeCN solution with the formation of thianthrene (Th). We used **4a** and **4a′** ($X^- = PF_6^-$) as models for studying this decomposition, which was followed mainly with NMR spectroscopy, including DEPT. The NMR spectrum of **4a** in CD_3CN, for example, changed completely during a period of 5 days. The aromatic ^1H signals of **4a** were replaced with the two

TABLE 1. Products 5a−u



compound[a]	A	B	C	D	R	R′	yield (%)[b]	method[c]
5a	Me	H	H	Me	Me	Me	30	2
5a							23	1
5b					Me	Et	25	2
5c					Me	Pr	20	1
5d					Me	*i*-Pr	13	1
5e					Me	Bu	24	1
5f					Me	cC_6[d]	9	1
5g					Et	Me	14	1
5h					Pr	Me	5	1
5i	Me	H	H	Et	Me	Me	10	1
5j					Me	Et	15	1
5k					Me	Pr	15	1
5l					Me	*i*-Pr	6	1
5m					Me	Bu	7	1
5n					Et	Me	6	1
5o	Me	Me	H	Me	Me	Me	6	2
5p					Me	Et	12	2
5q					Me	Pr	12	2
5r					Me	*i*-Pr	10	2
5s					Me	Bu	9	2
5t					Et	Me	8	2
5u	Me	H	H	Pr	Me	Me	15	1

[a] Series **5a**−**h** corresponds with isobutene; series **5i**−**n** with 2-methyl-1-butene; series **5o**−**t** with 2-methyl-2-butene; **5u** with 2-methyl-1-pentene. [b] Amount of **1a** that was converted into **5**. [c] In method 1, reaction of $Th^{\bullet+}ClO_4^-$ with alkene in RCN containing R′OH; in method 2, reaction of monoadduct with R′OH in RCN. [d] Cyclohexyl.

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characteristic dd of Th, while the alkyl signals were replaced with two singlets at δ 4.67 (2H) and 1.50 (6H) ppm. ^{13}C peaks related to the new ^{1}H spectrum, apart from those from Th, characterized with DEPT, were at δ 182.0, 85.2 (CH_2), 64.2 (quaternary), and 26.4 (CH_3) ppm. The data are consistent with the loss of **4a** and the formation of protonated **6** (**6-H**$^+$), the group on C-2 of **6** being CD_3 rather than CH_3.

An analogous experiment was carried out on a larger scale with **4a′** in MeCN. The solution was kept for 25 days after which the Th was removed from the recovered products by washing with ether. The remaining product, a sticky solid, was deduced to be the PF_6^- salt of **6-H**$^+$. That is, the ^{1}H NMR spectrum consisted of three singlets at δ 4.64 (CH_2), 2.33 (CH_3), and 1.49 (2 CH_3) ppm. This product was kept in CD_3CN for an additional 5 days, after which new signals appeared, accompanying the earlier signals, at 4.03 (CH_2), 2.08 (CH_3), and 1.35 (2 CH_3) ppm. The ^{13}C spectrum at this stage consisted of two sets of five peaks, the larger set at 177.9, 85.0, 64.2, 26.4, and 14.4 ppm and the smaller set at 171.3, 68.6, 56.3, 22.8, and 20.8 ppm. The two sets of ^{1}H and ^{13}C peaks are consistent with the formation of **6-H**$^+$ and, subsequently, **7-H**$^+$.

Preparation of 6-HClO$_4$. Crystalline **6-HClO$_4$**, mp 118−121 °C, was isolated with silica gel chromatography of a solution of **6** in 70% $HClO_4$. Its NMR spectra were recorded in CD_3CN and in D_2O, and these data were used in understanding the behavior of **4a** in CH_3CN. The changes that occurred in **6**, itself, when its solutions in CD_3CN and D_2O were acidified with $HClO_4$ were also used in understanding the behavior of **4a**.

Preparation of 7-HClO$_4$. Crystalline **7-HClO$_4$**, mp 117−118 °C, was isolated after complete conversion of **6-H**$^+$ into **7-H**$^+$ in D_2O. Its NMR spectra, recorded in CD_3CN and in D_2O were used along with those of **6-HClO$_4$** in understanding the behavior of **4a**. However, when a solution of **7-HClO$_4$** in D_2O was neutralized with solid NaOH, **7** was not formed. Instead, the solution's NMR spectrum was consistent only with the formation of **8**.

