The Decomposition of *t*-Butylperoxy *o*-Phenylbenzoate

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Bentrude and Martin[1] reported that the first-order thermal decompositions of some *o*-substituted *t*-butyl perbenzoates were very fast. Relative rates in chlorobenzene at 60°C varied with the *o*-substituents in the order:

$$\mathrm{PhS} > \mathrm{MeS} \ggg \mathrm{I} \gg (\mathrm{CH_3})_3\mathrm{C} > \mathrm{H}.$$

The tremendous rate enhancements observed with the first two of these peresters and the lesser effect accompanying the decomposition of the *o*-iodo perbenzoate were ascribed to the neighboring-group participation in a homolytic bond cleavage, the O-O bond cleavage being accompanied by simultaneous O-S (or O-I) bond formation.

It seems to be of great interest to investigate the decomposition of *t*-butylperoxy *o*-phenylbenzoate as to the possibility of the phenyl participation at the transition state of the decomposition, and this paper describes the results of the investigation of this perester.

Table 1 summarizes the kinetic data on *t*-butylperoxy *o*-phenylbenzoate together with those of *t*-butyl perbenzoate for comparison.

These very small acceleration of the decomposition (the ratio of the rate constants is 2.74 at 110°C and 2.56 at 130°C) seems to exclude the possibility of the *o*-phenyl participation at the transition state.

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[1] W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.,* **84**, 1561 (1962).

TABLE 1. DECOMPOSITION RATES OF PERESTERS $RCO_3C(CH_3)_3$

R	Solvent	First-order const. (sec^{-1})				$\Delta H^{\neq}$	$\Delta S^{\neq}$
		110°C	119.4°C	124°C	130°C	kcal/mol,	cal/deg
o-$C_6H_5C_6H_4$	Cumene	9.40×10^{-5}		2.71×10^{-4}	8.60×10^{-4}	35.8	15.6
C_6H_5	p-Chlorotoluene	3.42×10^{-5}	1.01×10^{-4}		3.36×10^{-4}	34.5	14.1[a]

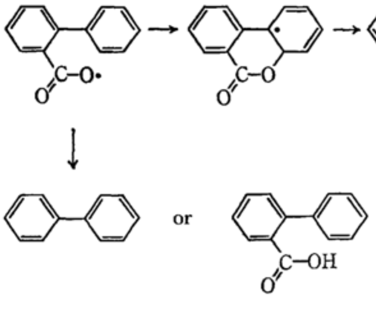
[a] A. T. Blomquist and A. F. Ferris, *J. Am. Chem. Soc.*, **73**, 3408 (1951).

TABLE 2. PRODUCTS OF DECOMPOSITION OF *t*-BUTYLPEROXY *o*-PHENYLBENZOATE IN CUMENE AT 125°C

	moles/mole of perester
Carbon dioxide	0.27
Acetone	0.23
t-Butyl alcohol	0.51
Fluorenone	0.11
o-Phenylbenzoic acid	0.22
3, 4-Benzcoumarin	0.32
Biphenyl	0.16
Bicumyl	0.20

The products of the decomposition of the perester in cumene at 125°C are listed in Table 2. It is interesting that about 32% of the perester was converted to 3, 4-benzcoumarin. This finding indicates that, even though the cleavage of the peroxide bond is not helped by the ortho phenyl π-system, the odd electron of the *o*-phenylbenzoyloxy radical formed reacts with the ortho phenyl π-system. The formation of fluorenone is rather difficult to explain. One speculation is that the perester decomposes to form fluorenone and *t*-butyl hydroperoxide, the latter being further decomposed to acetone and *t*-butyl alcohol.

The products of the decomposition of the perester indicate that the *o*-phenylbenzoyloxy radicals formed are converted into three products, namely, 3, 4-benzcoumarin, *o*-phenylbenzoic acid or biphenyl.



It is interesting to compare these findings with the studies on some of the peresters, the structures of which suggest the possibility of phenyl ring participation with the decomposition.

