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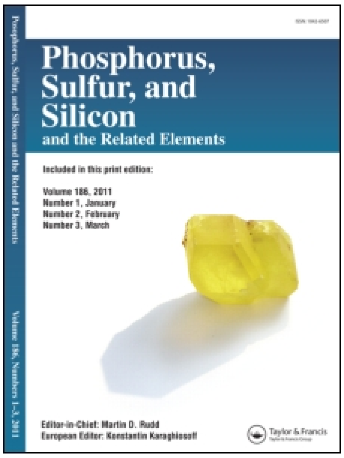

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OXYGEN TRANSFER FROM ALCOHOLS TO THE THIANTHRENE CATION RADICAL

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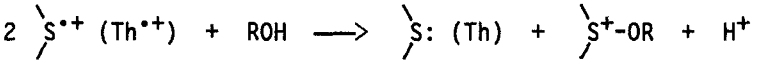
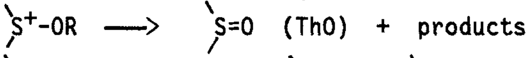
Abstract Thianthrene cation radical ($Th^{\bullet+}$) reacts cleanly with alcohols and diols in acetonitrile solution containing a hindered base. Products from $Th^{\bullet+}$ are thianthrene and thianthrene 5-oxide. Other products vary with the structure of the alcohol and diol.

The reaction of thianthrene cation radical ($Th^{\bullet+}$) with water was the first reaction of a cation radical with a nucleophile to be studied mechanistically.[1-3] It is surprising, then, that a systematic study of the analogous reaction of $Th^{\bullet+}$ with alcohols has never been reported until recently.[4] Reaction of $Th^{\cdot+}$ with alcohols is fast if a moderate excess of the alcohol is used. When carried out in acetonitrile (CH_3CN) solution, and in the presence of the hindered base 2,6-di-tert-butyl-4-methylpyridine (DTBMP) to prevent acid-catalyzed reactions, an acyclic or cyclic alcohol (ROH) gives quantitative yields of products of the classes alkene R(-H), ether ROR, and (after work up) amide CH_3CONHR, whose distributions depend on the nature of R. At the same time, thianthrene (Th) and thianthrene 5-oxide (ThO) are formed in equal amounts. The oxygen atom in ThO comes from ROH, as shown with [^{18}O]cyclohexanol, and the amount of ThO is equal to the sum of all products derived from R. The course of reaction is interpretable on the basis that a 5-alkoxythianthreniumyl ion is formed, shown symbolically in eq. 1, and leads to elimination and substitution reactions of the S_N1/S_N2

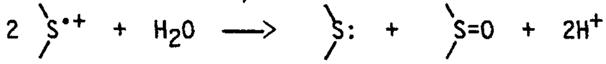
and E1/E2 types, eq. 2. These equations are analogous to the water reaction, eq. 3. We have studied and now report reactions with



$$2\ {>}S^{\bullet+}\ (Th^{\bullet+}) + ROH \longrightarrow {>}S{:}\ (Th) + {>}S^{+}{-}OR + H^{+} \qquad (1)$$



$$ {>}S^{+}{-}OR \longrightarrow {>}S{=}O\ (ThO) + \text{products} \qquad (2)$$



$$2\ {>}S^{\bullet+} + H_2O \longrightarrow {>}S{:} + {>}S{=}O + 2H^{+} \qquad (3)$$

cycloalkanols (C_5-C_8 and C_{12}), alkan-2-ols (C_3, C_5, C_6, C_8), 3-hexanol, neopentyl alcohol, a number of benzyl alcohols, dl- and (S)-1-phenylethanol, cyclopentyl- and cyclohexylmethanol, and the *exo*- and *endo*-borneols and norborneols. Significantly, the major product from the norborneols is nortricylene.

Acyclic-*α,ω*-diols, cyclic 1,2-diols and pinacols also react well with $Th^{\bullet+}$, again with a stoichiometry analogous to that of eq. 1-2. The *α,ω*-diols undergo cyclization in excellent yield; e.g., 1,5-pentanediol gave 98% of tetrahydropyran. *Cis*-cyclopentane-1,2-diol gave cyclopentanone whereas the *trans*-diol gave only cyclopentene oxide. A similar result was obtained with the cyclohexane-1,2-diols. Among the pinacols, rearrangement, epoxide formation and oxidative cleavage were experienced. All of these reactions, except oxidative cleavage, gave also the anticipated amount of Th and ThO and are understandable on the basis of intramolecular displacements or eliminations in a first-formed hydroxyalkoxythianthreniumyl ion, e.g., $HO(CH_2)_5O{-}\overset{+}{S}{<}$ from 1,5-pentanediol.

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