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A New Type of Induced Decomposition. IV.[1] Pyrolysis of *t*-Butyl Peroxy-3-butenoate in the Gas Phase

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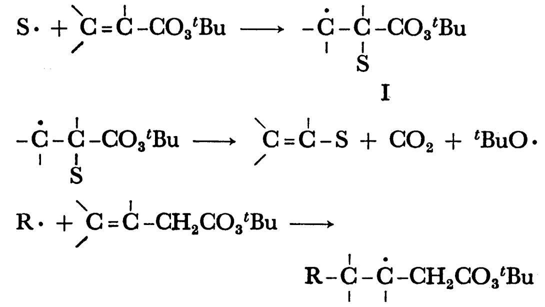
Synopsis. *t*-Butyl peroxy-3-butenoate decomposes in the gas phase at 115 °C to give carbon dioxide, 1-butene, acetone, 1,5-hexadiene, methane, and ethane. Experiments with iodine, an efficient radical scavenger, indicate the operation of induced decomposition. The mechanism of the formation of 1-butene and 1,5-hexadiene is discussed in terms of a new type of induced decomposition.

In previous communications[1] we reported that *t*-butyl peroxy-esters derived from α,β-unsaturated carboxylic acids undergo a new type of induced decomposition and proposed a mechanism, in which radicals (S·) derived from solvent (SH) by hydrogen-abstraction add to the unsaturated bond of a peroxide to give an intermediate radical (I) carrying an odd electron on the carbon atom β to the carboxyl group and this radical subsequently undergoes β-scission to afford an olefin, a molecule of carbon dioxide, and a *t*-butoxyl radical (Reactions 1 and 2 in the following scheme).



$$\mathrm{S\cdot + {>}C{=}\overset{|}{C}\text{-}CO_3{}^tBu \longrightarrow -\dot{C}\text{-}\underset{S}{\overset{|}{C}}\text{-}CO_3{}^tBu} \quad (1)$$

I

$$\mathrm{-\dot{C}\text{-}\underset{S}{\overset{|}{C}}\text{-}CO_3{}^tBu \longrightarrow {>}C{=}\overset{|}{C}\text{-}S + CO_2 + {}^tBuO\cdot} \quad (2)$$

$$\mathrm{R\cdot + {>}C{=}\overset{|}{C}\text{-}CH_2CO_3{}^tBu \longrightarrow R\text{-}\overset{|}{\underset{|}{C}}\text{-}\dot{\underset{|}{C}}\text{-}CH_2CO_3{}^tBu} \quad (3)$$

SH = solvent

Radicals similar to structure I can also be generated by addition of a radical to the γ-position of β,γ-unsaturated peroxy-esters (Reaction 3), which therefore may undergo β-scission in a way similar to Reaction 2. With the view of examining such a possibility the decomposition of *t*-butyl peroxy-3-butenoate was studied.

Results and Discussion

The results of the decomposition of *t*-butyl peroxy-3-butenoate (II) in the gas phase at 115 °C are summarized in Table 1. The major products identified by VPC were carbon dioxide, 1-butene, 1,5-hexadiene, acetone, methane, and ethane, and are readily explained by assuming the following series of reactions.[2] Acetone and ethane result from Reactions 5 and 6. Methane arises from methyl radicals by hydrogen-abstraction from some hydrogen donating species in the system (Reaction 7).

$$\underset{\text{II}}{\mathrm{CH_2{=}CHCH_2CO_3{}^tBu}} \longrightarrow \mathrm{CH_2{=}CHCH_2\cdot + CO_2 + {}^tBuO\cdot} \quad (4)$$

$$\mathrm{{}^tBuO\cdot \longrightarrow CH_3COCH_3 + CH_3\cdot} \quad (5)$$

$$\mathrm{2CH_3\cdot \longrightarrow CH_3CH_3} \quad (6)$$

$$\mathrm{CH_3\cdot + SH \longrightarrow CH_4 + S\cdot} \quad (7)$$

SH = hydrogen donor

Table 1. Products from pyrolysis of *t*-butyl peroxy-3-butenoate at 115 °C for 3 h

	Run 1	Run 2
Peroxybutenoate, mmol	0.585	0.519
Products, mmol		
Carbon dioxide	0.599 (1.02)[a]	0.512 (0.986)
1-Butene	0.160 (0.274)	0.138 (0.266)
Acetone	0.444 (0.759)	0.389 (0.749)
1,5-Hexadiene	0.136 (0.232)	0.120 (0.231)
Methane	0.054 (0.093)	0.053 (0.101)
Ethane	0.083 (0.144)	0.067 (0.129)

a) Yields in mol per 1 mol of the peroxybutenoate are given in parentheses.

The formation of 1-butene and 1,5-hexadiene is satisfactorily explained, as is anticipated in the introduction, thus:

$$\mathrm{CH_3\cdot + CH_2{=}CHCH_2CO_3{}^tBu \longrightarrow CH_3CH_2\dot{C}HCH_2CO_3{}^tBu}$$

$$\mathrm{CH_3CH_2\dot{C}HCH_2CO_3{}^tBu \longrightarrow CH_3CH_2CH{=}CH_2 + CO_2 + {}^tBuO\cdot} \quad (8)$$

$$\mathrm{CH_2{=}CHCH_2\cdot + CH_2{=}CHCH_2CO_3{}^tBu \longrightarrow CH_2{=}CHCH_2CH_2\dot{C}HCH_2CO_3{}^tBu}$$

$$\mathrm{CH_2{=}CHCH_2CH_2\dot{C}HCH_2CO_3{}^tBu \longrightarrow (CH_2{=}CHCH_2)_2 + CO_2 + {}^tBuO\cdot} \quad (9)$$

The addition of a methyl radical to the peroxy-3-butenoate gives 1-(*t*-butylperoxycarbonylmethyl)propyl radical, which then decomposes into 1-butene, a molecule of carbon dioxide, and a *t*-butoxyl radical (Reaction 8). 1,5-Hexadiene is given through a similar addition-elimination mechanism (Reaction 9).