Reaction of 6 in CD$_3$CN/HClO$_4$. When a solution of **6** in CD_3CN was acidified with an equimolar amount of $HClO_4$, the ^{1}H and ^{13}C NMR spectra of **6** changed quickly. The ^{1}H spectrum consisted of two sets of three singlets, the larger set at δ 4.64, 2.33, and 1.48 ppm and the smaller set at δ 4.03, 2.08, 1.36 ppm. Each set integrated for proton ratios of 2:3:6. The intensities of the larger set decreased with time, while those of the smaller set increased. This change was followed at 300 MHz. The ratio of peak intensities was 1/1 after 1 day and 1/5 after 16 days. The initial effect of $HClO_4$ on **6** was also seen in its ^{13}C NMR spectrum, divisible with the aid of DEPT and HMQC into two sets of five peaks. The larger set and its associated proton signals had δ 177.6, 84.9 (4.64), 64.3, 26.5 (1.48), and 14.5 (2.33) ppm, while the smaller set had δ 171.2, 68.5 (4.03), 56.7, 22.8 (1.36), and 20.8 (2.08 ppm). The two sets of ^{1}H and ^{13}C data are attributable to **6-H**$^+$ and **7-H**$^+$.

The solvent CD_3CN was evaporated from this solution and replaced with D_2O. The ^{1}H NMR spectrum was now identical with that when starting with **6** in D_2O/$HClO_4$.

Reaction of 6 in D$_2$O/HClO$_4$. The effect of $HClO_4$ on **6** in D_2O was analogous to but much faster than that in CD_3CN. Within 20 h, the initial ^{1}H spectrum of δ 4.56, 2.22, and 1.35 ppm had changed almost completely into δ 4.00, 2.02, and 1.25 ppm. The change was complete after 66 h, at which time the ^{13}C spectrum showed δ 173 (−C=O), 68.1 (CH_2), 53.0 (quat), 21.3 (2 CH_3), and 19.5 (CH_3) ppm. The ^{1}H spectrum was indentical with that reported for **7-HCl**.[5]

Reaction of 2-(Acetylamino)-2-methylpropanol (8) in CD$_3$CN/HClO$_4$. Addition of $HClO_4$ to a solution of **8** in CD_3CN caused an immediate shift in ^{1}H NMR peaks to δ 3.67 (CH_2), 2.28 (CH_3), and 1.35 (2 CH_3) ppm. The intensities of these peaks decreased over a period of 10 days, at which point they were too small to be integrated. During this period, peaks attributable to **6-H**$^+$ and **7-H**$^+$ appeared, those for **6-H**$^+$ being dominant at all times.

Discussion

Decomposition of 4: A. Formation of 5. The chemistry that we report here originates in the instability of selected monoadducts in MeCN solution. The instability of such a monoadduct is detectable when the monoadduct is used directly (method 2) and when it is formed in situ in method 1. The instability of **4c** was reported briefly earlier[3] but was not followed further. Among the others with which we are now concerned, **4a** was sufficiently stable in CD_3CN to allow reliable ^{1}H and ^{13}C NMR spectra to be recorded, **4b** was too unstable for time-consuming acquisition of ^{13}C NMR data and for preparing **5** in reasonable yields, and **4c** was usable for recording its ^{1}H NMR spectrum and for preparing **5o**−**t**; preparation of **4d** was not attempted. The formation of **5a**, discovered serendipitously with **4a**, prompted us to ask what happens to monoadducts that decompose in MeCN in the absence of R′OH. Therefore, the discussion that follows is largely concerned with that decomposition, which, when understood clearly, showed also how decomposition was divertible in part to **5** by adding R′OH to the solution. Decomposition of only **4a** was studied in depth, to serve as a model. We have not studied the analogous decompositions of **4b**,**c** in the absence or RO′H but regard them as being similar to that of **4a**, the link being that the decompositions of all four monoadducts (**4a**−**d**) in the presence of RO′H have a common pathway, leading to **5**.

There are several striking features in the reactions that lead to compounds **5**. First, the alkenes from which **5** can be obtained, and whose monoadducts (**4**) can lead to **5**, have two alkyl groups on C-2 (**4a**,**b**,**d**) or C-3 (**4c**). Second, the first product detectable with NMR spectroscopy in the decomposition of **4a** in the absence of R′OH was the d_3-analogue of protonated 2,4,4-trimethyl-2-oxazoline (**6-H**$^+$). That is, the C-2 of the former alkene (isobutene) was now bonded to the N atom of the solvent CD_3CN. Similarly, the final product of decomposition of a compound **4** in RCN containing R′OH is **5**, in which the C-2 (C-3) of a former alkene is again bonded to the solvent's N atom. Third, in the decomposition of **4**, the thianthrenium group is converted into thianthrene (Th); that is, it is reduced.

