Reactions of Thianthrene Cation Radical with Acyclic and Cyclic Alcohols[1]

Henry J. Shine* and Wang Yueh

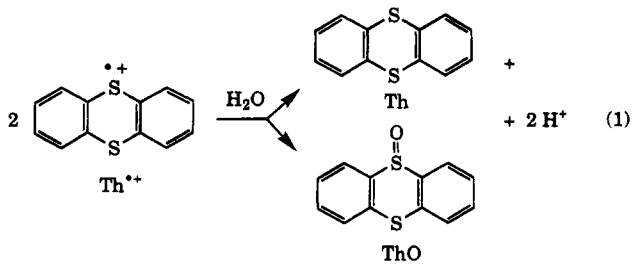
Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409

Received February 16, 1994®

Thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) reacted readily with cycloalkanols (C_5, C_7, C_8, and C_{12}), alkan-2-ols (C_3, C_5, C_6, and C_8), 3-hexanol, neopentyl alcohol, a number of benzyl alcohols, *dl*- and (*S*)-1-phenylethanol, cyclopentyl- and cyclohexylmethanols, the *exo*- and *endo*-borneols, and norborneols. Reactions were carried out with an excess of the alcohol in acetonitrile solution containing 2,6-di-*tert*-butyl-4-methylpyridine. Products were alkenes, ethers, and *N*-substituted acetamides, depending on the structure of the alcohol. Thianthrene (Th) and its 5-oxide (ThO) were formed in equal amounts. The sum of amounts of products from the alcohol was equal to the amount of ThO. All reactions are interpretable on the basis of the ultimate formation and further reactions of a 5-alkoxythianthreniumyl ion ($ROTh^+$). The predominant formation of nortricyclene from the norborneols is striking and is discussed. Swern–Moffatt-type oxidations of the alcohols were not observed.

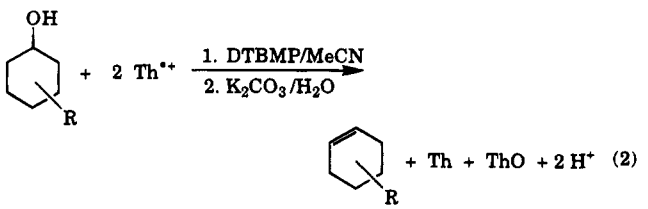
Introduction

Reactions of thianthrene ($Th^{\bullet+}$) and other organosulfur cation radicals with nucleophiles have been reported by a number of workers and have provided a foundation for understanding the chemistry of cation radicals as a class of reactive intermediates.[2-4] The very first of these reactions to be studied was of $Th^{\bullet+}$ with water. This simple reaction, whose products are equal amounts of thianthrene (Th) and its 5-oxide (ThO) (eq 1), eventually became the



(1)

prototype of the mechanistic complexity of reactions of $Th^{\bullet+}$, for which a solution was provided in time by Parker[3] and Vieil.[5] It is surprising, then, that no analogous study of reactions of $Th^{\bullet+}$ with alcohols has been reported. A study of this kind was, in fact, begun in these laboratories approximately 20 years ago but was thwarted by the lack of suitable GC and GC/MS equipment.[6] We have now carried out a systematic investigation of reactions of $Th^{\bullet+}$ with a number of classes of alcohols. Reactions of some cyclohexanols have already been reported briefly, and it was shown, particularly with use of [^{18}O]cyclohexanol, that the oxygen atom of a cyclohexanol was transferred to $Th^{\bullet+}$ with quantitative formation of ThO and a cyclohexene.[7] The reactions (eq 2) were, in fact, stoichiometric

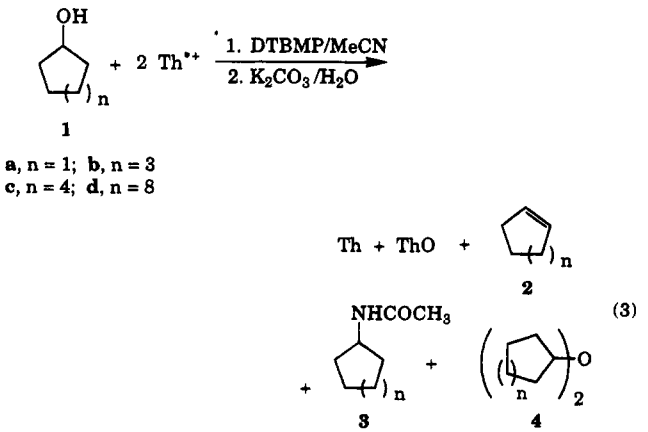


(2)

analogues of the water reaction (eq 1). We report now the reactions of $Th^{\bullet+}$ with a number of acyclic and cyclic alcohols, all carried out in acetonitrile solution in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) to prevent acid-catalyzed reactions of the alcohol. All of the results that follow can be understood on the basis that a 5-alkoxythianthreniumyl ion is formed and leads to substitution and elimination reactions of the S_N1/S_N2 and E1/E2 types.

Results and Discussion

Cyclopentan-, Cycloheptan-, Cyclooctan-, and Cyclododecanol (1a–d). Products of reaction were mostly cycloalkenes and *N*-cycloalkylacetamides (eq 3).



(3)

Cyclopentanol (**1a**) gave a small amount (4%) of dicyclo-

® Abstract published in *Advance ACS Abstracts,* June 1, 1994.

(1) Taken in part from the Ph.D. dissertation of Wang Yueh, Texas Tech University, Dec 1993.

(2) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 155–278.

(3) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55–157.

(4) Shine, H. J. In *The Chemistry of the Sulphonium Group*; Stirling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981; Chapter 14.

(5) Vieil, E.; Maurey-Mey, M.; Cauquis, G. *Electrochim. Acta* **1984**, *29*, 1009.

(6) By Dr. Kyongtae Kim, now at Seoul National University.

(7) Shine, H. J.; Yueh, W. *Tetrahedron Lett.* **1992**, *33*, 6583.

