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11. (3*S*,5*S*,6*R*)-2,3,5,6-Tetrahydro-3,5,6-triphenyl-1,4-oxazin-2-one (**5a**): This compound was identified by

comparison with the known enantiomer of **5a**.^{5d} ¹H NMR (300 MHz, CDCl₃, 298 K) δ 2.35 (br s, 1H), 4.72 (d, *J*=4.1 Hz, 1H), 5.22 (s, 1H), 5.71 (d, *J*=4.1 Hz, 1H), 6.92-7.63 (m, 15H). IR (KBr): 3374, 1748, 1214 cm⁻¹.

12. (3*S*,5*S*,6*R*)-4-(*tert*-Butyloxycarbonyl)-2,3,5,6-tetrahydro-3,5,6-triphenyl-1,4-oxazin-2-one (**4a**): mp 217-219 °C; [α]_D -78.2 (c 1, CH₂Cl₂); IR (KBr): 3075, 1748, 1692, 1451, 1386, 1234 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 298 K) δ [1.13 (s), 1.27 (s), 9H], [5.19 (d, *J*=2.7 Hz), 5.45 (s), 1H], [5.76 (d, *J*=2.8 Hz), 5.85 (s), 1H], [6.19 (s), 6.42 (s), 1H], 6.72-7.59 (m, 15H). For *syn*-oxazinone: ¹H NMR (300 MHz, CDCl₃, 298 K) δ 1.19 (s, 9H), 5.71 (s, 1H), 5.86 (d, *J*=2.9 Hz, 1H), 6.07 (d, *J*=3.0 Hz, 1H), 6.95-6.98 (m, 2H), 7.19-7.29 (m, 13H).

Oxidative Decarboxylation of Carbamates by Thianthrene Cation Radical

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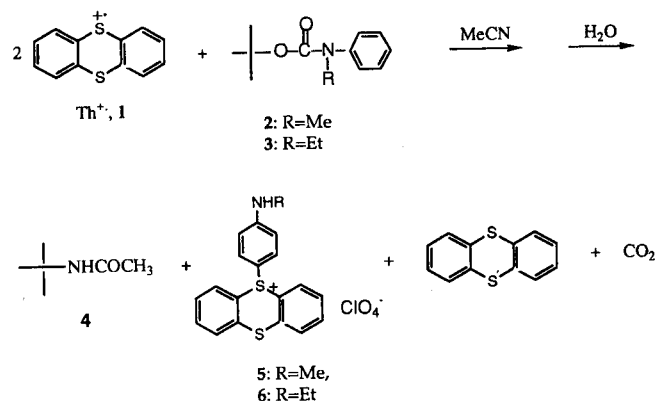
Cation radical induced oxidative decompositions have attracted wide attention in recent years.¹⁻⁴ For example, azoalkane such as 1,1'-azoadamantane (AA), was oxidized by thianthrene cation radical perchlorate (Th⁺·ClO₄⁻, **1**) in MeCN affording N₂ evolution with C,N bond cleavage.¹ In this 2:1 stoichiometry reaction of cation radical salts to AA adamantyl cation derived product was observed instead of product formed by free radical reaction. But, in the reaction of *tert*-butyl phenyl carbonate (Me₃COCOOPh) with **1**, CO₂ was produced with C,O bond cleavage.⁴ While adamantyl radicals formed from the first oxidation of AA were again oxidized into adamantyl cations, phenoxy radicals formed from the oxidative decomposition of carbonate were not oxidized but trapped by **1** to give 5-substituted thianthreniumyl perchlorate salts.

We report here the first observation of electron-transfer-mediated C,N and C,O bond activation in stable carbamates. The stoichiometry for oxidative fragmentation of carbamate requires at least 2 mol equiv of cation radical to fully consume 1 mol of carbamate. All of the results that follow can be understood on the basis that *tert*-butyl cation and amine radical were trapped by solvent nitrile and cation radical respectively.

Chemical oxidation of carbamates, *tert*-butyl *N*-methylphenyl⁵ (**2**) and *tert*-butyl *N*-ethylphenyl carbamate⁵ (**3**), by **1** in MeCN yields C,N and C,O bond cleavage products (Scheme 1). The major products were *N*-*tert*-butylacetamide (**4**) from *tert*-butyl cations and 5-substituted thianthreniumyl perchlorates, 5-(4-*N*-methylaminophenyl)- (**5**) and 5-(4-*N*-ethylaminophenyl)thianthreniumyl perchlorate (**6**), from am-

ine radicals respectively along with thianthrene (Th) and CO₂. Average product balances account for 72% of the *tert*-butyl groups which appear as cations, 84% of the amine radicals, and 86% of the cation radicals as determined by quantitative GC and GC/MS analyses. In addition to reduced oxidant Th, a small amounts (0.1%) of thianthrene 5-oxide (ThO) was also obtained.⁶ These products and their yields are listed in Table 1.

