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Reaction of Thianthrene Cation Radical with Alcohols: Isolation and Chemistry of 5-Cyclohexyloxythianthreniumyl Perchlorate

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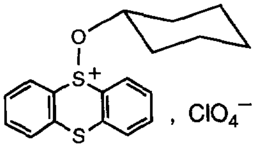
Abstract: 5-Cyclohexyloxythianthreniumyl perchlorate (**1**) was prepared by reaction of thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) with cyclohexanol in CH_2Cl_2. Cyclohexene and thianthrene 5-oxide (ThO) are formed when **1** is heated in solution. Reaction of **1** with H_2O/OH^- occurs at the 5-position and gives cyclohexanol and ThO. The chemistry of isolated **1** clarifies earlier work on the reaction of $Th^{\bullet+}ClO_4^-$ with cyclohexanol.

Recently, we reported the reactions of thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) with some cyclohexanols,[2] and with benzyl alcohols, neopentyl alcohol and some secondary alcohols.[3] These reactions in CH_3CN solution, led to the formation of alkenes, ethers and N-substituted acetamides, and they were attributed to the reactions of initially formed 5-alkoxythianthreniumyl perchlorates. None of these thianthreniumyl perchlorates could be isolated, the supposition being then that they underwent S_N1/S_N2 and E1/E2 type reactions soon after being formed.[2,3] We have, however, now been able to isolate 5-cyclohexyloxythianthreniumyl perchlorate (**1**) and have found it to be surprisingly stable in CH_3CN solution.



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Preparation of 1. To a solution of 250 mg (0.79 mmol) of $Th^{\bullet+}ClO_4^-$ in 10 mL of CH_2Cl_2, stirred under N_2 in a 50 mL septum-capped flask, was added a solution of 260 mg (2.6 mmol) of cyclohexanol in 10 mL of CH_2Cl_2. The mixture was stirred for 3 h and concentrated to 5 mL in a rotatory evaporator. To the concentrate was added 25 mL of dry ether. The precipitate that formed was washed with ether three times to give 80 mg (49%) of **1**, mp 80-81 °C (dec).[4]

Anal. Calcd. for $C_{18}H_{19}ClO_5S_2 \bullet H_2O$: C, 49.9; H, 4.86; Cl, 8.21; S, 14.8. Found: C, 50.2; H, 4.31; Cl, 7.96; S, 14.2. IR: 1085 cm^{-1} (ClO_4^-, strong). ^1H NMR ($CDCl_3$) δ (J in Hz): 8.668 (d, $2H_1$, J = 7.78), 7.923 (dd, $2H_4$, J = 7.94, 1.55), 7.836 (td, $2H_{2(3)}$, J = 7.17, 1.42), 7.730 (td, $2H_{3(2)}$, J = 7.46, 1.57), 4.690 (m, 1H), 1.912 (m, 2H), 1.401 (m, 8H). These NMR data for the thianthreniumyl portion of **1** show understandable downfield shifts as compared with the corresponding positions in ThO, namely δ : 7.936 (H_1), 7.640 (H_4), 7.565, 7.435 ($H_{2,3}$).