0022-3263/94/1959-3553$04.50/0

Table 1. Products of Reaction of Cycloalkanols (1a–d) with $Th^{\bullet+}ClO_4^-$

alcohol[a]	$Th^{\bullet+}ClO_4^-$, mmol × 10^2	products,[b] mmol × 10^2 (%)[c] Th	ThO	2, ene	3, amide	4, ether	R[d]
1a	81	41 (51)	40 (49)	38 (96)		1.6 (4.0)	99
1b	80	42 (53)	38 (48)	27 (73)	10 (27)		97
1c	80	42 (53)	39 (49)	31 (79)	8.1 (21)		100
1d	81	40 (49)	37 (46)	34 (100)			92

[a] Used in excess. **1a**, cyclopentanol (three runs); **1b**, cycloheptanol (four runs); **1c**, cyclooctanol (four runs); **1d**, cyclododecanol (three runs). [b] GC assay of all products was made with column A except for **2a** (column D) and **2b** (column E). [c] For Th and ThO, percent of $Th^{\bullet+}ClO_4^-$, for **2–4**, percent of sum of products **2–4**. [d] [mmol(**2–4**)/mmol ThO]100.

pentyl ether (Table 1). Cycloalkene **2** was obtained predominantly from **1a** and entirely from cyclododecanol (**1d**), whereas both cycloheptanol (**1b**) and cyclooctanol (**1c**) gave 20–30% of the acetamide (**3b** and **3c**). The results are understandable in the formation of an alkoxysulfonium ion ($ROTh^+$, R = cycloalkyl) (eq 4)

$$2Th^{\bullet+} + ROH \rightarrow Th + ROTh^+ + H^+ \qquad (4)$$

which then partitions into products, the partioning route depending on the structure of R. Formation of **3** (eq 3) calls for formation of the cycloalkyl carbenium ion and its Ritter reaction with the solvent. That occurs with the C_7 and C_8 but not with the C_5 and C_{12} cycloalkanols, a difference which is in accord with the different rates of acetolysis of their tosylates[8,9] and the solvolysis of the corresponding cycloalkyl halides.[10] That is, carbenium ion formation is favored by the C_7 and C_8 rings as compared with the C_5 and C_{12} rings. It is noted, also, that only cyclohexene was obtained from cyclohexanol,[7] whose tosylate solvolyzes at the lowest rate of all. Cyclohexene was the major product (70–80%) of the solvolysis of cyclohexyl tosylate in aqueous acetic, formic, and trifluoroacetic acids.[11] The formation of cycloalkene (**2**, eq 3) can be attributed to elimination encouraged by the presence of the good leaving group (OTh) and being mechanistically somewhere in the spectrum of the E2 types. The formation of 4% of **4a** is attributed to S_N2 displacement of the cyclopentyl group from $ROTh^+$ by cyclopentanol, a reaction not seen with the larger cycloalkyl reactants. The last column (R) in Table 1 (and in all of the other tables) relates the sum of the products to the amount of ThO. In principle, R should always be 100, since regardless of what product is formed from R in $ROTh^+$, the oxygen atom remains as ThO. Column 3 in Table 1 (and in other tables) reports the amount of Th. In principle, this, too, should be equal to the amount of ThO, and our results are close to that. For convenience, neither Table 1 nor any of the other tables reports error limits for our assays. These were in the order of 2–3% (i.e., 0.01–0.015 mmol for Th and ThO).[1] A small excess of Th (over the amount of ThO) was always obtained, which we attribute in part to its inclusion in $Th^{\bullet+}ClO_4^-$, isolated as a solid.

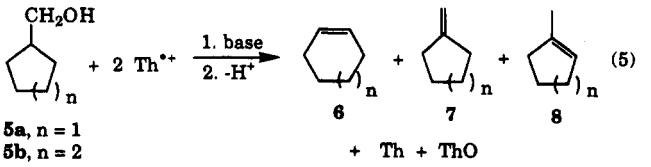
Cyclopentylmethanol (5a), Cyclohexylmethanol (5b), and 1-Methylcyclohexanol (MCH). The products

Table 2. Reaction of Cyclopentylmethanol (5a), Cyclohexylmethanol (5b), and 1-Methylcyclohexanol (MCH) with $Th^{\bullet+}ClO_4^-$

alcohol[a]	$Th^{\bullet+}ClO_4^-$, mmol × 10^2	products,[b] mmol × 10^2 (%)[c] Th	ThO	6	7	8	R[d]
5a	82	41 (50)	39 (48)	33[e] (86)	5.4[f] (14)		98
5b	80	41 (51)	38 (48)	3.7[g] (9.7)	2.5[h] (6.5)	32[i] (84)	101
MCH	80	40 (50)	40 (50)		0.9[h] (2.4)	37[i] (98)	95

[a] Used in excess. Number of runs averaged were for **5a** and **MCH** (four), **5b** (three). [b] GC assay of products was made with column A, except **6a**, **7a**, and **8a** (column B) and **6b**, **7b**, and **8b** (column F). [c,d] See Table 1 for protocol. [e] Cyclohexene. [f] Inseparable mixture of methylenecyclopentane and 1-methylcyclopentene. [g] Cycloheptene. [h] Methylenecyclohexane. [i] 1-Methylcyclohexene.

of these reactions with $Th^{\bullet+}$ are shown in eq 5 and listed in Table 2. It is not likely that the alkoxysulfonium ions



from **5a,b** will lose ThO and form the corresponding primary cycloalkylmethyl carbenium ions. The large amount of ring expansion product from **5a** (cyclohexene, **6a**) and the smaller amount (cycloheptene, **6b**) from **5b** must arise from expulsion of ThO by a migrating σ-bond. The secondary cycloalkyl carbenium ions that would arise from these migrations cannot have had a long enough existence as free carbenium ions for reaction with the solvent. Possibly, deprotonation by DTBMP was concomitant with rearrangement. We are unable to say whether only one or both of **7a** (methylenecyclopentane) and **8a** (1-methylcyclopentene) were obtained (14%) from **5a** since they were inseparable in our GC columns. On the other hand, **8b** amounted to 84% of the products from **5b** and must have arisen from hydride shift in accompanying an E1-like loss of ThO from $ROTh^+$. The absence of *N*-(cyclohexylmethyl)acetamide in the products, as well as the inherent disadvantages of a free, primary cyclohexylmethyl carbenium ion, speak against its formation. 1-Methylcyclohexene (**8b**), and a small amount of **7b**, were obtained also from MCH and are attributable to E1-like elimination in the corresponding tertiary $ROTh^+$.