An alternative mechanism for the formation of 1-butene and 1,5-hexadiene is the combination of the allyl and methyl radical (Reactions 10 and 11):

$$\mathrm{CH_2{=}CHCH_2\cdot + CH_3\cdot \longrightarrow CH_3CH_2CH{=}CH_2} \quad (10)$$

$$\mathrm{2CH_2{=}CHCH_2\cdot \longrightarrow (CH_2{=}CHCH_2)_2} \quad (11)$$

The exclusive operation of this mechanism, which does not involve any induced path, is ruled out by the experiments summarized in Table 2. The peroxy-3-butenoate was heated in the presence of iodine, an effective radical scavenger, or nitrogen, inert molecules towards radicals, at 115 °C for 1.0 h, and the amount of carbon dioxide evolved was measured. Since the peroxy-3-butenoate affords carbon dioxide quantitatively (Table 1), the amount of carbon dioxide obtained corresponds to that

TABLE 2. DECOMPOSITION OF *t*-BUTYL PEROXY-3-BUTENOATE IN THE PRESENCE OF IODINE OR OF NITROGEN[a)]

Run	Peroxy-butenoate mmol	I_2 mmol	N_2 mmol	CO_2 produced mmol
1	0.281	nil	0.897	0.244 (0.868)[b)]
2	0.286	nil	0.854	0.246 (0.860)
3	0.300	nil	0.890	0.261 (0.870)
4	0.289	0.168	nil	0.179 (0.620)
5	0.277	0.601	nil	0.034 (0.12)
6	0.294	0.564	nil	0.073 (0.25)
7	0.287	0.618	nil	0.056 (0.20)

a) At 115 °C, for 1.0 h, in the gas phase. b) Yields in mol per 1 mol of peroxide are given in parentheses.

of the peroxy-3-butenoate decomposed. Under the above conditions 87% of the starting peroxy-3-butenoate underwent the decomposition in the presence of 0.9 mmol of nitrogen, while only 62% of the peroxy-3-butenoate was decomposed in the presence of 0.17 mmol of iodine, and the extent decomposition further decreased with increasing iodine concentration. These findings indicate that iodine scavenges efficiently the free radicals which otherwise will cause induced decomposition of the peroxy-3-butenoate and thus support the operation of an induced pathway for the formation of 1-butene and 1,5-hexadiene.

Experimental

t-Butyl Peroxy-3-butenoate. 3-Butenoic acid[3)] (4.7 g), bp 69.0—70.0 °C/12 mmHg, was heated under reflux for 30 min with 1.2 molar equivalents of thionyl chloride, and the resulting 3-butenoyl chloride (3 g) was distilled, bp 95—96 °C. A solution of this chloride (1.68 g) in 8 ml of anhydrous pentane was added to a stirred solution of *t*-butyl hydroperoxide (bp 32 °C/12 mmHg, 1.91 g) and pyridine (1.36 g) in anhydrous pentane (7 ml) at −20—−25 °C over a period of 1.3 h. The resulting mixture was allowed to warm to 0 °C, the supernatant solution decanted into a vessel containing ice-water, the remaining pyridinium chloride washed twice with pentane, and the washings added to the ice-water. The organic layer was separated, washed successively with 4 ml of 5% sulfuric acid, 4 ml of 10% aqueous sodium carbonate, and water. and dried with anhydrous sodium sulphate. After removal of pentane under reduced pressure, the oily residue was distilled to give 1.5 g (59%) of *t*-butyl peroxy-3-butenoate, bp 16 °C/2 mmHg (Found: C, 60.60; H, 9.04%. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92%. Purity, 96% by iodometric titration[4)]), IR (neat) 1645 ($\nu_{C=C}$) and 1785 cm^{-1} ($\nu_{C=O}$).

Pyrolysis of t-Butyl Peroxy-3-butenoate. A typical run was as follows. *t*-Butyl peroxy-3-butenoate (0.58 mmol) was placed in a glass vessel (730 ml), which was then degassed (three freeze-thaw cycles), sealed and immersed in an oil bath maintained at 115 °C, and the peroxy-ester was allowed to decompose in the gas phase for 3 h. After cooling to room temperature, the vessel was attached to a vacuum system, and the products were transferred to a sampling tube for VPC analysis.

Analyses were carried out with a Perkin Elmer Vapor Fractometer Model 154-D by using helium as carrier gas and the following stainless steel column: 1) A 2m column packed with Silica gel, Type 15 at 51 °C for analysis for methane, ethane, and carbon dioxide; 2) a 2m column packed with dimethylsulfolane at 60 °C for analysis for 1-butene, 1,5-hexadiene and acetone. For authentic materials for comparison commercial products were used except 1,5-hexadiene, which was prepared according to a published procedure.[5)]

References

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2) The peroxybutenoate is thought to undergo a synchronous two-bond scission since the allyl radical is relatively stable [P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958)].

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