Benzyl Cation Formation from the Reaction of Benzyl Alcohol with Thianthrene Cation Radical

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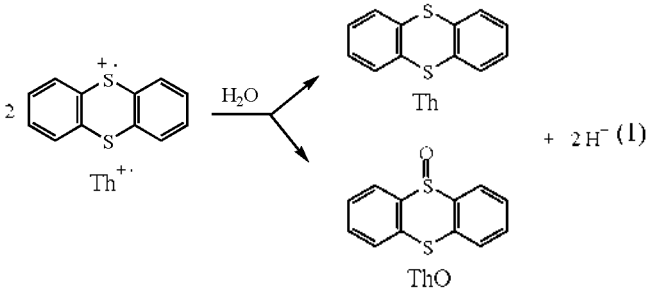
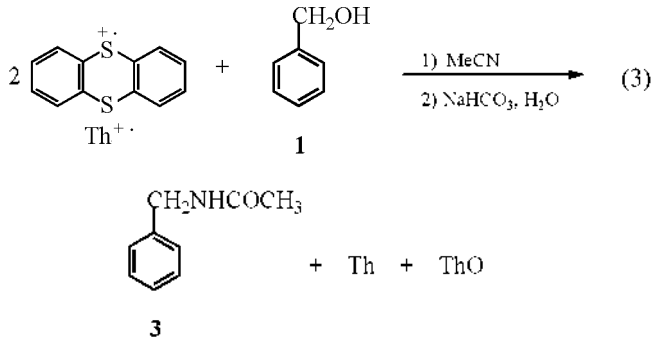
Mechanistic studies have been reported for the reactions of thianthrene cation radical ($Th^{+\cdot}ClO_4^-$) with nucleophiles such as water and alcohol. The simple reaction of $Th^{+\cdot}$ with water[1] generated equal amounts of thianthrene (Th) and its 5-oxide (ThO) (eq 1). The analogous study of reactions of $Th^{+\cdot}$ with



alcohols have reported by Yueh and Shine.[2,3] In their study of the reaction of $Th^{+\cdot}$ with benzyl alcohol (**1**), dibenzyl ether (100%), Th (52%), and ThO (48%) were obtained as products. The stoichiometry of the reaction was a molar ratio of 1.88-2.50: 1.00 of $Th^{+\cdot}$ to **1**, with the major products are not characteristic of benzyl cations but rather dibenzyl ether and without the formation of *N*-benzylacetamide. With the exception of **1**, all of the substituted benzyl alcohols ($X\text{-}C_6H_5\text{-}CH_2OH$, X = methyl, halogen) gave mixtures of the corresponding dibenzyl ether and *N*-benzylacetamide. Yueh and Shine suggested that dibenzyl ether was formed in an S_N2 displacement of ThO, whereas the amides were formed by S_N1 loss of ThO from the $ROTh^+$. Since our recent works[4,5] have cast doubt on formation of dibenzyl ether from **1** by $Th^{+\cdot}$, the reaction of **1** with $Th^{+\cdot}$ was reinvestigated in order to clarify the mechanism. We report here our new reaction mechanism proposed on the basis of our experimental results for the particular case of **1** and $Th^{+\cdot}$. Reactions were carried out at a 2:1 stoichiometry of the $Th^{+\cdot}$:**1**, in acetonitrile at room temperature. The products obtained were *N*-Benzylacetamide (**3**), Th, and ThO, as determined by quantitative GC and GC/MS analyses. *N*-Benzylacetamide (**3**) from the benzyl cation, isolated in a yield of 90%, Th (100%) and ThO (90%) were formed quantitatively, according to the results of the formation of an alkoxysulfonium ion in eq 2 (R = benzyl). Contrary to Yueh and Shine's report, in our reaction, no trace amounts of dibenzyl ether was obtained.

$$2\ Th^{+\cdot} + R\text{-}OH \longrightarrow Th + ROTh^+ + H^- \qquad (2)$$

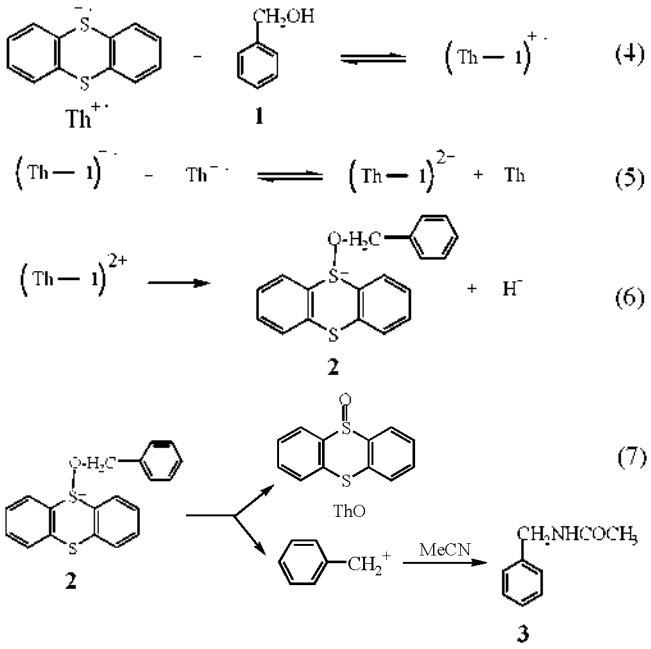
As expected from the stoichiometry of eq 3, there are equivalent amounts of Th, ThO and **3**.