These features suggest that the first step in the decomposition of **4** is the opening of the bond between

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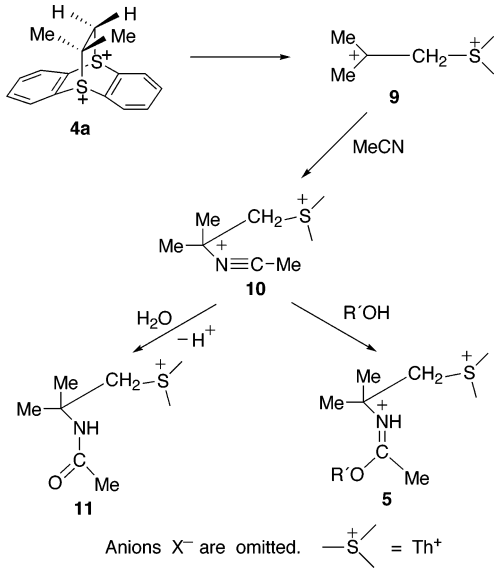
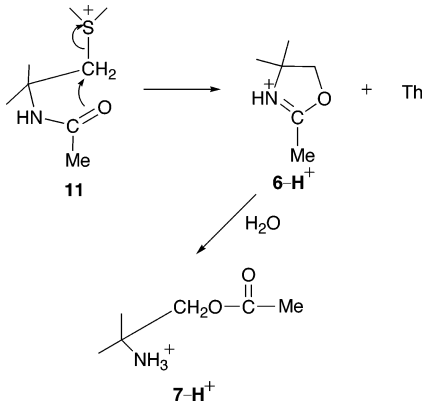
SCHEME 2



SCHEME 3



the geminally substituted C atom and the sulfur atom. This is shown with **4a** decomposing in MeCN (Scheme 2). The driving force for bond opening is the formation of the tertiary cation (**9**). Once formed, that reacts with the most available nucleophile present, the solvent, giving **10**. Direct attack of MeCN on **4a** does not occur, for if that were to occur, the position of attack should be the former alkene's C-1 carbon atom. If that mode of attack were to occur, furthermore, the same reaction should be expected of monoadducts of all unsubstituted alkenes; instead, they are stable to storage in MeCN.

In the presence of R′OH, **10** leads directly to **5**. In the absence of R′OH, **10** can react with the small amount of water in the incompletely dried solvent, forming **11**. We have seen no evidence in the NMR spectra, recorded while reactions are occurring in CD_3CN, that can be tied to the presence of **11** in solution. Consequently, it appears that once formed, **11** quickly cyclizes into **6-H**$^+$, a reaction (Scheme 3) that displaces (and thus reduces) the thianthrenium group. Subsequently, **6-H**$^+$ reacts slowly with residual water in solution to give **7-H**$^+$ (Scheme 3).

We do not know if the bond opening that gives **9** (Scheme 2) is reversible. That would be an interesting development in our work, because we have stressed in earlier reports that the configuration of alkenes is retained when monoadducts are formed.[1–3] Bond opening and reclosing would be detectable in a monoadduct whose configuration would change thereby. That is, an erythro adduct could be changed into a threo adduct, and vice versa. Unfortunately, that criterion cannot be applied to **4a**−**d**, whose configuration would not be changed by bond opening and reclosing. Adducts of *cis*-2-butene and *trans*-3-hexene, which we have made earlier,[3] would serve as tests for bond opening and reclosing, but they did not undergo the reactions now reported. Reactions of *cis*-2-butene and *trans*-3-hexene with **1a′** in MeCN containing MeOH gave only the monoadducts and none of **5**. Attempts to make testable adducts of other suitable alkenes such as (*E*)- and (*Z*)-3-methyl-2-pentene failed. Thus, we are not able to say now if bond opening is reversible.

B. Role of 6 and 7. The conversion of 2-substituted-2-oxazolines into esters of amino alcohols in acidic solution is reported in the older[6] and more recent literature.[7−10] These reports have guided us in deducing the behavior of **4a** in MeCN. To confirm the literature's guidance, we studied the chemistry of **6** in acid solutions and its conversion in such solutions into **7**. Thereby, we have been able to characterize authentic **6-H**$^+$ in CD_3CN. Similarly, having been able to convert **6-HClO$_4$** completely into **7-HClO$_4$**, we were able to isolate the latter and characterize authentic **7-H**$^+$ in CD_3CN, too. In these ways, we have been able to confirm our deductions (Schemes 2 and 3) about the decomposition of **4a** in MeCN, monitored with NMR spectroscopy in CD_3CN. The work with **4a** serves as a model for the decomposition of the other monoadducts (**4b**−**d**) and for understanding how, in the presence of R′OH, they were converted into their corresponding four-component adducts (**5**).