Reactions of 1. (**a**) **1** was found with ^1H NMR spectroscopy to be stable in dry CD_3CN at room temperature, but to be converted slowly at 50 °C, and rapidly at 100 °C into cyclohexene and thianthrene 5-oxide (ThO). The conversion of **1** into these products could be followed easily by the appearance of the cyclohexene's –CH=CH– peaks and also with the gradual replacement of the doublet for **1**, centered at δ = 8.417, with that for ThO, centered at 7.859 (in CD_3CN). (**b**) A solution of 0.192 mmol of **1** in 10 mL of dry CH_3CN was stirred for 1 h, after which all volatile material was pumped off at room temperature into a receiver cooled in liquid N_2. Only a trace of cyclohexene was found in the receiver. (**c**) A solution of 0.128 mmol of **1** and of 0.143 mmol of 2,6-di-tert-butyl-4-methylpyridine (DTBMP) in 10 mL of CH_3CN was heated at 100 °C for 30 min. GC[5] gave cyclohexene (0.114 mmol, 89%), ThO (0.116 mmol, 91%), Th (0.565 mmol, 4.4%) and DTBMP (0.137 mmol, 96%). (**d**) To a solution of 0.126 mmol of **1** and 0.792 mmol of DTBMP in 10 mL of CH_3CN, 0.4 mL of 2 M aqueous K_2CO_3 was added, and the solution was stirred for 2 h. GC gave a trace of cyclohexene, cyclohexanol (0.120 mmol, 95%), ThO (0.124 mmol, 98%), and Th (0.002 mmol, 1.6%). (**e**) To a solution of 0.042 mmol of **1** in 5 mL of CH_3CN was added 0.2 mL of $H_2{}^{18}O$ (50% ^{18}O) containing 56 mg of K_2CO_3. The solution was stirred for 4 h, and was found to contain (GC/MS) equal amounts of ThO and $Th^{18}O$.

These reactions show that **1** decomposed in solution into equal amounts of cyclohexene and ThO only if heated. It is likely, therefore, that the cyclohexenes reported in our earlier work,[2] were formed from the corresponding **1** in the injection GC port or on the GC column rather than in solution. The results (**e** and **d**) show, furthermore, that **1** reacted at sulfur with H_2O (or OH^-) in CH_3CN solution, rather than undergoing elimination of cyclohexene. The finding of reaction at sulfur corresponds with reactions of analogous alkoxysulfonium ions obtained from dimethylsulfoxide.[6]

We have found that the reactions of isolated **1** are replicated in the reactions of $Th^{\bullet+}ClO_4^-$ with cyclohexanol in CH_3CN solution. Thus, after stirring a solution of 0.341 mmol of $Th^{\bullet+}ClO_4^-$, 1.05 mmol of cyclohexanol and 0.373 mmol of DTBMP in 10 mL of CH_3CN for 1 h, the volatiles were removed by pumping and found to consist of CH_3CN and cyclohexanol only. The residue was dissolved in 10 mL of CH_3CN. An aliquot of the new solution gave (GC) the equivalent of 0.170 mmol (99.7%) of cyclohexene. The bulk of the new solution was heated at 100 °C for 30 min, cooled and, again, volatiles were removed at room temperature, and contained 0.155 mmol (91%) of cyclohexene. The residue from the second evaporation was dissolved once more in 10 mL of CH_3CN, and GC analysis, both before and after adding aqueous K_2CO_3, gave cyclohexene (0.024 mmol, 14%), ThO (0.175 mmol, 51%). These results show that **1** had been formed in the initial reaction between $Th^{\bullet+}ClO_4^-$ and cyclohexanol, and that it eliminated cyclohexene only when heated in solution. The stoichiometry of the formation and decomposition of **1** remain as proposed earlier.[2]

References and Notes:

1. On leave from the Institute of Photographic Chemistry, Academia Sinica, Beijing.
2. Shine, H. J.; Yueh, W. *Tetrahedron Letters* **1992**, *33*, 6583.
3. Shine, H. J.; Yueh, W. *J. Org. Chem.* **1994**, *59*, 3553.
4. Care should be exercised in handling this and other perchlorates. Although we have not heard of problems with the use of $Th^{\bullet+}ClO_4^-$ by other workers, it has exploded twice in this laboratory in the course of many years of usage. It should be prepared in small quantities. We do not recommend storing it or filtering it on sintered glass surfaces.
5. 10% carbowax 20 M on 80-100 mesh chrom WHP, 6 ft x 1/8 in stainless steel for cyclohexene; 10% OV-101 on 80-100 mesh chrom WHP, 4 ft x 1/8 in s.s. for all other products.
6. Khuddus, M. A.; Swern, D. *J. Am. Chem. Soc.* **1973**, *95*, 8393.

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