Cald. for $C_{16}H_{16}O_2$; C, 80.00%, H, 6.67%. Found; C, 79.13%, H, 6.57%.

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The First Example of Cation Radical Induced Decarboxylation from Carbonates

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In the course of our investigation of cation radical induced oxidation of carbonates, we have discovered that thianthrene cation radical perchlorate (**1,** $Th^{+} \cdot ClO_4^{-}$) readily oxidizes *tert*-butyl phenyl carbonate (**2**) in acetonitrile at room temperature. This is a novel reaction of carbonates, and offers the first example of cation radical induced decarboxylation. Carbonates, diester of carbonic acid, are known as stable organic compounds and as useful intermediates for a variety of industrial and synthetic applications. Alkyl aryl carbonates undergo the loss of carbon dioxide or are converted to diaryl carbonates at reasonable rates only if heated in the region 180-200 °C.[1] In contrast, the reaction (Scheme 1) of this very stable carbonate **2** with **1** at room temperature leads to rapid oxidative decarboxylation. Quantitative data are listed in Table 1. Product balances account for 88% of the *tert*-butyl groups which appear as cations, 91% of the phenoxy groups, and 95.1% of the cation radicals.

The major products are *N-tert*-Butylacetamide (**3**)[2] from *tert*-butyl cations, 5-(4-hydroxyphenyl)thianthreniumyl perchlorate (**4**)[3] from phenoxy radicals, thianthrene (Th) and carbon dioxide. Thus, the intermediates which are trapped in the course of oxidative decomposition were *tert*-butyl cations and phenoxy radicals. *tert*-Butyl cations reacted with

the solvent acetonitrile to give a Ritter-type intermediate ($Me_3CN=^{+}CMe$), which reacted with water during work-up, to give **3.** The simplest representation of the reaction of **1** with **2** and the formation of **3** and **4** is given in eq 1-5.

Table 1. Products of Reaction of Thianthrene Cation Radical Perchlorate with *tert*-Butyl Phenyl Carbonate in MeCN at Room Temperature[a]

Reactants, mmol x 10^2		Products (%),[b] mmol x 10^2			
1	2	3	4[c]	Th[d]	PhOH
100	50	44	45	49	0.5
		(88)	(45)	(49)	(1)

[a]Reaction was carried out by adding acetonitrile by syringe to a stirred, septum-capped round-bottomed flask containing 1.00 mmol of **1** and 0.50 mmol of **2** under argon atmosphere. The color of **1** was discharged within 10 minutes, but stirring was continued overnight. Water (5 mL) was added. The solution was neutralized with $NaHCO_3$ and extracted repeatedly with CH_2Cl_2 (4 x 20 mL). [b]Products were identified and quantified by GC, using the method of "standard addition" of authentic samples,[16] and by ^{1}H NMR and GC/MS. GC analyses were made with a 2 m x 1/8 in. stainless steel column packed with 10% OV-101 on Chrom W. Reaction was run four times, and the averaged yields of products are given. [c]Isolated yield. 100 x (mmol of product)/ initial mmol of $Th^{+} \cdot ClO_4^{-}$. This represents 90% of the phenoxy groups in the carbonate **2.** [d]A small amount (1.1%) of thianthrene 5-oxide (ThO) was also obtained.[17]

Scheme 1.

$$Th^{+} + Me_3COCOPh \rightleftharpoons Th + \left[Me_3COCOPh\right]^{+ \cdot} \quad (1)$$

$$\left[Me_3COCOPh\right]^{+ \cdot} \longrightarrow Me_3C^{+} + CO_2 + OPh \quad (2)$$

$$Me_3C^{+} + MeCN \longrightarrow Me_3CN=^{+}CMe \quad (3)$$

$$Me_3CN=^{+}CMe + H_2O \longrightarrow Me_3CNHCOMe + H^{+} \quad (4)$$

$$Th^{+} + OPh \longrightarrow 4 \quad (5)$$
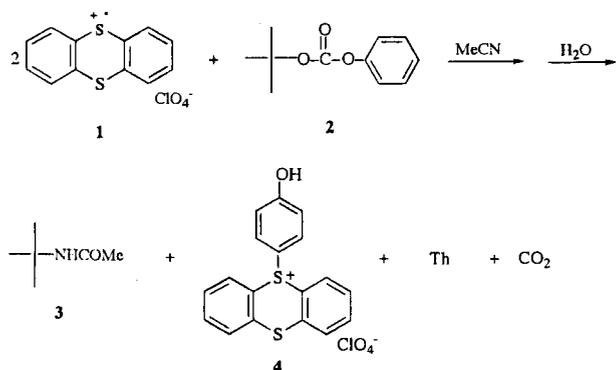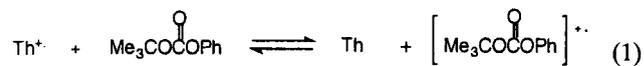
Compound **3** was also obtained in 76% and 31% yields, respectively when *tert-* butyl S-(4,6-dimethylpyrimidine-2-yl) thiolcarbonate and *N-(tert-* butoxycarbonyl)glycine reacted with **1** in acetonitrile. Further separation of products proved not to quantitative and their complete assay was not pursued.

Analogous studies on the aromatic cation radicals induced oxidative decomposition for azoalkanes have been reported.[4–6] 1,1'-Azoadamantane,[4] *meso-* azobis- α -phenylethane[5] and cyclic azoalkanes[6] were oxidized rapidly and quantitatively by **1** at room temperature to give nitrogen plus cation derived products instead of products formed by free radical reactions. While alkyl radicals formed from the first oxidation of azoalkanes in these reactions were again oxidized into alkyl cations, phenoxy radicals formed from the oxidative decomposition of carbonate (eq 2) were not oxidized to phenoxonium ion but trapped by **1** to give **4** in excellent yield (eq 5).

A question arose as to whether or not the reaction involved electron transfer and formation of radicals, which, being trapped by **1,** gave products 5-substituted thianthreniumyl perchlorates. Evidences for these steps were found in the reaction of **1** with dialkylmercurials[7,8] phenylmagnesium chloride,[9] organotins,[10] cyclohexanols,[11,12] and 2,2'-azo-2-methyl-6-heptene.[13] Thus, without doubt, the fate of phenoxy radicals is primarily to be trapped by cation radicals and leads to the formation of **4.** An earlier report[14] showed that **1** reacted with phenol to form **4** and the mole ratio of **1** to phenol was 2 : 1.

Although the major products are rationalized by eq 1-5, the origin of the 1.0% phenol remains uncertain. We can exclude the formation of phenoxonium ion because free phenoxonium ion could not be formed from mono- and disubstituted phenols.[15] Moreover, neither amide nor hy - droquinone from the reaction of phenoxonium ions with solvent or with water was found. Control reaction of perchloric acid and **2** in acetonitrile was carried out to know if the decomposition is catalyzed by acid that is formed in incompletely dried solvent instead of oxidative decomposition of the carbonate. Only a trace of phenol was obtained from the control experiment. This result indicates that not only the reaction is proceeding by electron transfer and not by acid catalysis but phenol may be formed by acid that is formed in incompletely dried solvent.

In conclusion, a thermally stable carbonate has been shown to undergo facile oxidative decarboxylation under mild conditions and both carbonations and free radicals were trapped by solvent and cation radical respectively. The new oxidative decomposition of *tert-* butyl phenyl carbonate further enlarges the chemistry of the versatile carboxylic linkage.

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