Our searches of the literature have failed to find the isolation and characterization of **7** itself. The preparation, but not isolation and characterization, of **7** by transesterification of 2-amino-2-methylpropanol with ethyl 2-(2,4-dinitrophenyl)aceto acetate (**12**) has been reported recently.[11] We tried to prepare **7** by that method, but in our hands, the reaction gave only a mixture of **6** and **8**. This was shown with column chromatography of products formed in $CHCl_3$ and also by following the reaction in $CDCl_3$ with NMR spectroscopy rather than with isolation. The possibility that, in our hands, **7** had been formed and had rearranged immediately into **8** cannot be ruled out; but we found that *tert*-butylamine, used as a model, was acetylated when heated with **12** in $CDCl_3$, so that by analogy direct N-acetylation of 2-amino-2-methylpropanol by **12** may also have occurred. Earlier reports on the relationships between 2-oxazolines and the corresponding esters of amino alcohols show that the esters are stable in acidic solution but isomerize easily into isomeric acylamino alcohols as the pH of the solution is increased.[7,8,10] Thus, it may be questionable that **7** itself was prepared as reported.[11]

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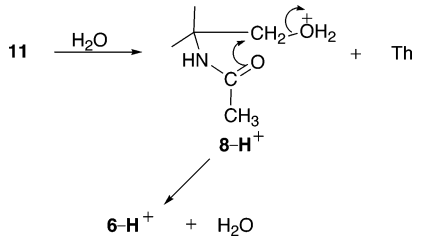
SCHEME 4



The preparation and isolation of **7-HCl** have been described in detail,[5] however, and NMR results in D_2O were given. Our data for **7-HClO$_4$**, recovered from CD_3CN and placed in D_2O, are in perfect agreement with those for **7-HCl**. Furthermore, the NMR data for **7-HClO$_4$**, obtained by conversion of **6** in D_2O, agree with these results. Isomerization of **7** into **8** apparently occurred when we attempted to neutralize **7-HClO$_4$**.

C. Role of 8. At one time, we considered also that 2-acetylamino-2-methylpropanol (**8**), possibly derived from **11** (as **8-H**$^+$) by reaction with water in the solvent (Scheme 4), may have been the source of **6-H**$^+$ in the decomposition of **4a** in MeCN. We found, indeed, that **8** was converted into **6-H**$^+$, but only very slowly, when $HClO_4$ was added to its solution in CD_3CN. Over a period of 10 days, the signals from **8-H**$^+$ decreased until they were no longer measurable. The solution then contained **6-H**$^+$ and a smaller amount of **7-H**$^+$. However, in none of the experiments in which we followed the decomposition of **4a** in CD_3CN with NMR spectroscopy were we able to detect peaks attributable to **8-H**$^+$. Had **8-H**$^+$ been formed from **11** (Scheme 4), its slow conversion into **6-H**$^+$ and **7-H**$^+$ should have made it detectable. Instead, the first signals to appear in the decomposition of **4a** were those of **6-H**$^+$. Consequently, **8** was not a participant in the decomposition of **4a**.

Structures of 5. The Ortep diagrams (Figures S1−S15, Supporting Information) leave no question as to the structures of these new compounds. Further, in each of these diagrams, it can be seen that the H atom attached to N and the adjacent R′O group (attached to C) have the anti configuration on the C=N bond. That configuration diagnoses the trans addition of R′OH to the C−N triple bond of **10** (Scheme 2).

The NMR spectra (Supporting Information) reveal patterns of structure among the three major groups of **5**, even in solution. The three major groups are **5a**−**h** (from isobutene), **5i**−**n** (from 2-methylbutene), and **5o**−**t** (from 2-methyl-2-butene). The aromatic proton signals in **5a**−**h** are typical of a symmetrically placed thianthenium (Th$^+$) group,[3] consisting of two dd (the 1,9- and 4,6-protons) and two td (the 2, 8- and 3, 7-protons), each multiplet representing 2H with J values of about 8.0 and 1.5 Hz. The aromatic ^{13}C signals complement this indication of symmetry, there being mainly six peaks per spectrum. In contrast, the aromatic proton spectra of most of **5i**−**n** and, more markedly, **5o**−**t**, show signals from eight individual H atoms in four sets of dd and four sets of td. That is, the 1,9- and 4,6-protons, etc., are no longer equivalent. Correspondingly, the aromatic ^{13}C spectra of these compounds show mainly 12 peaks.

The spectral characteristics of the alkyl portions of the three groups of **5** also reflect differences in symmetry. In **5a**−**h**, the methylene protons on C-1 and the methyl groups on C-2 of the alkyl chain are singlets. In **5i**−**n**, the methylene protons on C-1 are no longer equivalent, as reflected in two 1H d with J = 14−15 Hz. Similarly, the methylene protons on C-3 show inequivalence in the two sets of 1H dq, with J = 14.5−15 and 7.0−7.5 Hz. The two methyl groups on C-3 of **5o**−**t** appear as separate singlets. Inequivalence is also revealed within the (alkylidene)ammonio groups of **5i**−**u**, where, for example, the $-CH_2O$ proton signals appear as two dq or two dt, depending on the alkyl group attached to the CH_2.

Finally, the yields of **5** (Table 1) are quite small. It is probable that formation of **5** competes poorly with the other routes of decomposition of **4**. We have made no efforts to optimize yields of **5**.

