The *tert*-Butylperthiyl Radical[1]

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How does one characterize a perthiyl radical? This question has intrigued chemists for some time,[2-10] in part because such radicals may be formed when disulfide bridges in proteins are destroyed photochemically or radiolytically. Electron paramegnetic resonance (EPR)[2-7] or UV-vis spectra[8-10] will not generally yield sufficient information for an unequivocal assignment, since perthiyl radicals are likely to show broad, structureless absorption bands, in common with many other sulfur-centered radicals.[11] Moreover, the use of disulfides[2,3,5,7-10] as photochemical precursors is likely to yield inconclusive results because radicals I–III are all possible products, eq 1–3.

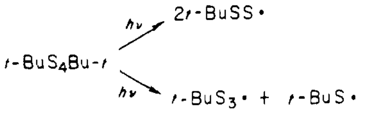
$$\mathrm{RSSR} \xrightarrow{h\nu} \underset{\mathrm{I}}{2\mathrm{RS}\cdot} \qquad (1)$$

$$\mathrm{RSSR} \xrightarrow{h\nu} \underset{\mathrm{II}}{\mathrm{RSS}\cdot} + \mathrm{R}\cdot \qquad (2)$$

$$\mathrm{RSSR} + \mathrm{RS}\cdot \rightarrow \underset{\mathrm{III}}{\mathrm{R\dot{S}(SR)_2}} \qquad (3)$$

In an attempt to resolve these problems, we have used a variety of techniques for the generation and detection of perthiyl radicals so that the combined weight of evidence was sufficient to allow unequivocal spectroscopic assignments.

Laser flash photolysis[12] (excimer laser, 308 nm, 80 mJ) of cyclopentane solutions containing *tert*-butyl tetrasulfide[13] (ca. 10^{-5} M) gave the spectrum shown in Figure 1. By contrast, only a very weak spectrum was obtained by photolysis of carefully purified *tert*-butyl disulfide under similar conditions.[14] These results suggest that photolysis of the tetrasulfide gave either t-BuSS· or t-BuSSS·, eq 4 and 5. However, since the central S–S bonds in tetrasulfides are longer[15] and presumably weaker[10] than the others, it follows that the spectrum was most likely due to the perthiyl radical t-BuSS·.



$$t\text{-BuS}_4\text{Bu-}t \xrightarrow{h\nu} 2\,t\text{-BuSS}\cdot \qquad (4)$$

$$t\text{-BuS}_4\text{Bu-}t \xrightarrow{h\nu} t\text{-BuS}_3\cdot + t\text{-BuS}\cdot \qquad (5)$$

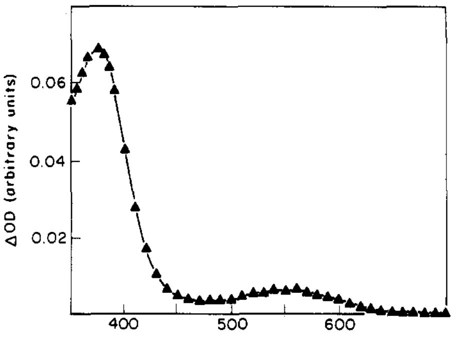


Figure 1. Spectrum of the *tert*-butylperthiyl radical obtained by photolysis of *tert*-butyl tetrasulfide.

A similar spectrum was observed by Itoh and Matsuda[17] by flash photolysis of *tert*-butyl disulfide and was assigned to the *tert*-butylthiyl radical. Our results suggest that this assignment is incorrect and that the observation[17] was due to photolysis of tri- and tetrasulfides, which are significant impurities in commercially available disulfide samples.

