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\(^+\)ClO\(_4\)) with nucleophiles such as water and alcohol. The simple reaction of Th\(^+\) with water\(^1\) generated equal amounts of thianthrene (Th) and its 5-oxide (ThO) (eq 1). The analogous study of reactions of Th\(^+\) with alcohols have reported by Yueh and Shine\(^2\) in their study of the reaction of Th\(^+\) 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\(^+\) 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-C\(_6\)H\(_5\)-CH\(_2\)OH, X = methyl, halogen) gave mixtures of the corresponding dibenzyl ether and N-benzylacetamide. Yueh and Shine suggested that dibenzyl ether was formed in an SN2 displacement of ThO, whereas the amides were formed by SN1 loss of ThO from the ROTh\(^+\) (eq 2), whereby the oxygen atom of 1 was transferred to Th\(^+\) with quantitative formation of ThO and 3.

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

\[
\begin{align*}
\text{2 Th}^+ & \quad \text{R-OH} \quad \text{Th} + \text{ROTh}^+ + \text{H}^+ \quad \text{(2)} \\
\text{Th}^+ & \quad \text{CH}_2\text{OH} \quad 1) \quad \text{MeCN} \\
\text{CH}_3\text{NHCOCCH}_3 \quad 2) \quad \text{NaHCO}_3, \text{H}_2\text{O} \\
\text{3} & \quad \text{Th} + \text{ThO} \quad \text{(3)}
\end{align*}
\]

It is evident that Th\(^+\) cannot oxidize 1 because of the lower oxidation potentials of Th (~ 1.3 V vs SCE\(^6\)) relative to alcohols (> 2 V). Alternatively, analogous to the anisylation of Th\(^+\), complexation of an 1 with Th\(^+\) must occur, and leads ultimately to an unstable alkoxysulfonium ion, from which benzyl cation is derived by S$_2$1 loss of ThO from the ROTh\(^+\) (eq 2), whereby the oxygen atom of 1 was transferred to Th\(^+\) with quantitative formation of ThO and 3.

In general, ThO is obtained as a side product from the hydrolysis of Th\(^+\) by water, either adventitiously in the solvent or added during work-up of the reaction of Th\(^+\). 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\(^+\) with nitrite and nitrate ions, oximes, cyclic alcohols, 2,3-dimethyl-2,3-butanediol, and azodioxide. Without doubt, 3 arose from hydration, during work-up, from a Ritter-type intermediate (C\(_6\)H\(_5\)CH\(_2\)N=+CMe), from the reaction of C\(_6\)H\(_5\)CH\(_2\) + with MeCN solvent. The chemical characteristics of the t-butylium cation from the cation radical-induced oxidative decomposition of nucleophiles has been documented extensively, but that of the benzyl cation, known to be less stable than the t-butylium 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\(^+\) with 1 (eq 4) to produce a species more easily oxidized than Th\(^+\), where electron transfer (eq 5) produces a thianthrene dication-benzyl alcohol complex (Th-1)$^{12}$ 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$_2$1 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⁺· ClO₄⁻.** A general procedure was adopted. Solid Th⁺· ClO₄⁻ (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⁺· ClO₄⁻ disappeared within 30 min, but the mixture was stirred overnight. Thereafter, 10 mL of water was added followed by aqueous NaHCO₃ to neutralize HClO₄ that had formed during the reaction. The solution was extracted with 3 × 30 mL portions of CH₂Cl₂. The CH₂Cl₂ solution was dried over MgSO₄ and evaporated. The residue was dissolved in 10 mL of CH₂Cl₂. Portions of this solution were used for quantitative analysis by GC and for identification of products by GC/MS (CDCl₃). 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) and N-benzylniacetamide (3) were prepared as described in the literature.

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**References and Notes**

5. Unpublished work, N-benzylniacetamide was obtained from the reaction of benzyl phenyl ether and thianthrene cation radical.