(20) Similar species have been invoked in cross couplings effected with *stoichiometric* amounts of organonickel reagents, see: (a) M. F. Semmelhack, *Org. React.*, **19**, 155 (1972); (b) R. Baker, *Chem. Rev.*, **73**, 487 (1973); (c) A. Nakamura and S. Ohtsuka, *Tetrahedron Lett.*, 463 (1974).

(21) (a) A. Tamaki, S. A. Magennis, and J. K. Kochi, *J. Am. Chem. Soc.*, **96**, 6140 (1974); (b) Cf. also for Pt(IV): M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J. Chem. Soc., Dalton Trans.*, 2457 (1974).

(22) (a) For structural factors in equilibria involved in 4- and 5-coordinate Ni(II) complexes with monodentate phosphines: L_nNiX_2 ($n = 2, 3$) see E. C. Alyea and D. W. Meek, *J. Am. Chem. Soc.*, **91**, 5761 (1969); Cf. also J. W. Dawson et al., *ibid.*, **96**, 4428 (1974). (b) The very rapid isomerization of a cis precursor is not precluded by our results. (c) Interestingly, reductive elimination from alkylgold(III) also proceeds from a 3-coordinate species (see ref 21a).

(23) Cf. J. F. Garst in "Free Radicals", J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 9; G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, *Adv. Chem. Ser.* **51**, 112 (1965).

(24) H. R. Ward, R. G. Lawler, and R. A. Cooper in "Chemically Induced Magnetic Polarization", A. R. Lepley and G. L. Closs, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 7. See also S. Bank and D. A. Juckett, *J. Am. Chem. Soc.*, **97**, 567 (1975).

(25) (a) Cf. M. M. Baizer, Ed., "Organic Electrochemistry", Marcel Dekker, New York, N.Y., 1973, (b) R. J. Rogers, H. L. Mitchell, Y. Fujiwara, and G. M. Whitesides, *J. Org. Chem.*, **39**, 857 (1974).

(26) (a) H. O. House and M. J. Umen, *J. Am. Chem. Soc.*, **94**, 5495 (1972); (b) H. C. Gardner and J. K. Kochi, *ibid.*, **97**, 1885 (1975); (c) W. A. Nugent, F. Bertini, and J. K. Kochi, *ibid.*, **96**, 4945 (1974); (d) L. S. Hegedus and L. L. Miller, *ibid.*, **97**, 459 (1975); (e) E. C. Ashby, I. G. Lopp, and J. D. Buhler, *ibid.*, **97**, 1964 (1975); (f) I. H. Elson, D. G. Morrell, and J. K. Kochi, *J. Organomet. Chem.*, **84**, C7 (1975).

(27) (a) J. Halpern, M. S. Chan, J. Hanson, T. S. Roche, and J. A. Topich, *J. Am. Chem. Soc.*, **97**, 1607 (1975); (b) S. N. Anderson, D. H. Ballard, J. Z. Chrzastowski, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 685 (1972); (c) J. K. Kochi, *Acc. Chem. Res.*, 7, 351 (1974); (d) G. Costa, A. Puxeddu, and E. Reisenhofer, *Bioelectrochem. Bioenerg.*, **1**, 29 (1974).

(28) A stable 5-coordinate σ-phenylnickel(II) species is described [P. Dapporto and L. Sacconi, *Inorg. Chim. Acta*, **9**, 62 (1974)].

(29) (a) Cf. H. O. House and M. J. Umen, *J. Org. Chem.*, **38**, 3893 (1973). (b) Based strictly on oxidation potentials, the oxidation of the nickelate complex in eq 23 is likely to be faster than that of the neutral complex in eq 21.

(30) Equation 24 represents one extreme of a charge transfer interaction of I with an acceptor in which electron transfer is complete and reactions subsequently proceed from the ion–radicals. On the other hand, an acceptor can *perturb* a donor such as I and cause labilization of the organometal bond by lowering of the energies of the d orbitals.[31] The latter has been described well by Yamamoto et al.[32] for the reductive elimination of butane from diethyl(dipyridyl)nickel(II) enhanced by various olefins and included in Kumada's original formulation.[1,7] From our work, the scrambling of aryl groups observed during the reaction of I and ArBr supports the first formulation and not the second. However, pending more extensive studies, we do not feel that a *rigorous* distinction between the two processes can be made at this juncture.