Whether or not ring expansion occurs in cyclopentylmethyl and cyclohexylmethyl derivatives has been reviewed by Gutsche and Redmore.[12] **5a**-brosylate solvolyzes in acetic acid nearly six times faster than isobutyl brosylate, leading to the conclusion that σ-bond migration participated in ring-expansion solvolysis,[13] from which at 80 °C 71% of cyclohexene, 15% of cyclohexyl acetate, and 9% of cyclopentylmethyl acetate were formed.[14] In comparison, reaction of cyclopentylmethylamine with nitrous acid gave 76% of cyclohexanol, 19% of 1-methylcyclopentanol, and 5% of cyclopentylmethanol.[15] These results correspond in character with ours in that not only

(8) Heck, R.; Prelog, V. *Helv. Chim. Acta* **1955**, *38*, 1541.
(9) Brown, H. C.; Ham, G. *J. Am. Chem. Soc.* **1956**, *78*, 2735.
(10) Schotsmans, L.; Fierens, P. J. C.; Verlie, Th. *Bull. Soc. Chim. Belg.* **1959**, *68*, 580.
(11) Lambert, J. B.; Putz, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 6313.
(12) Gutsche, C. D.; Redmore, D. *Carbocyclic Ring Expansion Reactions*. In *Advances in Alicyclic Chemistry*; Hart, H., Karabatsos, G. J., Eds.; Academic Press: New York, 1968; Suppl. 1, pp 29–57.
(13) Felkin, H.; LeNey, G. *Bull. Soc. Chim. Fr.* **1957**, 1169.
(14) LeNey, G. *Compt. Rend.* **1960**, *250*, 368.
(15) Smith, P. A.; Baer, D. R.; Ege, S. N. *J. Am. Chem. Soc.* **1954**, *76*, 4564.

Table 3. Products of Reaction of Benzyl Alcohols ($XC_6H_4CH_2OH$, 9a–g) with $Th^{\bullet+}ClO_4^-$

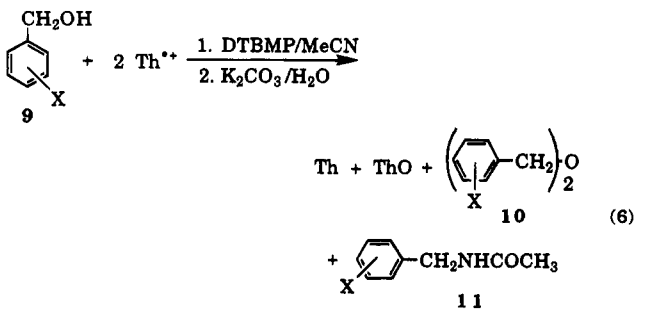
X	alcohol[a]	$Th^{\bullet+}ClO_4^-$, mmol × 10^2	products,[b] mmol × 10^2 (%)[c] Th	ThO	10	11	R^d
H	**9a**	81	42 (52)	39 (48)	35 (100)		90
o-Me	**9b**	80	39 (49)	40 (50)	14 (35)	26 (65)	100
m-Me	**9c**	80	41 (51)	39 (49)	18 (47)	20 (53)	97
p-Me	**9d**	82	42 (51)	41 (50)	17 (41)	25 (61)	102
p-F	**9e**	80	41 (51)	38 (48)	9 (25)	27 (75)	95
p-Cl	**9f**	80	41 (51)	36 (45)	21 (55)	17 (45)	106
p-Br	**9g**	81	41 (51)	39 (48)	11 (28)	28 (72)	100

[a] Used in excess. The number of runs averaged was four (**9a–c,e–g**) and three (**9d**). [b] GC assay of all products with column A. [c,d] See Table 1 for protocol.

a large amount of ring expansion but also isomerization of the incipient cyclopentylcarbinyl cation to the 1-methylcyclopentyl cation (our **7a/8a** and Smith's[15] 1-methylcyclopentanol) must have occurred. Insofar as the cyclohexylmethyl system is concerned, Kotani has reported that **5b**-mesylate at reflux in 50% aqueous acetic acid containing a small amount of sodium acetate gave 5% of ring expansion (**6b** and cycloheptanol), 51% of unrearranged products (**5b** and its acetate), and 43% of unexpanded but rearranged products, primarily **8b** (27%) and 1-methylcyclohexanol (15%).[16] Kotani regards the formation of **5b** and its acetate as arising from direct S_N2 reaction rather than from the unlikely formation of the cyclohexylcarbinyl cation. Others have found that **5b**-tosylate[17] and -mesylate[18] solvolyze in acetic acid without rearrangement. In contrast with **5a**-brosylate, **5b**-brosylate solvolyzes in acetic acid more slowly than isobutyl brosylate,[13] and with no trace of ring expansion, the major products being **5b**-acetate and **8b**.[14]

Thus, our results with the thianthreniumyl derivatives of **5a** and **5b** are in line with earlier experiences with more traditional leaving groups. Our obtaining none of the *N*-(cycloalkylmethyl)acetamides reflects the probable absence of the free primary carbenium ions, and the formation of only alkenes **6–8** reflects the presence of DTBMP in our solutions.

Benzyl Alcohols (9a–g). With the exception of benzyl alcohol (**9a**) all of these alcohols gave mixtures of the corresponding dibenzyl ether (**10a–g**) and *N*-benzylacetamide (**11b–g**), eq 6, Table 3. The formation of



(6)

acetamides **11** encourages us to propose that the corresponding benzyl carbenium ions were formed, stabilized by the electron-donating groups present in the rings. That **9a** gave only **10a** and none of **11a** suggests that **10a** and other ethers were formed in an S_N2 displacement of ThO whereas the amides were formed by S_N1 loss of ThO from the $ROTh^+$.

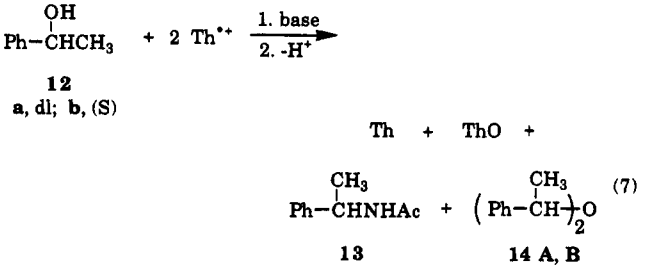
From the effect of pressure on rates of solvolysis of benzyl, *o*-methylbenzyl, and *p*-methylbenzyl chlorides in aqueous ethanol, Kwun and co-workers have deduced that the reactions occur by the S_N1 route.[19] Aronovitch and Pross have also studied solvolyses of benzyl halides and note that in the history of such studies the borderline nature of the solvolyses has made the assignment to either S_N1 or S_N2 processes particularly difficult. In their own work the transition through intimate, solvent-separated and free ion pairs is encountered.[20] Of course, with benzoxythianthreniumyl ions from the reactions of **9a–g** with $Th^{\bullet+}$, ion pairs are not involved.

