A Novel Organic Peroxyester as an Exclusive Source of *tert*-Butyl Radicals

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A novel peroxyester, 1,1,2,2-tetramethylpropyl peroxypivalate **1b**, has been synthesized and thermolyzed in cumene. The kinetic data show that the decomposition rate constant of **1b** is about three times higher than that of *tert*-butyl peroxypivalate. The radical trapping technique employing 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl has been used to study the decomposition mechanism of **1b**. The results show that the thermolysis of **1b** in cumene generates *tert*-butyl radicals exclusively.

There have been many papers concerning the reactions of alkyl radicals with substrates such as toluene and vinyl monomers such as styrene and methyl methacrylate.[1-5] Among a variety of alkyl radicals, *tert*-butyl radical is one of the well-studied alkyl radicals and several routes to generate it, *i.e.* the photolysis of 2,2'-azoisobutane,[2] 2-methyl-2-nitroso-propane,[3] and di-*tert*-butylketone,[2a, 4] and the thermolysis of *tert*-butyl peroxypivalate **1a** (R = Me in **1**),[5] have been employed. Generation by the photolysis or thermolysis of dipivaloyl peroxide is possible but not practical, because this peroxide decomposes by an ionic mechanism even at 10 °C.[6] Thus most of the peroxide is wasted.

In this letter, the synthesis and thermolysis of a novel peroxyester, 1,1,2,2-tetra-methylpropyl peroxypivalate **1b** (R = Bu^t in **1**), as a source of *tert*-butyl radicals are described. *tert*-Alkyl peroxypivalates **1** are known to generate an equimolar amount of *tert*-butyl radicals and the corresponding *tert*-alkoxyl radicals **2** via a concerted two-bond scission accompanied by the cage reaction (about 50%) in a solvent such as cumene.[7] *tert*-Alkoxyl radicals having an alkyl group larger than a methyl group at tertiary carbon are known to be susceptible to β-scission to form a ketone and alkyl radicals at a significant rate.[8] However, very little is known about the rate of β-scission for 1,1,2,2-tetramethylpropoxyl radicals **2b** (R = Bu^t in **2**) to generate *tert*-butyl radicals.[8b]

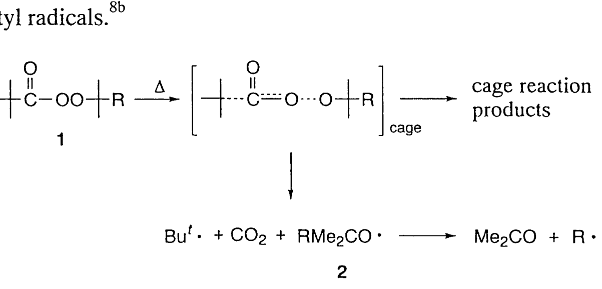


Chart 1.

Following the synthesis of 1,1,2,2-tetramethylpropyl hydroperoxide **3** from the corresponding alcohol, peroxypivalate **1b** was prepared by the reaction of pivaloyl chloride with **3** in alkaline solution.

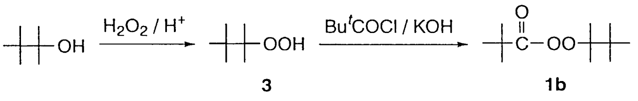


Chart 2.

Thus, 1,1,2,2-tetramethylpropanol[9] (11.6 g, 0.10 mol) in dichloromethane (12 ml) was added dropwise with stirring at 5-10 °C to a mixture of 50% hydrogen peroxide (28.6 g, 0.42 mol) and 98% sulfuric acid (20.0 g, 0.20 mol). Stirring was continued for 1.5 h at 0-5 °C. The organic layer was separated, washed with 10% $NaHCO_3$ and water, and dried over anhydrous Na_2SO_4 and $MgSO_4$. After the evaporation of the solvent under vacuum, a crude product of 10.7 g was obtained. The purification by the isolation of the sodium salt from hexane followed by regeneration gave white crystal (7.0 g). The purity was determined by iodometric titration using isopropyl alcohol and acetic acid as the solvent, and saturated potassium iodide as the source of iodide. The purity and yield of **3** were 97.8% and 53.0%, respectively [mp = 110 °C (lit. mp = 112-113 °C,[10a] 114 °C[10b])]. Pivaloyl chloride (12.1 g, 0.10 mol) was added dropwise over a period of 10 min with stirring at 0-5 °C to a mixture of 97.8% 1,1,2,2-tetramethylpropyl hydroperoxide (10.8 g, 0.08 mol), 30% KOH (31.7 g, 0.14 mol), and dichloromethane (11.0 g). Stirring was continued for 2 h at 5 °C, and then cold water (20 g) was added to the mixture. The organic layer was washed with 5% NaOH, with a buffer solution containing Na_2SO_3, acetic acid and sodium acetate, and then washed with water, and dried over anhydrous Na_2SO_4 and $MgSO_4$. Evaporation of dichloromethane gave 17.2 g of viscous liquid (crystallized at < -20 °C) in 80.0% of yield. The purity was determined by the following titration method. Acetic acid (0.2 ml), isopropyl alcohol (20 ml), and saturated potassium iodide (2 ml) were added to a 0.2 M KOH-methanol solution containing the peroxide sample (0.2 g) at room temperature. The mixture was refluxed for 3 min. The liberated iodide was titrated with aqueous sodium thiosulfate solution. Thus, the purity of the peroxyester was determined as 98.0%. The structures of **3** and **1b** were consistent with their NMR and IR spectra.[11]