The decarboxylation of carbamates has not very well known. The *tert*-butoxy carbonyl (Boc) group is removed by treating the protected amino acid or peptide with anhydrous acid,⁷ such as trifluoroacetic acid or hydrogen chloride in acetic acid, base,⁸ and catalysts.⁷ The initial reaction



Scheme 1

Table 1. Products (mmol) of Reactions of Carbamates in MeCN at Room Temperature^a

Run	Reactants, mmol × 10 ²		Products (%) ^b , mmol × 10 ²			
	Carbamate	Th ⁺ ·ClO ₄ ⁻	4	salt ^c	Th	amine
1	1, 50	100	38 (76)	5, 40 (40)	49 (49)	0.7 (1.4)
2	2, 50	100	34 (68)	6, 44 (44)	49 (49)	4.0 (8.0)

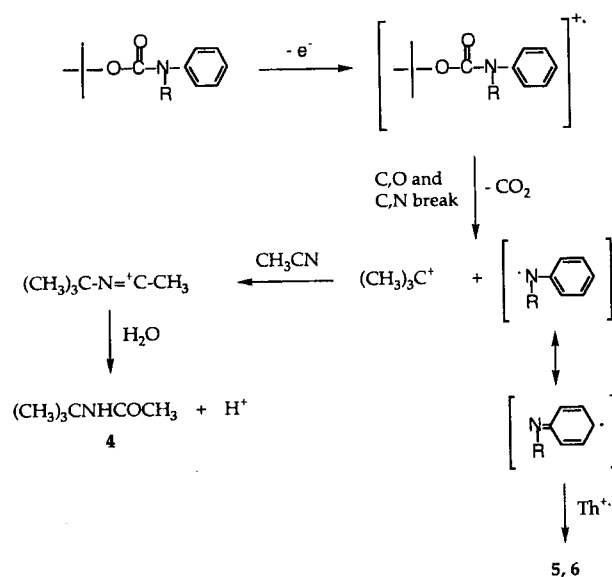
^a Carbamates (1.00 mmol) and Th⁺·ClO₄⁻ were placed in a round-bottomed flask, containing a stirrer magnet bar, and the flask was purged with dry argon after capping with a septum. Dry MeCN (20 mL) was introduced by syringe, and the mixture was stirred overnight. Next, water (5 mL) was added into the mixture, neutralized with NaHCO₃, and extracted repeatedly with CH₂Cl₂ (4 × 20 mL). ^b Products were identified and quantified by GC and by ¹H NMR and GC-MS. GC analyses were made with a 2 m × 18 in. stainless steel column packed with 10% OV-17 on 80-100 mesh Chrom W. Reactions were repeated three times, and the results tabulated are averages. ^c Isolated yield. 100 × (mmol of product)/initial mmol of Th⁺·ClO₄⁻. This represents 80, 88% of the amine radical recoverage in the carbamate respectively.

is cleavage of the C,O bond to give the relatively stable *tert*-butyl cation and a carbamic acid. The resulting carbamic acid then decarboxylates, giving the amine.

Carbamates undergo conventional thermolysis into corresponding amine, alkene, and CO₂ in various hydrocarbon solvents at reasonable rates only if heated in the region 250-320 °C.⁹ In contrast, these carbamates reacted with **1** at room temperature with rapid and evolution of CO₂. Chemical oxidation of carbamates (**2**, **3**) shows that 2^{•+} and 3^{•+} are prone to facile decarboxylation. Upon aqueous workup, *N*-*tert*-butylacetamide (**4**) is formed. Scheme 2 shows our proposed mechanism for oxidative C,N and C,O bond cleavage of **2** and **3**. The stoichiometry of the reaction requires 2 mol of equiv of oxidant and is that which is commonly seen in reactions of thianthrene cation radical, that is, in which half of the amount of cation radicals is converted into perchlorate salt and half into the parent compound, Th. 5-(4-*N*-Alkylaminophenyl)thianthreniumyl perchlorates (**5**, **6**) are obtained from amine radicals, being generated by the decomposition of *tert*-butyl *N*-alkyl *N*-phenyl carbamates, which, followed rearrangement and being trapped by **1**. In this case, the intermediate amine radical next to the benzene ring rearranges to the more stable phenyl radical much more rapidly than it react with **1** to give the corresponding S-arylsulfonium salt.

Evidences for the radical trapping by **1** to form 5-substituted thianthreniumyl perchlorate were observed in other works.^{2,10-12} An earlier report showed that **1** reacted with alkyl- and arylamine to form 5-substituted thianthreniumyl perchlorate.^{13,14} When control reaction of aqueous perchloric acid (*ca.* 70%) with carbamates in MeCN was conducted, only a trace of starting amines (<2%) was obtained. These observations indicate that the oxidative decomposition of the carbamate is not catalyzed by acid which is generated from electron transfer (ET) reaction but is proceeded exclusively by ET mechanism.

In conclusion, thermally stable carbamates have been shown to undergo facile oxidative decarboxylation yielding *tert*-butyl cation, CO₂, and amine radical by very effective one-electron oxidant, thianthrene cation radical perchlorate.

**Scheme 2**

Thus, ET-mediated C,N and C,O bond breaking is found for carbamates.

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