Table 4. Products of Reaction of *dl*- (12a) and (*S*)-1-Phenylethanol (12b) with $Th^{\bullet+}ClO_4^-$

alcohol[a]	$Th^{\bullet+}ClO_4^-$, mmol × 10^2	products,[b] mmol × 10^2 (%)[c] Th	ThO	13	14A	14B	R^d
12a	81	41 (51)	40 (49)	15 (37)	14[e] (34)	12[e] (29)	103
12b	83	42 (51)	40 (48)	16 (40)	14[f] (35)	10[f] (25)	100

[a] Used in excess. Two runs for **12a**, one run for **12b**. [b] GC assay of all products with column E. [c,d] See Table 1 for protocol. [e] One of these is the *dl*-isomer and the other the meso-isomer. Distinguishing between them was not pursued. [f] One of these is the (*S,S*)-isomer and the other the meso-isomer.

1-Phenylethanol (12a,b). The products (Table 4 and eq 7) were *N*-(1-phenylethyl)acetamide (**13**) and a mixture



(7)

of bis(1-phenylethyl) ethers (**14A** and **14B**) and are diagnostic of an S_N1 reaction. That is, the *dl*-alcohol (**12a**) gave 37% of **13** and 63% of two ethers. The two ethers were evident and separated, but not at the base-line level, in our GC traces. They are numbered as **14A** and **14B**. The same products will be formed whether the *dl*-alkoxysulfonium ion reacts with **12a** by S_N1 or S_N2 routes, namely racemic **13** and a mixture of racemic and *meso*-**14**. Although two ethers were obtained from **12a**, we are unable to distinguish one from the other under our experimental conditions and GC assay. But, distinction is not critical to our deduction. The use of **12b** was sufficiently diagnostic for our purpose. If **12b** reacted with its alkoxysulfonium ion in an S_N2 way, only *meso*-**14** could be formed. Reaction by an S_N1 route must give both meso- and (*S,S*)-**14**. The latter cannot be distinguished from the racemate by GC, so that the same GC peaks should be observed as from using **12a**. This was the case

(16) Kotani, R. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1767.
(17) Huisgen, R.; Seidl, G. *Chem. Ber.* **1963**, *96*, 2740.
(18) Bly, R. B.; Dryden, H. L., Jr. *Chem. Ind.* **1959**, 1287.
(19) Kwun, O. C.; Kyong, J. B.; Shin, Y. K. *J. Korean Chem. Soc.* **1985**, *30*, 40. Kwun, O. C.; Kyong, J. B. *Bull. Korean Chem. Soc.* **1985**, *6*, 259.
(20) Aronovitch, H.; Pross, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 540.

Table 5. Products of Reaction of *exo*- (15a) and *endo*-Norborneol (15b) and *exo*- (20a) and *endo*-Borneol (20b) with $Th^{\cdot+}ClO_4^-$

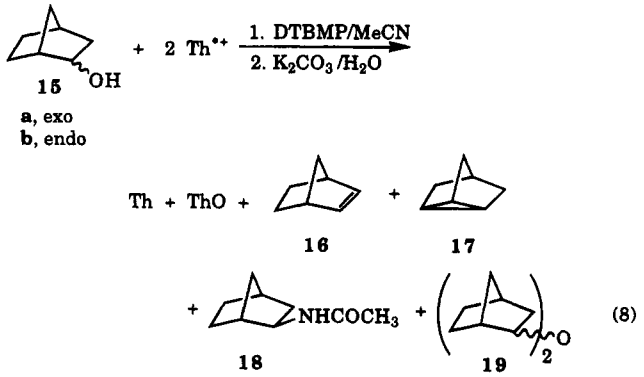
alcohol[a]	$Th^{\cdot+}ClO_4^-$, mmol × 10^2	products,[b] mmol × 10^2 (%)[c]								R^d
		Th	ThO	16	17	18	19	21	22	
15a	81	41 (51)	39 (48)	2.9 (7.5)	20 (51)	11 (28)	5.0 (13)			100
15b	81	41 (51)	40 (49)	4.3 (11)	31 (77)		5.1 (13)			101
20a	82	43 (52)	38 (46)					tr	36 (100)	95
20b	81	42 (52)	38 (47)					0.7 (1.9)	37 (98)	99

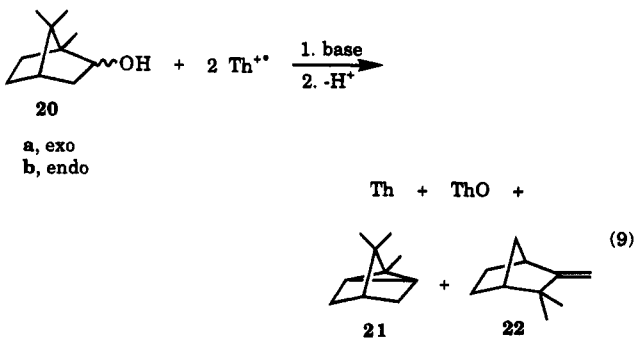
[a] Used in excess. Four runs were averaged for **15a,b** and **20b**; three runs for **20a**. [b] Column A was used for all products except **16** and **17** (column D). [c,d] See Table 1 for protocol.

(Table 4). One would anticipate that in S_N1 routes equal amounts of *meso*- and *dl*-**14** should be obtained from **12a**, and equal amounts of *meso*- and (*S,S*)-**14** from **12b**, and that each should give the same amount of **13**. These relationships are seen reasonably well for **13** from **12a,b** and for the ethers from **12a**, but not so well from **12b**, a result possibly arising from incomplete base-line separation of the gc peaks.

From deuterium-[21] and ^{13}C-kinetic isotope[22] effects, it has been deduced that solvolyses of 1-phenylethyl halides in alcohol and aqueous alcohol occur by an S_N1 mechanism.