(31) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959); See also P. Cossee, *J. Catal.*, **3**, 80 (1964).

(32) T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **93**, 3350, 3360 (1971).

(33) F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959); D. Dolphin and K. Endo, *Anal. Biochem.*, **36**, 338 (1970).

(34) Selected Mass Spectral Data, American Petroleum Institute, Texas A and M University, College Station, Texas, 1969.

The Decomposition of Phenolic Peresters. II. *tert*-Butyl 3,5-Di-*tert*-butyl-2-hydroxyperbenzoate and *tert*-Butyl 5-Methyl-3-*tert*-butyl-2-hydroxyperbenzoate[1]

John T. Barbas and J. E. Leffler*

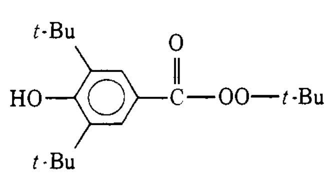
Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306.

Received May 1, 1975

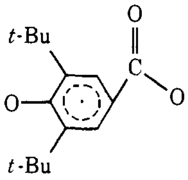
Abstract: The *o*-hydroxy-substituted *tert*-butyl perbenzoates **3a** and **3b** contrast remarkably with the *p*-hydroxy perester **1**[2] in two ways. First, the introduction of the hydroxyl group in the ortho position, unlike the introduction in the para position, causes a large increase in the first-order rate constant for the spontaneous decomposition of the perester. Second, the *o*-hydroxy-substituted peresters are quite insensitive to radicals and to bases, whereas such reagents induce a rapid decomposition of the para compound by abstracting H· or H^+ from its *p*-hydroxyl group. The rapid spontaneous decomposition of **3a** and **3b** is attributed to the intramolecular transfer of a hydrogen atom from OH to the carbonyl oxygen, an atom to which it is already hydrogen bonded. The same hydrogen bond protects the *o*-hydroxyl group from attack by external reagents.

The first paper of this series[2] was concerned with compound **1**, a *p*-hydroxy-substituted *tert*-butyl perbenzoate. The reason for our interest in **1** was its use as a model for induced decomposition and carboxy inversion reactions of peroxides.

Compound **1** is sensitive both to radicals, which remove hydrogen atoms from the phenolic OH, and to bases, which remove protons. In both cases the intermediate produced is believed to be the triplet diradical **2**.[3]



1

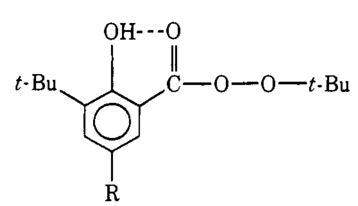


2

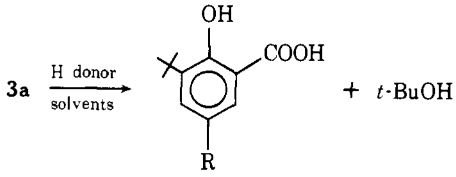
In contrast to the radical or base induced decomposition, the rate of the spontaneous decomposition of **1** is unexceptional and consistent with the substituent effects observed for ordinary *tert*-butyl perbenzoates.

In the present paper, we describe the almost precisely opposite behavior of *o*-hydroxy substituents.

Reaction Products. The products from the decomposition of the *o*-hydroxy-substituted peresters **3a** and **3b** are consistent with a simple homolysis. Thus the decomposition of 0.1 *M* **3a** in degassed tetrahydrofuran at 70° proceeds essentially according to eq 1. The yield of the acid **4a** is 92%, and



3a, R = methyl
3b, R = *tert*-butyl



(1)

4a, R = CH_3
4b, R = t-Bu

no acetone is formed. In solvents less susceptible to hydrogen atom abstraction, the acyloxy moieties are increasingly decarboxylated, though never completely decarboxylated, and the *tert*-butoxy radicals undergo extensive β-cleavage to acetone. In benzene, $CHCl_3$, and CCl_4, the yields of acid are 84, 60, and 38%, respectively. Besides CO_2 and acetone, the products in benzene included 1.8 mol % of biphenyl and several unidentified carbonyl compounds. The formation of acetone in CCl_4 solution is suppressed by added 0.2 *M* 4-methyl-2,6-di-*tert*-butylphenol.