Laser photolysis of t-BuSSCl[18] (10^{-5} M) in cyclopentane again gave the absorption spectrum of Figure 1, supporting the assignment of the spectrum to t-BuSS·, eq 6.

$$t\text{-BuSSCl} \xrightarrow{h\nu} t\text{-BuSS}\cdot + \mathrm{Cl}\cdot \qquad (6)$$

While direct photolysis of *tert*-butyl disulfide did not efficiently cleave the carbon–sulfur bond, Kampmeier and his colleagues[19] have shown that this cleavage can be brought about by triplet sensitization. In laser flash photolysis experiments (nitrogen laser, 337 nm, 10 mJ), we found that triplet benzophenone was quenched by *tert*-butyl disulfide. The quenching rate constant k_7, was related to those for the pseudo-first-order decay of the triplet in the presence and absence of the disulfide (k_{obsd} and k_0, respectively) via eq 7 and 8.

$$\mathrm{Ph_2CO^*} + t\text{-BuSSBu-}t \rightarrow \mathrm{Ph_2CO} + t\text{-BuSS}\cdot + t\text{-Bu}\cdot \qquad (7)$$

$$k_{\mathrm{obsd}} = k_0 + k_7[t\text{-BuSSBu-}t] \qquad (8)$$

At 25 °C, k_7 was found to be $(1.5 \pm 0.1) \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$ in benzene solvent. However, the most important result from the present point of view is that the decay of triplet benzophenone led to the growth of a new spectrum identical with that shown in Figure 1 and which can therefore confidently be assigned to the perthiyl radical with $\lambda_{\max} \simeq 366$–$370$ nm. The result confirms earlier but tentative assignments of the spectra of perthiyl radicals.[9,10] Interestingly, CIDNP studies[20] support the view that C–S cleavage in disulfide photolysis derives from a triplet excited state.

Photolysis of frozen solutions of t-BuS$_4$Bu-t or t-BuSSCl (20% v/v in toluene at −160 °C) gave anisotropic EPR spectra[21] with $g_x = 2.058$, $g_y = 2.027$, $g_z = 2.002$, and $g_{\mathrm{av}} = 2.029$.[4] The value of g_{av} and the substantial difference between g_x and g_z is a characteristic of spectra for which the perthiyl structure has been considered a possibility[3,5,6-8] or a probability.[2,4,5]

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It is noteworthy that photolysis of *tert*-butyl disulfide under similar conditions also gave a weak spectrum of the perthiyl radical, which was substantially enhanced when benzophenone (ca. 0.05 M) was present in the mixture. Clearly, the matrix is capable of preserving the perthiyl radicals even though they are formed with a low quantum yield.

Finally, thermolysis of t-BuS$_4$Bu-t [250 °C (10^{-3} torr)] in an apparatus consisting of a quartz furnace, an electron monochromator, and quadrupole mass spectrometer[22] gave a good yield of t-BuSS·. The ionization potential of the radical was found to be 8.25 eV.

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Registry No. t-BuS$_4$Bu-t, 5943-35-1; t-BuSSCl, 6009-05-8; t-BuSSBu-t, 110-06-9; t-BuSS·, 71256-14-9.

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Electrooxidative Transformation of Aldehydes to Esters Using Mediators[1]

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Oxidative transformation of aldehydes **1** to esters **2** under mild conditions is often requisite in organic synthesis, and hence much effort has been devoted to find new methods or new reagents effective for this type of oxidation.[2] In our continuing study on anodic oxidation using mediators,[3] we have found that this electrooxidation is a convenient tool for the transformation of **1** to **2**.

$$\underset{1}{\mathrm{RCHO}} \xrightarrow[\mathrm{R'OH}]{-2e} \underset{2}{\mathrm{RCO_2R'}} \qquad (1)$$

The electrooxidation of **1** to the corresponding methyl ester is remarkably simple as briefly described below. Namely, methyl esters **5a–10a** were easily prepared by passing a constant current at room temperature through a solution of aldehydes **5–10** in methanol containing KI or KBr.[4] The results are shown in Table I.