Norborneols (15a,b) and Borneols (20a,b). The products obtained from these bicyclic alcohols are listed in Table 5 and shown in eqs 8 and 9. It is clear from the





predominant formation of camphene (**22**) and small amounts of tricyclene (**21**) from both **20a** and **20b** that the reaction follows along customary S_N1 lines. Solvolyses of the corresponding chlorides, for example, gave mainly **22** and small amounts of **21**. In alcohol solvents some of the ethers expected from carbenium ion formation were also obtained.[23-25] In our reactions of **20a,b**, rearrangement following or coincident with formation of the 2-bornyl carbenium ion (with departure of ThO) is responsible for the large amount of **22**. We saw no formation of ethers or acetamides, a finding that is attributable to the ease of deprotonation of the tertiary carbenium ion formed in the rearrangement, particularly by the action of added DTBMP and the bulky nature of the alcohol.

In contrast with **20a,b** the results of reactions of the norborneols (**15a,b**) are quite unlike most of those in the extensive literature of norbornyl esters and halides. This literature, beginning with some of its earliest mechanistic works,[26,27] shows that in almost all solvolyses of unsubstituted exo- and endo-derivatives, the predominant (often exclusive) product is the solvent-substituted exo-derivative.[28]

The data in Table 5 show, however, that the dominant product of the $Th^{\cdot+}ClO_4^-$ reactions is nortricyclene (**17**). Certainly, substitution has occurred in the formation of 28% of *exo*-*N*-norbornylacetamide (**18**) from **15a** and 5% of norbornyl ether (**19**) from both **15a** and **15b**, but **17** is by far the major product. As far as we are aware, the only other reports of large amounts of nortricyclenes in norbornyl reactions are by Grob and co-workers from solvolyses in 70% aqueous dioxane.

From solvolyses of the tosylates of **15a** and **15b**, themselves, **17** was obtained in 6% and 7% yields, along with 94% and 93% of **15a** and **15b**, respectively. However, solvolyses of some 6- and 7-substituted norbornyl tosylates, frequently in the presence of added triethylamine, gave very large yields of the corresponding nortricyclenes.[29-34] Sargent[35] records the formation of mixtures of **17** and **16** (norbornene) from acetolyses of **15a**-brosylate. At 75 °C, 12.7% of the mixture was obtained, with a **17**/**16** ratio of

(21) Shiner, V. J., Jr.; Buddenbaum, W. E.; Murr, B. L.; Lamaty, G. *J. Am. Chem. Soc.* **1968**, *90*, 418.
(22) Stothers, J. B.; Bourns, A. N. *Can. J. Chem.* **1960**, *38*, 923.
(23) Beltrame, P.; Bunton, C. A.; Dunlop, A.; Whittaker, D. *J. Chem. Soc.* **1964**, 658.
(24) Bunton, C. A.; O'Connor, C. *Chem. Ind.* **1965**, 1182.
(25) Beltrame, P.; Bunton, C. A.; Whitaker, D. *Chem. Ind.* **1960**, 557.
(26) (a) Winstein, S.; Trifan, D. *J. Am. Chem. Soc.* **1952**, *74*, 1147, 1154. (b) Winstein, S.; Clippinger, E.; Howe, R.; Vogelfanger, E. *J. Am. Chem. Soc.* **1965**, *87*, 376.
(27) Roberts, J. D.; Lee, C. C.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 4501.
(28) Norlander, J. E.; Gruetzmacher, R. E.; Kelly, W. J.; Jindal, S. P. *J. Am. Chem. Soc.* **1973**, *96*, 181.
(29) Fuso, F.; Grob, C. A.; Sawlewicz, P.; Yao, G. W. *Helv. Chim. Acta* **1986**, *69*, 2098.
(30) Flury, P. Grob, C. A. *Helv. Chim. Acta* **1983**, *66*, 1971, 1991.
(31) Grob, C. A.; Herzfeld, D. A. *Helv. Chim. Acta* **1982**, *65*, 2443.
(32) Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 87.
(33) Grob, C. A.; Günter, B.; Hanreich, R. *Helv. Chim. Acta* **1981**, *64*, 2312.
(34) Fischer, W.; Grob, C. A.; Hanreich, R.; von Sprecher, G.; Waldner, A. *Helv. Chim. Acta* **1981**, *64*, 2298.
(35) Sargent, G. D. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience, New York, 1972; Vol. III, Chapter 24.

Table 6. Reaction of Acyclic Secondary Alcohols 23a–d with $Th^{\bullet+}ClO_4^-$

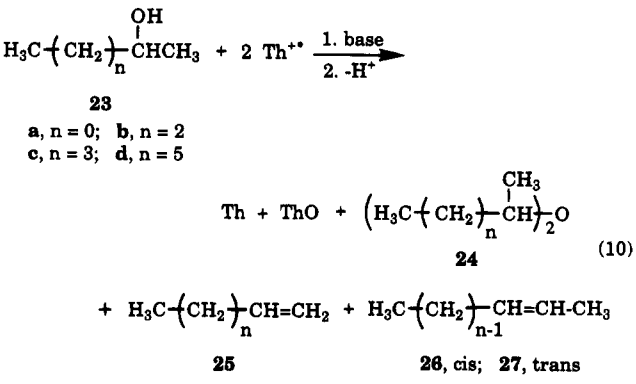
alcohol[a]	$Th^{\bullet+}ClO_4^-$, mmol × 10^2	products,[b] mmol × 10^2 (%)[c] Th	ThO	24	25	26	27	R^d
23a	80	41 (51)	36 (45)	8.6 (24)	27 (76)			99
23b	82	43 (52)	42 (51)		3.6 (8.8)	37[e] (91)		97
23c	81	42 (52)	40 (49)		4.9 (12)	14 (35)	21 (53)	100
23d	79	41 (52)	37 (47)		5.5 (16)	11 (32)	18 (52)	93

[a] Used in excess. Four runs were averaged in each case. [b] Column A for Th and ThO, column D for **24a** and **25a**, column B for all others. [c,d] See Table 1 for protocol. [e] The cis- and trans-isomers could not be separated in the GC columns that were used.

39:1.[36] Gassman and Marshall[37] obtained 29% of 7-nortricylenone from solvolysis of 7,7-dimethoxy-*endo*-norbornyl tosylate.