Greene *et al.*2) studied the decomposition of *o*-phenylbenzoyl peroxide, and found that *o*-phenyl ring did not participate at the transition state but reacted with the carboxy radical to form 3, 4-benzcoumarin.

It seems worth commenting on the facile cyclization of *o*-phenylbenzoyl chloride to form fluorenone, the phenomenon observed when the acid was being converted into the acid chloride. Since a general method for preparation of an acid chloride is to reflux an acid with thionyl chloride, *o*-phenylbenzoic acid was refluxed with excess thionyl chloride for one hour. The product was fluorenone, not *o*-phenylbenzoyl chloride. Therefore, this reaction was further investigated at 30°C. Since the use of unpurified thionyl chloride resulted in the faster cyclization, hydrogen chloride was suspected to be the catalyst for this Friedel-Crafts reaction. When 0.02 g of water was carefully added into the mixture of 0.091 g of the acid and 0.331 *ml* of thionyl chloride in order to increase the content of hydrogen chloride in the mixture, the cyclization was faster. The reaction was followed by the changes of carbonyl absorptions in the infrared, and the results were shown in Fig. 1. Hydrogen chloride, though not reported as a catalyst for Friedel-Crafts reaction in literatures, could function as the catalyst.

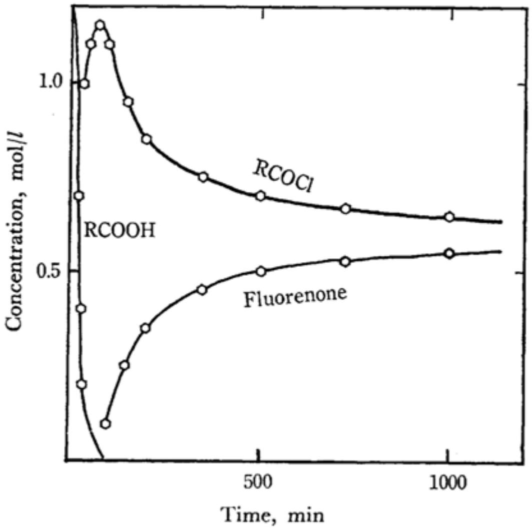


Fig. 1. Conversion of acid chloride to fluorenone.
RCOOH = 0.091 g, $SOCl_2$ = 0.331 *ml*,
H_2O = 0.02 g, 30.0°C

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2) F. D. Greene, G. R. Van Norman, J. C. Cantrill and R. D. Gilliom, *J. Org. Chem.*, **25**, 1790 (1960).

The suppression of this Friedel-Crafts cyclization was investigated, and it was found that the addition of weak proton acceptor such as diethyl ether or diphenyl ether resulted in the almost complete suppression of the cyclization and the formation of the acid chloride in a good yield.

Experimental

***o*-Phenylbenzoic Acid.** *o*-Phenylbenzoic acid was prepared from fluorenone by the method of Huntress and Seikel.[3]

Mp 114°C (lit[4] 114°C).

***o*-Phenylbenzoyl Chloride.** Usually acid chlorides are prepared by heating acids with thionyl chloride. Greene *et al.*[2] reported that *o*-phenylbenzoyl chloride was prepared by the action of thionyl chloride on the acid and the distillation at 99.5—101°C/0.3 mmHg. They observed that some closure to fluorenone occurred during distillation (weak carbonyl absorption in the infrared at 1728 cm^{-1}).

However, when the acid was refluxed in thionyl chloride at 80°C for one hour almost all the acid was converted into fluorenone. After various attempts, the following method was found to be the best. A mixture of 1 g of the acid, 1 g of diethyl ether and 2.60 m*l* of thionyl chloride was let to react in an oil bath at 30°C for 120 min. Then the excess thionyl chloride was evaporated by aspirator. The residual oil was the acid chloride with a very small amount of fluorenone. The distillation at 99.5—101°C/0.3 mmHg yielded the pure acid chloride.