The products from *tert*-butyl 3,5-di-*tert*-butyl-2-hydroxyperbenzoate (**3b**) in benzene are CO_2, acetone, *tert*-butyl alcohol, the corresponding acid (**4b**) in 82% yield, 2,4-di-*tert*-butylphenol (4.1%), biphenyl (1.4%), and phenyl 3,5-di-*tert*-butyl-2-hydroxybenzoate (1.1%).

Although the perester **3a** is clearly a source of radicals, it and its phenolic decomposition products are also inhibitors. Decomposing in styrene at 70°, the net effect of **3a** is to inhibit rather than promote the polymerization of the styrene.

No CIDNP proton signals were observable when **3a** was decomposed in hexachloroacetone at 140° at 8000 G.

Kinetics. In contrast to the perester **1**, the *o*-hydroxy-substituted peresters show no evidence of acceleration by reagents that might remove either a hydrogen atom or a proton from the phenolic OH group.

The first-order rate constants (Table I) are insensitive to increases in the initial concentration of perester, the runs are precisely first order with no sign of autocatalysis, and the rate constants are not very different in the solvents benzene (a poor chain-transfer agent) and tetrahydrofuran (a good chain-transfer agent). Solid MnO_2 added to a benzene solution of **3a** at room temperature had no effect. The k_{HO}/k_{DO} isotope effect in benzene is only 1.30, which also indicates that chains involving the removal of a phenolic hydrogen atom are unimportant. The k_{HO}/k_{DO} for the *p*-hydroxy compound **1** was not significantly different from unity for dilute solutions but ranged up to 13 for more concentrated solutions.

There is also no sign of the extreme sensitivity to base shown by **1**. Whereas pyridine in tetrahydrofuran caused a rapid decomposition of **1** even at −20°, **3a** shows no appreciable change in the carbonyl infrared band after 1.5 hr at room temperature, either in 1:6 pyridine-THF or in neat pyridine. In benzene, pyridine caused a moderately fast decomposition of **1** at room temperature but has no effect on the rate of decomposition of **3a** even at 50°.

Table I. Decomposition Kinetics in Degassed Solvents

Solvent	T, °C	Initial concn, M	10^5k_1, sec^{-1}	$\Delta H^‡$, kcal/mol	$\Delta S^‡$, cal/(mol deg)
tert-Butyl 5-Methyl-3-*tert*-butyl-2-hydroxyperbenzoate (3a)					
Benzene	70.0	0.050	36.2	24.4	−3.4
	50.5	0.049	3.94		
	70.0	0.100	38.7		
	70.0	0.062	28.9[a]		
CCl_4	70.0	0.070	26.9		
		0.100	26.1[b]		
THF	70.0	0.050	30.2		
		0.100	30.7		
tert-Butyl 3,5-Di-*tert*-butyl-2-hydroxyperbenzoate (3b)					
Benzene	70.0	0.050	30.2	24.2	−4.3
	50.5	0.050	3.35		

[a] *tert*-Butyl 5-methyl-3-*tert*-butyl-2-deuterioxyperbenzoate, k_H/k_D = 1.30. [b] In the presence of 0.2 *M* 4-methyl-2,6-di-*tert*-butylphenol.

Table II. Effects of Ortho Substituents in *tert*-Butyl Perbenzoates

Substituent	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, cal mol^{-1} deg^{-1}	$k_{rel}60°$[c]
2-CH_3S–[a]	22.6	−5.0	18500
2-C_6H_5S–[b]	23.0	−3.4	22700
2-HO-3,5-di-t-Bu[d]	24.2	−4.3	2280
2-HO-5-Me-3-t-Bu[d]	24.4	−3.4	2700
2-($(C_6H_5)_2C{=}CH$)–[b]	26.3	−5.0	69
2-I[b]	28.0	−0.8	44
2-$C_6H_5SCH_2$–[b]	32.2	7.2	4.3
H[b]	34.1	10.0	1.0 (4.44×10^{-8})[e]
2-t-Bu[b]	34.4	12.5	2.2
2-CH_3SO_2–[b]	38.0	19.5	0.33

[a] Reference 8, in chlorobenzene. [b] Reference 9, in chlorobenzene. [c] Relative to H = 1, calculated from the activation parameters. [d] This paper, in benzene. [e] Calculated k in sec^{-1}.