Experimental Section

Thianthrene cation radical perchlorate (**1a**) was used for almost all of the present work. Therefore, all of the new compounds **5** that are reported are diperchlorates. **1a** is the easiest thianthrenium salt to prepare in reproducible yields, but it is temperamental toward explosion.[12] We have used it for many years without trouble, only to have it explode occasionally without apparent reason. It has been prepared also by other workers many years ago and none of them has reported having had trouble with it. We have now abandoned its use in favor of Th$^{\bullet+}PF_6^-$ (**1a′**).

Preparation of 1a′. To get reliable yields of **1a′** in reaction of Th with $NOPF_6$, it was found necessary to remove NO as it was formed. Th (2.1 g, 9.7 mmol) and $NOPF_6$ (1.9 g, 10.6 mmol) were placed side by side under argon in a 500 mL flask capped with a septum, through which 60 mL of dry MeCN was injected. Argon was bubbled through the solution, while it was stirred for 2 h. The solution was then cooled in ice, and 250 mL of dry ether was added in portions. The dark blue precipitate was removed, washed with dry ether and dried under vacuum to give 2.7 g (7.5 mmol, 76%) of **1a′**.

2-Acetylamino-2-methylpropanol (8). Prepared as described, mp 87−87.5 °C; lit. mp 87.5−88 °C.[13] NMR (CD_3CN), δ (J), ^1H: 6.64, br s, 1H; 4.52 (6.0), t, 1H; 3.45 (5.5), d, 2H; 1.85, s, 3H; 1.21, s, 6H. ^{13}C: 172.5 (−C=O), 71.0 (CH_2), 56.9 (quat), 25.0 (2 CH_3), 24.4 (CH_3). ^1H NMR (D_2O), δ: 3.47, s, 2H; 1.78, s, 3H; 1.08, s, 6H.

Preparations of 4: A. 4a. 1a (319 mg, 1.01 mmol) and 4 mL of MeCN were placed in a septum-capped flask that had been flushed with argon. The flask was cooled in ice, and into it was injected a cold solution of 343 mg (6.1 mmol) of isobutene in 4 mL of MeCN. After the mixture was stirred for 40 min, the color of **1a** had faded. Dry ether (60 mL) was added dropwise, causing precipitation of a white solid. Filtration and washing with ether gave 151 mg (0.32 mmol, 63%) of product, shown with NMR spectroscopy to be **4a**, mp 118−118.5 °C (dec). GC of the filtrate gave 0.616 mmol (61%) of Th. NMR (CD_3CN), δ (J), ^1H: 8.59, m, 4H; 8.17 (7.6, 1.7), td, 2H overlapping 8.15 (7.6, 1.7), td, 2H; 4.01, s, 2H; 1.63, s, 6H. ^{13}C: 137.0, 136.9, 136.7, 136.4, 124.7, 123.4, 65.1, 48.0, 26.7.

4a′. A similar procedure with 704 mg (1.95 mmol) of **1a′** and 1.5 g (27 mmol) of isobutene gave 315 mg (0.560 mmol, 58%) of **4a′**.

B. 4b (129 mg, 0.27 mmol, 40%), mp 88−89 °C (dec), was obtained from reaction of 358 mg (1.14 mmol) of **1a** with 0.7 mL (6.5 mmol) of 2-methylbutene. Attempts to purify **4b** by reprecipitation caused its decomposition. ^1H NMR (CD_3CN), 300 MHz, δ (J): 8.61−8.56, m, 4H; 8.19−8.14, m, 4H; 3.96 (1.5), d, 2H; 1.87−1.63, m, 2H; 1.54, s, 3H; 1.12 (7.4), t, 3H.

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C. 4c. To a suspension of 416 mg (1.32 mmol) of **1a** in 5 mL of MeCN cooled in ice was added 4 mL of a 2 M solution of 2-methy-2-butene in THF. Reaction was fast. Addition of 80 mL of ether and washing of the filtered product with ether gave 174 mg (0.358 mmol, 54%) of **4c**, mp 103−105 °C (dec). Although quite unstable in MeCN,[3] **4c** was able to be used to prepare **5o**−**t**. We were also able to record its ^{1}H NMR (CD_3CN) spectrum, the aromatic portion of which, however, was poorly resolved; δ (*J*): 8.67−8.65, m, 1H; 8.63−8.57, m, 3H; 8.21−8.17, m, 4H; 4.20 (7.0), q, 1H; 1.68, s, 3H; 1.58 (7.5), d, 3H; 1.47, s, 3H.