***t*-Butylperoxy *o*-Phenylbenzoate.** A solution of 3.163 g (35.14 mmol) of *t*-butyl hydroperoxide in 10 m*l* of petroleum ether was added to a solution of 1 g (5.02 mmol) of the acid chloride in 10 m*l* of petroleum ether. 3.033 g (38.4 mmol) of pyridine in 10 m*l* of petroleum ether was then added slowly to this ice-cooled mixture. The solution was stirred at 0°C by a magnetic stirrer until the precipitation of pyridinium chloride was complete. The mixture was washed with a cold 10% sulfuric acid solution, a 5% sodium carbonate solution and water. The perester solution was then dried with anhydrous sodium sulfate. The evaporation of petroleum ether and other low-boiling impurities under vacuum yielded 1.13 g (83.4%) of the perester as a yellow oil. The infrared spectrum of this oil showed the strong absorption of the perester at 1765 cm^{-1}. When this oil in petroleum ether was passed down through a short chromatographic column packed with alumina, the decomposition of the perester occurred on the column. However, since the perester freed from low-boiling impurities was found to be of fair purity, this perester was used for kinetic and product studies. (Found: C, 76.03, H, 6.50%. Calcd for $C_{17}H_{18}O_3$, C, 75.53, H, 6.71%.).

Kinetic Procedure. A weighed quantity of perester was dissolved in cumene. The concentration of the solution was calculated to bring the concentration of the perester within the range of about 20 to 80% transmission as to the carbonyl absorption at the infrared.

The solution was transferred to about ten small test tubes. The tubes were then sealed at atmospheric pressure without degassing and placed in the thermostated oil bath at each decomposition temperature. The initial solution was taken as the zero time sample. At suitable intervals one of the tubes was subsequently withdrawn and cooled rapidly in ice. The infinity sample was left in the bath for about ten half lives. Each sample was stored at −5°C until the infrared analysis was carried out.

A Hitachi Infrared Spectrophotometer was used with cells of 0.1 mm thickness for the determination of the amount of the perester remaining.

The relative concentration at time t was calculated from the equation:

$$P/P_0 = \frac{\log T_\infty - \log T_t}{\log T_\infty - \log T_0}$$

Where T_∞ is the percentage transmission of the sample at infinite time against pure solvent, and T_0 is the percentage transmission of the initial sample.

Product Studies. 1.285 g (4.76 mmol) of the perester was dissolved in 10 m*l* of cumene in a decomposition flask and was attached onto a vacuum system. The solution was degassed three times by alternately freezing with dry ice-methanol mixture and evacuating the flask. The flask was sealed under vacuum and immersed in an oil bath at 125°C for about ten half lives until the perester decomposition was complete. The flask was again attached to the vacuum system. The amount of the gas not condensible with liquid nitrogen, which was presumably methane, was not determined. After the non-condensible gas was evacuated, the pressure of carbon dioxide released from the flask to the vacuum system was read on the manometer. The vacuum distillation of the solution yielded the liquid products and the non-distillable residue.

From the pressure of the gas and the known volume of the vacuum system, the number of moles of carbon dioxide formed was determined.

The volatile products in the solvent were identified to be acetone and *t*-butyl alcohol by the gas chromatography, and their amounts were quantitatively determined by a Shimadzu Gas Chromatograph Type GC-2B.

The infrared spectrum of the non-distillable residue indicated the presence of 3, 4-benzcoumarin (1747 cm^{-1}), *o*-phenylbenzoic acid (1690 cm^{-1}) and fluorenone (1717 cm^{-1}). The residue was chromatographed on alumina. The fractions were identified by the comparison of their infrared spectra and melting points with those of the authentic samples. The products found were biphenyl, bicumyl, fluorenone, 3, 4-benzcoumarin and *o*-phenylbenzoic acid.

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[3] E. H. Huntress and M. K. Seikel, *J. Am. Chem. Soc.*, **61**, 816 (1939).

[4] "Kagaku Daijiten," Vol. VII, Kyoritsu, Tokyo (1961), p. 497.