The decomposition of **1b** (0.1 M) was carried out in cumene at the temperatures listed in Table 1, was measured by monitoring its disappearance by iodometric titration, and was found to satisfy first-order kinetics at all of the temperatures. The rate constants are shown in Table 1, together with that of the *tert*-butyl analogue **1a**. It can be seen that the decomposition rate constant of **1b** is about three times higher than that of **1a** and the half-life of **1b** is

Table 1. Decomposition kinetics of *tert*-alkyl peroxypivalates **1** in cumene

R in **1**	Temp. (°C)	$k_R \times 10^5$ (s^{-1})	$\Delta H^{\ddagger}$ ($kJ\,mol^{-1}$)	$\Delta S^{\ddagger}$ ($JK^{-1}\,mol^{-1}$)
Bu^t (**1b**)	40	0.689		
	45	1.36		
	50	2.51		
	55	5.01		
	60^a	9.10	109.4	5
Me (**1a**)	60^b	2.70	111.6	2

^{a} Calculated value. ^{b} Calculated value from data in ref. 12.

estimated to be 2.1 h at 60 °C.

The decomposition mechanism of **1b** was investigated using the radical trapping technique with the scavenger, 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl (TEMIO),[5b, 13] which reacts with carbon-centred radicals at close to diffusion controlled rate to produce stable alkoxyamines.[14] In previous work, we have shown that TEMIO does not influence the thermal decomposition of **1**.[5b] Thus, following the thermolysis of **1b** (0.02 M) in cumene at 60 °C for 1 h and in the presence of excess of TEMIO, the reaction mixture was analyzed by HPLC and was shown to contain *tert*-butoxyamine **4**,[5b] methoxyamine **5**[5b] and 1,1-dimethyl-benzyloxyamine **6**[15] (relative yields: 99.7, 0.1, 0.2%, respectively.)

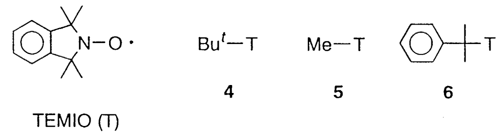
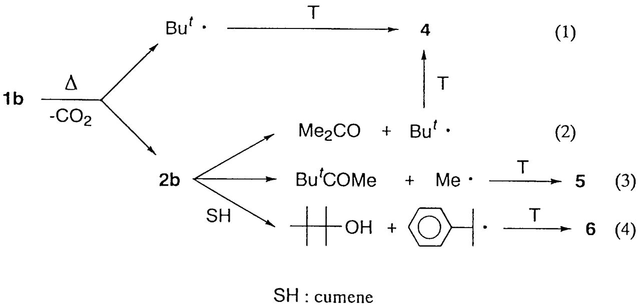


Chart 3.

A postulated reaction mechanism is shown in Scheme 1. The thermolysis of **1b** generating *tert*-butyl and *tert*-alkoxyl radicals **2b** is followed by β-scission of the great majority (> 99%) of alkoxyl radicals **2b** to *tert*-butyl radicals and acetone, and trapping of all the *tert*-butyl radicals by TEMIO to form alkoxyamine **4** (eqs 1 and 2). β-Scission of **2b** to form methyl radicals (eq 3) and hydrogen abstraction from cumene by **2b** (eq 4) occurred to a very small extent (< 0.5%). Thus, the β-scission of **2b** to generate *tert*-butyl radicals competes extremely effectively with abstraction from cumene.



Scheme 1.

In summary, we have found that **1b** is a low temperature active organic peroxide and that *tert*-butyl radicals are generated from 1,1,2,2-tetramethylpropoxyl radicals **2b** as well as from acyl groups in the decomposition of **1b**. Therefore, **1b** can be used as an exclusive source of *tert*-butyl radicals. This also indicates that **1b** is expected to be a very useful polymerization initiator for monomers such as methyl methacrylate because alkyl radical initiation proceeds exclusively by addition.[16] Thus the formation of unsaturated end groups in the resulting polymer by abstraction is minimized. A detailed study of the reaction of **1b** with solvents and monomers is in progress.

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11 Spectroscopic data: **3**; ^{1}H NMR (270 MHz, $CDCl_3$) δ = 0.93 (9H, s, Me), 1.20 (6H, s, Me), and 9.64 (1H, s, OH); IR (neat) ν 3552, 3421, 2913, 2875, 1457, 1419, 1398, 1321, 1166, 1164, 1143, 948, 850, 782, and 750 cm^{-1}; GC-MS (70eV) m/z 117 (0.4), 99 (7), 75 (7), and 57 (100). **1b**; ^{1}H NMR (270MHz, $CDCl_3$) δ = 1.01 (9H, s, Me), 1.23 (9H, s, Me), and 1.26 (6H, s, Me); ^{13}C NMR ($CDCl_3$) δ = 20.57, 25.89, 27.29, 37.80, 38.86, 89.48, and 175.32; IR (neat) ν 2975, 2913, 2877, 2877, 1768, 1479, 1463, 1398, 1378, 1369, 1261, 1228, 1182, 1166, 1141, 1095, 1024, 958, 956, 941, 890, 850, 809, and 779 cm^{-1}.

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15 The compound **6** was isolated by preparative HPLC and characterized by HPLC-MS and NMR. Spectroscopic data: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.24 (6H, s, 2 × ring Me), 1.33 (6H, s, 2 × ring Me), 1.70 (6H, s, 2 × benzylic Me), 7.04-7.09, 7.20-7.40, and 7.58-7.63 (9H, m, ArH); HPLC-MS m/z 332 $(M + Na)^+$ 310 $(M + H)^+$.

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