Solvolyses of norbornyl derivatives gave rise to the concept of the nonclassical norbornyl cation[26,27] and the great controversy over its validity. Recently, what could be the last emphatic denial[38] and just as emphatic validation of the nonclassical ion have appeared.[39] It is not our purpose to take up the pros and cons of this controversy. Suffice it to note, though, that Lenoir and co-workers[39] have pointed out that all of the solvents used in solvolyses of **15a,b** (and analogues) have been nucleophilic and have participated by their nucleophilicity in affecting the exo/endo rate ratio. These workers have deduced (in support of the nonclassical ion) that as the ionizing power of a solvent increases and its nucleophilicity decreases the transition state resembles more closely the intermediate cation so that σ-participation becomes more pronounced and the exo/endo rate ratio increases. Grob and co-workers deduce analogously[29] that the similarity in the distribution of products (substituted **15a** and substituted **17**) obtained from their series of *exo*- and *endo*-tosylates suggests that a common intermediate is involved, namely the bridged 2-norbornyl cation, and that this also favors formation of the nortricylenes, a point also made earlier by Winstein.[26b] Thus, our reactions of **15a,b** with $Th^{\bullet+}ClO_4^-$ in acetonitrile may exemplify the conditions needed for formation of a bridged ion that is not readily captured by the poorly nucleophilic solvent, and consequently, in the presence of DTBMP, moreover, ends up as **17**. Walling looks upon the 2-norbornyl cation as a corner-protonated cyclopropane,[40] and this, too, would suit our product findings well. We have a problem, however, in that **18** (28%) was formed from **15a** but not from **15b**, which, instead, led to the greater yield of **17** (77% vs 51%). It may be that the difference is in the ready formation of the longer-lived bridged ion from **15a** as contrasted with concomitant deprotonation and cyclization of an as yet unbridged ion from **15b**. Table 5 shows also that small amounts (7.5% and 11%) of norbornene (**16**) were obtained. This, too, is not a customary product in solvolyses of unsubstituted derivatives of **15a,b**. Brown obtained 99.5% of **16** and 0.5% of **17** from **15a**-tosylate in a deliberately contrived exo-cis E2 reaction.[41] It is evident then, by analogy, that our reactions do not have that character and that our **16** must originate from competitive deprotonation (by DTBMP) of the cation formed with the departure of ThO from an alkoxythianthreniumyl ion. Substantial amounts of substituted **16** were obtained from solvolyses of 6-substituted-**15a** tosylates, also in the presence of added base (Et_3N),[33] and the factors responsible for formation of norbornenes in these cases may be the same as those in ours.

Secondary Alcohols (23a–d and 28). With the exception of 2-propanol (**23a**) all of the 2-alkanols (**23b–d**) gave only alkene products. **23a** gave 24% of diisopropyl ether and 76% of propene. The other alcohols gave larger amounts of 2-alkenes than 1-alkene, and among the 2-alkenes more of the *trans*-isomer than the *cis*-isomer was obtained (Table 6 and eq 10). These results are typical



(10)

of Saytzeff-type eliminations. The fact that *N*-alkylacetamides were not obtained indicates that long-lived free carbenium ions were not formed and suggests that elimination was concerted, albeit with advanced loss of the good leaving group, ThO. The diisopropyl ether obtained from 2-propanol is attributed to S_N2 displacement, a reaction inhibited with **23b–d** by the size of the larger 2-alkanols. Similar elimination results were obtained with 3-hexanol (**28**) and are described in the Experimental Section. Both 2- and 3-hexene were obtained in the ratio 69:31.

Neopentyl Alcohol (32). A mixture of 2-methyl-2-butene (**33**) and 2-methyl-1-butene (**34**) was obtained in which the ratio of **33/34** was 70:30. The results are similar to those in the literature for the solvolyses of neopentyl derivatives in which the 2-methyl-2-butylcarbenium ion is formed by concerted migration of a methyl group and departure of the leaving group. Neopentyl tosylate, for example, in aqueous acetic acid gave **33** and **34** in the

(36) Vogelfanger, E. Ph.D. dissertation, UCLA 1963. *Diss. Abstr.* **1963**, *24*, 982. We have been unable to find other published reports of these data, but lesser amounts of **16** and **17** obtained at 25 °C have been reported.[26b]

(37) Gassman, P.; Marchall, J. *Tetrahedron Lett.* **1968**, 2429, 2433.

(38) Brown, H. C.; Rei, M.-H.; Chandrasekharan, J.; Somayaji, V. *J. Org. Chem.* **1985**, *50*, 5578. Brown, H. C.; Rothberg, I.; Chandrasekharan, J. *J. Org. Chem.* **1985**, *50*, 5574. Brown, H. C.; Vander Jagt, D. L.; Rothberg, J.; Hammer, W. J.; Kawakami, J. H. *J. Org. Chem.* **1985**, *50*, 2179. Brown, H. C.; Ikegami, S.; Vander Jagt, D. L. *J. Org. Chem.* **1985**, *50*, 1165.

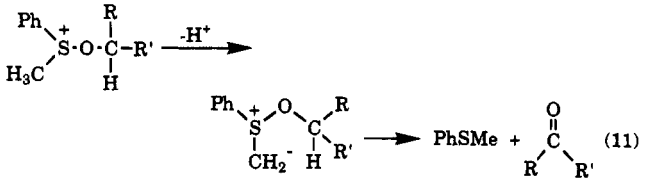
(39) Lenoir, D.; Apeloig, Y.; Arad, D.; Schleyer, P. v. R. *J. Org. Chem.* **1988**, *53*, 661.

(40) Walling, C. *Acc. Chem. Res.* **1983**, *16*, 448.

(41) Brown, H. C.; Liu, K.-T. *J. Am. Chem. Soc.* **1970**, *92*, 200.

ratio 75:25. In that case both isoamyl alcohol and acetate were also obtained.[42] Diazotization of neopentylamine in acetic acid gave **33** and **34** in the ratio 57:43. When the optically active 1-deuterioamine was used, activity (58%) was retained in **34**, indicative of concerted migration of the methyl group.[43] Support for the rearrangement route has been provided more recently with carbon and deuterium kinetic isotope effects and ab initio calculations.[44-46] Again, in our reactions, deprotonation of the rearranged carbenium ion has turned out to be faster than its capture by solvent acetonitrile.