Preparation of 5 (Method 2). An example is given with **5a**, 5-[2-[(1-methoxyethylidene)ammonio]-2-methylpropyl]-thianthrenium diperchlorate. **4a** (89 mg, 0.19 mmol) was placed in a three-necked, septum-capped flask that had been flushed with argon. Dried MeCN (10 mL) was injected through the septum, followed by 0.10 mL (2.5 mmol) of MeOH. The mixture was stirred at room temperature for 24 h, and the solvent was removed with a current of air. The residue was shown with NMR spectroscopy not to contain **4a**. The residue was dissolved in MeCN, and ether was added to precipitate 30 mg (0.055 mmol, 30%) of **5a**. Reprecipitation and drying gave **5a**, mp 164−165 °C (dec). Anal. Calcd for $C_{19}H_{23}NO_9Cl_2S_2$: C, 41.9; H, 4.23; N, 2.57; Cl, 13.1; S, 11.8. Found: C, 42.2; H, 4.35; N, 2.62; Cl, 13.7; S, 11.6. NMR (CD_3CN), δ (*J*), ^{1}H: 9.33, br s, 1H; 8.25 (8.0, 1.5), dd, 2H; 8.06 (8.0, 1.0), dd, 2H; 7.90 (7.6, 1.2), td, 2H; 7.80 (7.8, 1.2), td, 2H; 4.22, s, 2H; 4.12, s, 3H; 2.23, S, 3H; 1.59, S, 6H. ^{13}C: 181.6, 137.5, 136.2, 135.0, 131.3, 131.2, 118.2, 63.1, 59.0, 48.1, 26.4, 18.9.

Preparation of 5a (Method 1). A suspension of 406 mg (1.28 mmol) of **1a** in 5 mL of MeCN was cooled in ice. A cold solution of 1.04 g (18.6 mmol) of isobutene and 0.15 mL(3.7 mmol) of MeOH in 5 mL of MeCN was added to the suspension of **1a**. The mixture was stirred for 1 h at 0 °C and at room temperature overnight. Addition of 60 mL of dry ether gave 80 mg (0.147 mmol, 23%) of a white solid, shown with NMR spectroscopy to be **5a**.

Preparation of 5g (Method 1). A similar experiment with 378 mg (1.20 mmol) of **1a** in EtCN and with stirring only at 0 °C for 1 h gave a mixture of **4a** and **5g** in a 4/1 ratio. This mixture was redissolved in MeCN, to which ether was added dropwise to precipitate first 115 mg of **4a** and then 22 mg (0.039 mmol, 7%) of **5g**, mp 148−149 °C (dec). Anal. Calcd for $C_{20}H_{25}NO_9Cl_2S_2$: C, 43.0; H, 4.48; N, 2.51; Cl, 12.7; S, 11.5. Found: C, 42.8; H, 4.53; N, 2.37; Cl, 13.1; S, 11.1. NMR (CD_3CN), δ (*J*), ^{1}H: 8.94, br s, 1H; 8.19 (8.0, 1.5), dd, 2H; 8.02 (8.0, 1.0), dd, 2H; 7.86 (7.8, 1.0), td, 2H; 7.75 (7.6, 1.2), td, 2H; 4.18, s, 2H; 4.14, s, 3H; 2.51 (7.5), q, 2H; 1.55, s, 6H; 1.17 (7.5), t, 3H. ^{13}C: 184.9, 137.5, 136.2, 135.0, 131.8, 131.3, 62.9, 59.4, 48.6, 26.5, 25.6, 9.75.

All other **5** products were prepared by one of these methods. Each of the products **5i**−**n** from 2-methylbutene, when first precipitated, was found with NMR spectroscopy to contain a small amount of the corresponding product (**5o**−**t**), from 2-methyl-2-butene. For example, **5i** contained some **5o**, and **5j** contained some **5p**. Each of **5i**−**n** was freed of its contaminant by reprecipitation and crystallization. The cause of the contamination of series **5i**−**n** by series **5o**−**t** was traced to isomerization of 2-methybutene to 2-methyl-2-butene during reaction by method 1, and not, as was first feared, from contamination of our 2-methylbutene by 2-methyl-2-butene. Isomerization of the former alkene into the latter by $HClO_4$ in MeCN was shown to occur independently. NMR data and melting points of **5** are listed in Supporting Information.

Decomposition of 4a and 4a′: A. 4a in CD_3CN. A solution of **4a** was kept in a foil-wrapped NMR tube for 5 days. The NMR spectra then were δ ^{1}H 4.67, s, 2H; 1.50, s, 6H and δ ^{13}C 182.0 (−C=O), 85.2 (CH_2), 64.2 (quat), 26.4 (CH_3) ppm.

On a larger scale, a solution of 174 mg (0.369 mmol) of **4a** in 8 g of CD_3CN was monitored with NMR spectroscopy until the signals from **4a** were no longer visible. The solvent was removed under vacuum, and the residue was washed with ether to remove Th, leaving a sticky solid whose NMR spectrum consisted of four major peaks, divisible with integration into two sets of two peaks, namely, δ: 4.67 and 1.50 ppm and 4.02 and 1.46 ppm. The solid was placed on a column of silica gel, which was eluted with petroleum ether/dichloromethane to remove remaining Th and next with ethyl acetate to give a sticky solid whose NMR spectrum was consistent with the formation of 2-(d_3-acetylamino)-2-methylpropanol, namely: δ ^{1}H 6.41, br s, 1H; 4.53, br s, 1H; 3.43, s, 2H; 1.18, s, 6H and δ ^{13}C 172.5 (−C=O), 70.2 (CH_2), 56.3 (quat), 24.3 (2 CH_3) ppm.