It is evident that $Th^{+\cdot}$ cannot oxidize **1** because of the lower oxidation potentials of Th (~1.3 V vs SCE[6]) relative to alcohols[7] (> 2V). Alternatively, analogous to the anisylation of $Th^{+\cdot}$,[8] complexation of an **1** with $Th^{+\cdot}$ must occur, and leads ultimately to an unstable alkoxysulfonium ion, from which benzyl cation is derived by S_N1 loss of ThO from the $ROTh^+$ (eq 2), whereby the oxygen atom of **1** was transferred to $Th^{+\cdot}$ with quantitative formation of ThO and **3**.

In general, ThO is obtained as a side product from the hydrolysis of $Th^{+\cdot}$ by water, either adventitiously in the solvent or added during work-up of the reaction of $Th^{+\cdot}$.[7] However, in this study, the ThO is a primary product rather than a side product. The formation of ThO as a primary product of oxygen transfer from nucleophiles, has been reported widely from the reaction of $Th^{+\cdot}$ with nitrite and nitrate ions,[9] oximes,[10] cyclic alcohols,[5] 2,3-dimethyl-2,3-butandiol,[11] and azodioxide.[12] Without doubt, **3** arose from hydration, during work-up, from a Ritter-type intermediate ($C_6H_5CH_2N{=}{}^-CMe$), from the reaction of $C_6H_5CH_2^+$ with MeCN solvent. The chemical characteristics of the *t*-butyl cation from the cation radical-induced oxidative decomposition of nucleophiles[12-18] has been documented extensively, but that of the benzyl cation, known to be less stable than the *t*-butyl cation, affords very few examples of Ritter-type product, **3**.

A mechanism that fits the formation of such products involves the initial complexation of $Th^{+\cdot}$ with **1** (eq 4) to produce a species more easily oxidized than $Th^{+\cdot}$, where electron transfer (eq 5) produces a thianthrene dication-benzyl alcohol complex $(Th\text{-}\mathbf{1})^{2-}$ that undergoes a rate-determining bond formation with expulsion of a proton (eq 6) to produce **2**. *N*-Benzylacetamide (**3**) is subsequently formed by S_N1 loss of ThO from **2**.



In conclusion, a stable benzyl cation was obtained from the complexation of benzyl alcohol with a thianthrene cation radical under mild conditions. The postulated intermediate, the benzyl cation, has received scant attention because of very few examples of Ritter-type reaction from the cation radical reactions. The new reaction described herein further expands the characteristic benzyl cation chemistry induced by cation radicals.

Experimental Section

Reaction of benzyl alcohol (1) with $Th^{+\cdot}ClO_4^-$. A general procedure was adopted. Solid $Th^{+\cdot}ClO_4^-$ (315.6 mg, 1.0 mmol) was weighed into a 50-mL rounded-bottomed flask containing a magnetic bar and capped with a septum. The flask was purged with dry argon through a syringe needle, and into it was injected 15 mL of acetonitrile. The solution was stirred for 10 min, and to it was added, by syringe, a solution of benzyl alcohol (54.07 mg, 0.5 mmol) in 5 mL of acetonitrile. The dark purple color of $Th^{+\cdot}ClO_4^-$ disappeared within 30 min, but the mixture was stirred overnight. Thereafter, 10 mL of water was added followed by aqueous $NaHCO_3$ to neutralize $HClO_4$ that had formed during the reaction. The solution was extracted with 3 × 30 mL portions of CH_2Cl_2. The CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated. The residue was dissolved in 10 mL of CH_2Cl_2. Portions of this solution were used for quantitative analysis by GC and for identification of products by GC/MS and ^{1}H-NMR ($CDCl_3$). The GC column used was a 15 m × 0.25 mm capillary column with CP-Sil 5CB, with naphthalene as an internal standard. Concentration factors for all products were determined with authentic materials.

Thianthrene 5-oxide (ThO)[19] and ***N*-Benzylacetamide (3)**[20] were prepared as described in the literature.

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