Discussion

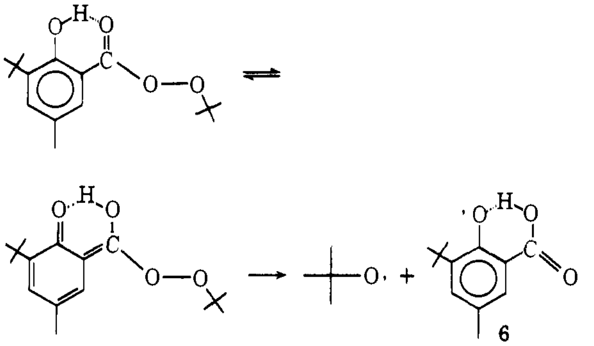
The important structural difference between peresters **3a** or **3b** and the *p*-hydroxy compound **1** is the presence of an intramolecular hydrogen bond between the hydroxyl group and the adjacent carbonyl in the *o*-hydroxy peresters. The presence of this bond is shown by broad infrared bands at 3200 (**3b**) and 3160 cm^{-1} (**3a**) and carbonyl bands at 1690 (**3b**) and 1700 cm^{-1} (**3a**).[4] In other perbenzoates, the carbonyl absorption occurs near 1750 cm^{-1}. On replacing the hydrogen of the OH with deuterium, there is a further shift from 1700 cm^{-1} (**3a** in $CHCl_3$) to 1692 cm^{-1}, as expected for an intramolecular hydrogen bond.[5] The ^1H NMR signals from the OH in **3a** and **3b** also substantiate the chelated structure. They are sharp singlets at δ 11.00 (**3b**) and 10.93 (**3a**), well down field from the usual phenolic OH position. These signals remain sharp down to −100° indicating that there are no stable or slowly equilibrating hydrogen bonded or zwitterionic isomers.

The apparently complete insensitivity of **3a** and **3b** to bases or H-atom abstractors, in contrast to the extreme sensitivity of **1** to the same reagents, is probably the result of the internal hydrogen bonds in **3a** and **3b**. It can be assumed that the hydrogen bond must also be broken by any reagent that might break the covalent bond of the hydroxyl hydrogen. Considerations of entropy and some intermolecular model compounds suggest an equilibrium constant in the neighborhood of 10^{-5} to 10^{-6} for the opening of the cyclic H bond. This should provide enough of an additional energy barrier to account for the insensitivity of the *o*-hydroxy perester to external reagents.[6]

Although the *o*-hydroxyl in **3a** or **3b** fails to impart any unusual sensitivity to base or radical induced decomposition, it does increase the rate of the spontaneous decomposition by more than three orders of magnitude.[7] For the most part, ortho substituents in peresters fall into two classes, both of which are exemplified by data in Table II.[8,9] Substituents without available electron pairs on the α-atom have very little effect on the rate. Substituents such as *o*-phenylthiyl, on the other hand, accelerate the reaction by several orders of magnitude. These anchimeric effects have been attributed to concerted bond formation or to electron transfer.

Although *o*-hydroxy resembles the latter substituents in its effect on the rate, there are important differences, both phenomenological and structural. Medium effects on the rate of decomposition of **3a** are much smaller than those for *tert*-butyl *o*-phenylthiylperbenzoate[10] and are not correlated with any of the usual measures of solvent polarity. The important structural differences are the hydrogen bond to carbonyl oxygen and the fact that the α-atom of the hydroxy substituent is oxygen. Anchimeric participation in which oxygen must expand its octet can be ruled out, while several otherwise similar mechanisms that avoid this difficulty are too highly polar for the observed medium effects.