B. 4a′ in MeCN. A solution of 315 mg (0.560 mmol) of **4a′** in 25 mL of MeCN was kept for 25 days at room temperature. The solvent was removed with a current of air, and the residue was washed with ether to remove Th, leaving a sticky solid whose ^{1}H and ^{13}C NMR spectra were divisible into two sets of peaks consistent with the presence of **6-H**$^+$ and **7-H**$^+$. That is, for **6-H**$^+$: δ ^{1}H 4.64, 2.34, 1.49 and δ ^{13}C 177.9, 85.0, 64.2, 26.4, 14.4 ppm. For **7-H**$^+$: δ ^{1}H 4.03, 2.08, 1.35 and δ ^{13}C 171.3, 68.6, 56.3, 22.8, 20.8 ppm. The ^{1}H NMR spectra now show the presence of the methyl group from solvent MeCN, differing from spectra of reaction in CD_3CN.

Reaction of 6 in $CD_3CN/HClO_4$. The NMR spectra of a solution of **6** in CD_3CN were recorded at 500 MHz. δ ^{1}H: 3.85, s, 2H; 1.83, s, 3H; 1.16, s, 6H. δ ^{13}C: 162.9, 79.6, 68.0, 28.6, 14.0. After addition of an equimolar amount of $HClO_4$, the spectra were recorded again, including DEPT, HQMC, and HMBC. Two groups of peaks were discernible. The larger group (**6-H**$^+$) had δ ^{1}H 4.64, s, 2H; 2.33, s, 3H; 1.48, s, 6H and δ ^{13}C 177.6, 84.9, 64.3, 26.5, 15.0 ppm. The smaller group (**7-H**$^+$) had δ ^{1}H 4.03, s, 0.26H; 2.08, s, 0.28H; 1.36, s, 0.55H and δ ^{13}C 171.2, 68.5, 56.6, 22.8, and 20.8 ppm. The NMR spectra were then recorded at 300 MHz over a period of 16 days, during which time the ratio of peaks **7-H**$^+$/**6-H**$^+$ increased as follows: 0.1 (1 day), 1.0 (5 days), 2.0 (9 days), 3.3 (12 days), and 5.5 (16 days).

Preparation of 2,4,4-Trimethyloxazolinium Perchlorate (6-$HClO_4$). A solution of 0.25 mL (2.0 mmol) of **6** in 0.17 mL (2.0 mmol) of 70% $HClO_4$ was placed on a column of silica gel. Elution with ethyl acetate gave first 134 mg of a sticky solid, shown with ^{1}H NMR to be a mixture of **6-H**$^+$ and **7-H**$^+$ in a 3/4 ratio. Continued elution and evaporation of the solvent gave 275 mg (1.29 mmol) of crystalline **6-$HClO_4$**, mp 118−121 °C. NMR (CD_3CN), δ ^{1}H: 4.67, s, 2H; 2.35, s, 3H; 1.50, s, 6H. ^{13}C: 178.2 (−C=O), 85.2 (CH_2), 64.3 (quat), 26.4 (2 CH_3), 14.6 (CH_3) ppm. NMR (D_2O), δ ^{1}H: 4.53, s, 2H; 2.20, s, 3H; 1.36, s, 6H.

Preparation of 7-$HClO_4$. A solution was made of 2 mL (0.016 mmol) of **6** in 1.4 mL (0.016 mmol) of $HClO_4$ in 10 mL of D_2O. One drop of this solution was dissolved in D_2O, and the ^{1}H NMR spectrum was recorded at 300 MHz at timed intervals. In 20 h, the initial spectrum of δ 4.56, s, 2H; 2.22, s, 3H; 1.35, s, 6H had changed almost completely into δ 4.00, s, 2H; 2.02, s, 3H; 1.25, s, 6H. The original peaks were visible but too small to be integrated. After 66 h, only peaks at 3.99, 2.01, and 1.24 ppm were visible. At 500 MHz, the ^{13}C NMR (DEPT) spectrum was 173.0 (−C=O), 68.1 (CH_2), 53.0 (quat), 21.3 (2 CH_3), and 19.5 (CH_3). Neutralization of a sample of this solution with solid NaOH resulted in the formation of **8**, as shown by NMR spectra δ ^{1}H 3.46, s, 2H; 1.78, s, 3H; 1.08, s, 6H and δ ^{13}C 173.4 (−C=O), 66.6 (CH_2), 54.3 (quat), 22.5 (2 CH_3), 22.4 (CH_3).