Moffatt–Swern Oxidations and the Current Results. We interpret the results of the reactions of alcohols with $Th^{\bullet+}$ as stemming from intermediate, as yet unisolated or characterized, 5-alkoxythianthreniumyl ions. An extensive literature exists of the oxidations of primary and secondary alcohols brought about by reaction with dimethyl sulfoxide (DMSO) and a promoting agent, such as acetic or trifluoroacetic anhydride or a carbodiimide. The scope of these oxidations was brought out particularly by Moffatt and by Swern.[47] The key intermediate in these oxidations is an alkoxydimethylsulfonium ion from which an ylide is formed, and it is within the ylide that intramolecular oxidation of the alcohol (the alkoxy group) occurs. The DMSO is reduced to dimethyl sulfide. In our reactions, ylide formation is impossible, so that oxidation of the Moffatt–Swern type cannot occur. Shono and coworkers, have, in fact, carried out successful oxidations of secondary alcohols, in benzonitrile solution containing 2,6-lutidine, with mediation by the anodic, catalytic formation of the thioanisole cation radical or dication.[48] Alkoxysulfonium ions were formed in which ylide formation and intramolecular oxidation *were* possible (in contrast with those from $Th^{\bullet+}$), eq 11. Whereas we obtained



only cyclododecene (Table 1), Shono obtained 75% of cyclododecanone from cyclododecanol, and where we obtained camphene (Table 5), Shono obtained 68% of camphor. In Shono's work the thioanisole mediator is catalytic and, in principle, fully recoverable. Yet, losses occurred, to a large extent in the formation of methyl phenyl sulfoxide. Sulfoxide formation was attributed to reaction of thioanisole cation radical (as in eq 1) or dication with water, but it now seems possible that elimination side reactions of the alkoxydimethylsulfonium ion, analogous to ours and initiated by 2,6-lutidine, may also have occurred.

(42) Silver, M. S. *J. Am. Chem. Soc.* **1961**, *83*, 3482.
(43) Guthrie, R. D. *J. Am. Chem. Soc.* **1967**, *89*, 6718.
(44) Ando, T.; Yamataka, H.; Morisaki, H.; Yamawaki, J.; Yukawa, Y. *J. Am. Chem. Soc.* **1981**, *103*, 430.
(45) Yamataka, H.; Ando, T. *J. Am. Chem. Soc.* **1982**, *104*, 1808.
(46) Yamataka, H.; Ando, T.; Nagase, S.; Hanamura, M.; Morukuma, M. *J. Org. Chem.* **1984**, *49*, 631.
(47) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: NY 1985; pp 1081–1082.
(48) Shono, T.; Matsumura, Y.; Mizoguchi, M.; Hayashi, J. *Tetrahedron Lett.* **1979**, 3861.

Experimental Section

Thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) was prepared from thianthrene (Fluka) as described earlier.[49] The thianthrene was first purified on a column of silica gel followed by crystallization from acetone.[1] Iodometric assay gave $Th^{\bullet+}$ content in the range 96–99%. Acetonitrile (Eastman, anhydrous grade) was dried by distillation from P_2O_5 under N_2. The following columns were used for GC analyses, with a Model 3700 Varian Associates FID-detector gas chromatograph and Model SP-4290 Spectra-Physics computer integrator: A, 10% OV-101 on 80–100-mesh Chrom WHP, 4-ft × 1/8-in. stainless steel (ss), B, 20% BEEA on 60–80-mesh Chrom PAW, 13-ft × 1/8-in. ss, attached to a similar 6-in. guard column; C, SE-30 Bondapak capillary, 15 m × 0.25 mm; D, 10% Carbowax-1540 on 80–100-mesh Chrom WHP, 6 ft × 1/8-in. ss, attached to a similar 6-in guard column; E, 10% OV-17 on 80–100-mesh Chrom QII, 6 ft × 1/8-in. ss; F, 20% QC2 Carbowax-20M capillary, 25 m × 0.25 mm. Quantitative analyses were performed with the use of authentic compounds and internal standards. The standards were naphthalene, dibutyl ether, and dibenzyl ether for columns A, C, and E, cyclohexene for B, and cyclohexane for D and F. A response factor was measured for each authentic compound and was used for analyses in a standard way. Mass spectra, for identification of products, were measured with a Hewlett-Packard instrument, Model 5995, in both GC and direct-insertion-probe modes. All of the cyclic and acyclic alcohols and all products, unless otherwise stated, were purchased from Aldrich Chemical Company.

All ethers except bis(*exo*-norbornyl) ether were prepared by adding a solution of the appropriate halide in 15 mL of dimethyl sulfoxide (DMSO) to a stirred, cold solution of a base, usually KOH, and the corresponding alcohol in 100 mL of DMSO and refluxing overnight. The resulting, cooled mixture was poured onto 200 mL of ice/water. The aqueous phase was extracted twice with benzene (100 mL), and the benzene solution was worked up for either distillation of liquid ethers or crystallization (hexane) of solid ethers. Thus, 3.6 g (29 mmol) of **9b**, 3 g of KOH, and 6.9 g of *o*-methylbenzyl bromide gave 3.8 g of **10b**, mp 42–43 °C (lit.[50] mp 47 °C). Analogous ethers were **10c**, bp 146–148 °C/3 Torr (lit.[51] bp 315–321 °C); **10d**, mp 57–58 °C (lit.[52] mp 63–64 °C); **10f**, bp 178–181 °C/0.1 Torr, mp 52–54 °C (lit.[53] mp 54–55 °C); **10g**, bp 205–211 °C/2 Torr, mp 84–85 °C (lit.[53] mp 85–86 °C). **10a** was from Aldrich. **10e**: bp 125–127 °C/2 Torr; ^1H NMR ($CDCl_3$) δ 7.94–7.89 (m, 4 H), 7.68–7.60 (m, 4 H), 5.05 (s, 4 H). The NMR spectrum was complicated by F couplings, and resolution was not pursued. **14** had bp 125–127 °C/0.3 Torr (lit.[54] bp 335–338 °C) and gave two GC peaks, for the meso- and *dl*-isomers. Distinguishing between them was not pursued, and the peaks were labeled **14A** and **14B** for assay purposes. They were assumed to have the same response factor and, hence, in the preparation their GC ratio was 1.3. Diisopropyl ether (**24**) was from Aldrich.