On the other hand, butyl esters **7b**, **9b**, and **11b–15b** were successfully prepared by carrying out the electrooxidation of aldehydes **7**, **9**, and **11–15** under the conditions of a two-phase system consisting of an aqueous layer containing KI or KBr and an organic one containing **1** and butanol, since the low electric conductivity of butanol did not allow its use as a sole solvent. Yields of butyl esters are summarized in Table II. An ester of n-hexyl alcohol was also prepared by a similar method (run 10 in Table II).

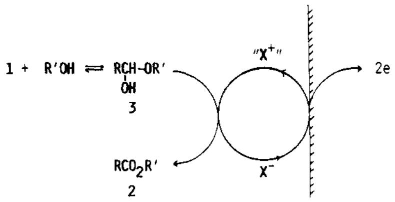
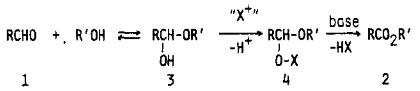


Figure 1. Electrooxidative transformation of **1** to **2**.

The reaction may proceed through the pathway described in eq 2 and 3.[3a,e] A positively charged active species "X$^+$" generated by the anodic oxidation of a halide ion X$^-$ attacks on aldehyde hemiacetals **3** to yield **4**.[5] Since a base may be formed as the cathodic reaction,[8] it abstracts hydrogen halide from **4** to afford **2** while regenerating X$^-$. Accordingly, the overall process can schematically be represented by Figure 1 in which the conversion of **1** to **2** proceeds with a catalytic amount of halide ion. In fact, even 0.1 mol equiv of KI was enough to complete the transformation of **1** to **2** (run 5 in Table I).

$$\mathrm{X^-} \xrightarrow{-2e} \text{"}\mathrm{X^+}\text{"} \qquad (2)$$



$$\underset{1}{\mathrm{RCHO}} + \mathrm{R'OH} \rightleftharpoons \underset{3}{\underset{\mathrm{OH}}{\mathrm{RCH{-}OR'}}} \xrightarrow[-\mathrm{H}^+]{\text{"}\mathrm{X^+}\text{"}} \underset{4}{\underset{\mathrm{O{-}X}}{\mathrm{RCH{-}OR'}}} \xrightarrow[-\mathrm{HX}]{\text{base}} \underset{2}{\mathrm{RCO_2R'}} \qquad (3)$$

This electrochemical method for the oxidation of **1** to **2** possesses high potentiality in organic synthesis, since (1) no special oxidizing reagent is required, (2) the procedures of the electrooxidation and subsequent workup are simple and easy, and (3) the reaction conditions are so mild that aldehydes having a carbon–carbon double bond (runs 8 and 9 in Table II) or an epoxy group (run 11 in Table II) can selectively be oxidized to the corresponding esters with these functional groups intact.

Experimental Section

IR spectra were taken with a Hitachi 215 spectrometer. ^{1}H NMR spectra were recorded on a Varian Associates EM-390 spectrometer using tetramethylsilane as an internal standard. Elemental analyses were determined by the Center for Instrumental Analysis of Kyoto University. Boiling points were uncorrected. Electrochemical oxidation was carried out using DC Power Supply (GP0502) of Takasago Seisakusho, Ltd.

Materials. Aldehydes **5–14**, **5a–8a**, and **12b** and potassium halides were commercially available. Epoxy aldehyde **15** was prepared by the oxidation of **14** with m-chloroperbenzoic acid and isolated by column chromatography (silica gel, AcOEt, hexane) in 68% yield: IR (film) 2950, 2930, 2730, 1715, 1380, 1120 cm^{-1}; NMR (CCl$_4$) δ 1.0 (d, J = 4 Hz, 3 H), 1.23 (s, 3 H), 1.26 (s, 3 H),

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[5] It has been known that aldehyde is generally equilibrated with its hydrated form in an aqueous solution,[6] and also the latter is the actual substrate in the chromic acid oxidation of aldehyde in an aqueous solution.[7]

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