D_2O was removed from the bulk of the solution under reduced pressure. The viscous residue was triturated with ether, and the ether was evaporated with a current of air to leave 3.6 g (0.016 mmol, 100%) of white solid, **7-$HClO_4$**, mp 117−118 °C. NMR (CD_3CN), δ, ^{1}H: 6.5, br s; 4.03, s, 2H; 2.09, s, 3H; 1.36, s, 6H. ^{13}C (DEPT): 171.1, 68.4 (CH_2), 56.8 (quat), 22.7 (2 CH_3), 20.8 (CH_3).

Reaction of 8 in $CD_3CN/HClO_4$. The NMR spectra of a solution containing equimolar amounts of **8** and $HClO_4$ were recorded and consisted of three sets of peaks attributable to

8-H$^+$, **6-H**$^+$, and **7-H**$^+$ as follows. **8-H**$^+$, δ ^{1}H: 3.67, s, 2H; 2.28, s, 3H; 1.35, s, 6H. ^{13}C: 177.6 (−C═O), 68.2 (CH_2), 61.3 (quat), 23.3 (2 CH_3), 21.1 (CH_3). **6-H**$^+$, δ ^{1}H: 4.66, s, 0.12H, 2.33, s, 0.19H; 1.49, s, 0.37H. **7-H**$^+$, δ ^{1}H: 4.03, s, 0.03H, 2.08, s, 0.05H; 1.35 overlap with the peak from **8-H**$^+$. The ^{1}H NMR spectrum was recorded at 300 MHz over a period of 10 days. Overlap of the peaks from **7-H**$^+$ and **8-H**$^+$ at 1.35 ppm prevented their diagnostic use. Integrations of the remaining peaks showed the decrease in intensity of those from **8-H**$^+$ and increase mainly of those from **6-H**$^+$. After 10 days, the peaks from **8-H**$^+$ were too small to integrate. The ratio of **6-H**$^+$**/7-H**$^+$ was 5/1.

Attempted Preparation of 7: A. In $CHCl_3$. A solution of 936 mg (3.16 mmol) of **12** and 0.3 mL (3.14 mmol) of 2-amino-2-methylpropanol was heated at 80 °C in a sealed vessel for 7 days.[11] The solvent was distilled off, and the residue was placed under high vacuum to give 83 mg (0.736 mmol, 23%) of **6**, as shown by its ^{1}H NMR spectrum. The remainder of the residue was placed on a column of silica gel, 60−200 mesh. Elution with dichloromethane gave 740 mg (2.91 mmol, 92%) of ethyl (2, 4-dinitrophenyl) acetate as a red oil. Continued elution with ethyl acetate gave 239 mg (2.01 mmol, 64%) of **8**, as shown by its ^{1}H NMR spectrum. When **8** was heated in $CDCl_3$ at 80 °C, its ^{1}H NMR spectrum changed slowly into that of **6**. The ratio of **6/8** was 15/85 (1 day), 30/70 (3 days) and 65/35 (7 days).

B. In $CDCl_3$. A similar solution in $CDCl_3$ was heated for 3 days. A drop of the solution was diluted with $CDCl_3$ for NMR spectroscopy. The complex ^{1}H spectrum showed the presence of **12** and ethyl (2,4-dinitrophenyl) acetate in a 25/75 ratio. Despite the complexity of the spectrum, it was possible with the use of data from authentic compounds to detect the signals from 2-amino-2-methylpropanol, **6**, and **8**. The dominant component was **8**.

A solution of 592 mg (2.0 mmol) of **12** and 0.21 mL (2.0 mmol) of *tert*-butylamine in 20 mL of $CHCl_3$ was heated at 80 °C. An aliquot was taken periodically and diluted with $CDCl_3$ for 300 MHz ^{1}H NMR spectroscopy. Peaks attributable to *tert*-butylacetamide appeared slowly at δ 1.91, s, 3H; 1.32, s, 9H.[15] After 7 days, 50% of **12** had reacted.

Ethyl 2-(2,4-Dinitrophenyl)acetoacetate (12) was prepared as described,[11] mp 93.5−95 °C; lit. mp 93−94 °C.[14] Its NMR spectra (Supporting Information) were recorded for use in following its reactions with 2-amino-2-methylpropanol.

X-ray Crystallography. Details are given in Supporting Information.

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Supporting Information Available: General experimental procedures, ^{1}H and ^{13}C NMR data for compounds **5b**−**f**, **5h**−**u**, **6**−**8**, **12**, Figures S1−S15 (Ortep diagrams), and tables giving X-ray crystallographic data for compounds **5a**−**c**, **5e**−**g**, **5i**−**l**, **5n**−**r**. This material is available free of charge via the Internet at http://pubs.acs.org.

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