Bis(*exo*-norbornyl) Ether (19). In a modification of a literature procedure,[55] 4.0 g (29 mmol) of anhydrous $ZnCl_2$[56] was added to a solution of 3.0 g (27 mmol) of *exo*-norborneol (**15a**) in 100 mL of CH_2Cl_2 in a 150-mL round-bottomed flask. The mixture was refluxed for 24 h under drying-tube protection. After workup with NaCl solution, the solvent was removed

(49) Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368. Solid $Th^{\bullet+}ClO_4^-$ may explode if it is shocked in handling. It should be prepared only in small quantities and used after preparation even though it can be stored for months without trouble. The cause of its detonation, twice in many years of usage, is not known. It should not, we believe, be filtered on and scraped from sintered glass.
(50) Grigoryan, D. V.; Arutyunyan, N. S.; Martyrosyan, G. T.; Babayan, A. T. *J. Org. Chem. USSR* **1967**, *3*, 1430.
(51) Szperl, L. *Roczniki Chem.* **1926**, *6*, 728.
(52) Feldstein, A.; Vanderwerf, C. A. *J. Am. Chem. Soc.* **1953**, *76*, 1626.
(53) Lapkin, I. I.; Povarnitsyna, T. N. *Zh. Obshch. Khim.* **1968**, *38*, 643.
(54) Wang, C. C. *J. Org. Chem.* **1963**, *28*, 2941.
(55) Kim, S.; Chung, K. N.; Yang, S. *J. Org. Chem.* **1987**, *52*, 3917.
(56) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. In *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980; p 548.

from the dried ($MgSO_4$) solution. The ether (**19**) was separated from **15a** on a column of silica gel by elution with hexane/ethyl acetate (98:2) to give 1.35 g (13.5 mmol, 49%) of **19**: mp 65–66 °C; ^1H NMR ($CDCl_3$) δ 3.38–3.36 (m, 2 H), 2.26–2.23 (m, 2 H), 2.20 (m, 2 H), 1.60–1.28 (m, 10 H), 1.09–0.92 (m, 6 H). Anal. Calcd ($C_{14}H_{22}O$): C, 81.5; H, 10.8. Found: C, 81.7; H, 10.8.

N-Substituted acetamides were prepared with one of three standard methods, abbreviated here as ROH/CH_3CN/H_2SO_4 (**3b,c, 11g, 18**), ROH/pyridine/AcCl (**11b,c,e**), and RNH_2/Ph_3P/THF/Ac_2O (**11d,f, 13**). Products obtained were **3b**, bp 150–152 °C/3 Torr (lit.[57] bp 147–148 °C/3 Torr); **3c**, bp 152–154 °C/3 Torr (lit.[57] 162 °C/4 Torr); **11b**, mp 68–69 °C (lit.[58] mp 69 °C); **11c**, bp 233–235 °C (lit.[59] bp 235–240 °C); **11d**, mp 111–112 °C (lit.[60] 112–113 °C); **11f**, mp 106 °C (lit.[61] mp 109.5 °C); **11g**, mp 112–114 °C (lit.[62] mp 113 °C); **13**, mp 96–99 °C (lit.[63,64] mp 104 °C for the (*S*)-isomer and 103–104 °C for the (*R*)-isomer; and **18**, mp 139–140 °C (lit.[65] mp 140–141 °C).

11e, mp 94–96 °C, was not found in the literature: ^1H NMR ($CDCl_3$) δ 7.86–7.81 (m, 2 H), 7.64–7.56 (m, 2 H), 4.83 (d, J = 6.04 Hz, 2 H), 2.79 (br s, 1 H), 2.44 (s 3 H). Anal. Calcd ($C_9H_{10}FNO$): C, 64.6; H, 6.0; N, 8.4. Found: C, 64.7; H, 6.0; N, 8.0.

Reactions of $Th^{\bullet+}ClO_4^-$ with Alcohols. Approximately 0.80 mmol of solid $Th^{\bullet+}ClO_4^-$ was weighed into a 25-mL volumetric flask containing a magnetic stirrer, which was then capped with a septum. The flask was purged with N_2 or argon through a syringe needle, and into it was injected 20 mL of acetonitrile. The solution was stirred for 5 min, and to it was added by syringe a solution of 164 mg (0.80 mmol) of DTBMP and an excess (1.5–2.0 mmol) of the appropriate alcohol in 1 mL of acetonitrile. Acetonitrile was then added to the mark. The color of $Th^{\bullet+}$ disappeared usually within 5–30 min, but the mixture was stirred for several hours, as convenient. The solution was by then usually pale yellow in color. To it 1 mL of 4 M aqueous K_2CO_3 was added by syringe. GC and GC/MS analyses were then carried out with the solution. The results are listed for the several classes of alcohols in Tables 1–6. In addition, reaction of $Th^{\bullet+}ClO_4^-$ (81 mmol) with 3-hexanol (**28**) gave 43 mmol (53%) of Th, 39 mmol (48%) of ThO, 12 mmol (29%) of a mixture of *cis*- and *trans*-3-hexene (**29**), which was inseparable on our GC columns, 11 mmol (27%) of *cis*-2-hexene (**30**), and 18 mmol (44%) of *trans*-2-hexene (**31**). Reaction of $Th^{\bullet+}ClO_4^-$ (83 mmol) with neopentyl alcohol (**32**) gave 45 mmol (54%) of Th, 38 mmol (46%) of ThO, 27 mmol (71%) of 2-methyl-2-butene (**33**), and 11 mmol (29%) of 2-methyl-1-butene (**34**). The results of five runs were averaged.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant D-028) for support.

(57) Murakami, M.; Akagi, K.; Mori, Y. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 11.
(58) Strassmann, H. *Chem. Ber.* **1888**, *21*, 576.
(59) Bromme, R. *Chem. Ber.* **1888**, *21*, 2700.
(60) Parris, C. L.; Christenson, R. M. *J. Org. Chem.* **1960**, *25*, 1888.
(61) Williams, G. *J. Chem. Soc.* **1930**, 37.
(62) Shoppee, C. W. *J. Chem. Soc.* **1931**, 1225.
(63) Campbell, A.; Kenyon, J. *J. Chem. Soc.* **1946**, 25.
(64) Tsuchihashi, G.; Iriuchijima, S.; Maniwa, K. *Tetrahedron Lett.* **1973**, *36*, 3389.
(65) Gevorkyan, G. G.; Ordubadi, M. D.; Belikova, N. A.; Pekhk, T. I. *J. Org. Chem. USSR* **1986**, *22*, 1693.