As an alternative to the usual electron-sharing or electron-transfer mechanisms, we would like to propose eq 2 in



(2)

which the hydrogen atom is transferred in a reversible ketonization step that is only partly rate determining. The mechanism represented by (2) requires no polar medium effects and is quite compatible with the low[11] k_H/k_D ratio of 1.30 if the rate is largely determined by the second step. An alternative explanation in which the hydrogen bond of **3** is nearly symmetrical and very similar to the bond in the transition state seems less likely.

We also note that the hydrogen bonded phenoxyl radical **6**, as opposed to an acyloxy radical, should be quite resistant to decarboxylation. Thus the acid **4a** is still formed in 38% yield even in CCl_4. Added I_2 plus water in CCl_4, a well-known trap for benzoyloxy radicals,[12] does not change this yield significantly.

Experimental Section

***tert*-Butyl 3,5-Di-*tert*-butyl-2-hydroxyperbenzoate (3b).** To a cold solution of 38 g (0.14 mol) of 3,5-di-*tert*-butyl-2-hydroxybenzoyl chloride in 650 ml of *n*-hexane was added at 0–5°, 12.6 g (0.14 mol) of *tert*-butyl hydroperoxide. A solution of 11.1 g of pyridine (0.14 mol) in 200 ml of hexane was then added dropwise (1 hr) also at <5°. After stirring at room temperature for an additional 5 hr, the solution was filtered from the pyridine hydrochloride precipitate, washed several times with H_2O, several times with 10% HCl, and finally several times with H_2O. The hexane solution was concentrated to an oil in vacuo after drying over $MgSO_4$. The oil was crystallized from a small amount of *n*-pentane: yield after six recrystallizations 40 g (88%), with an iodometric titer of 99.5 ± 0.4%; mp 69–70°; ir (CCl_4) 1690 cm^{-1} (C=O), 3200 cm^{-1} (OH, broad); ^1H NMR (CCl_4) δ 1.30 (singlet, 9.00, *tert*-butyl), 1.43 (singlet, 18.00, ring *tert*-butyl groups), 7.50 (singlet, 2.00, aromatic H), 11.00 (sharp singlet, 1.00, OH). On exposure to the laboratory light and air, the crystals turn green.

***tert*-Butyl 5-Methyl-3-*tert*-butyl-2-hydroxyperbenzoate (3a).** To a solution of 27.1 g (0.12 mol) of the corresponding acid chloride in 300 ml of *n*-pentane and 300 ml of cyclohexane at 0–5° was added 13.95 g (0.155 mol) of *tert*-butyl hydroperoxide. A solution of 12.25 g (0.155 mol) of pyridine in 100 ml of cyclohexane was added dropwise (1 hr) at <5°. The faintly yellow solution was then stirred at the same temperature for 5 hr, washed twice with 250-ml portions of 10% HCl and four times with 250-ml portions of H_2O. After drying over Na_2SO_4 and concentrating in vacuo, the residual oil was crystallized from small amounts of *n*-pentane. Yield after four recrystallizations: 30.9 g (92 %), iodometric assay 99.3 ± 0.4%; mp 63.5–64.5°; ir (CCl_4) 1700 (C=O), 3160 cm^{-1} (OH, broad); ^1H NMR (CCl_4) δ 1.37 (overlapping singlets, 18.00, *tert*-butyl groups), 2.26 (singlet, 3.00, CH_3), 7.22 (m, 2.00, ArH), 10.93 (sharp singlet, 1.00, OH); uv$_{max}$ (hexane) 322 nm (ϵ_{max} 4720).

***tert*-Butyl 5-Methyl-3-*tert*-butyl-2(*d*-hydroxy)perbenzoate.** The desired concentration of the HO compound was prepared in an organic solvent transferred to a drybox. Typically 5 ml of D_2O was added to 20 ml of the 0.1 *M* perester, the solution stirred for 20 min, the organic layer removed, and the treatment with D_2O repeated. The deuterated perester was dried over 4 Å molecular sieves: ir (CCl_4) 1692 (C=O), 2400 cm^{-1} (OD, broad).

Product Analysis. Most products were isolated by GLC and identified by means of authentic samples (NMR, ir, and mass spectra). Acids were determined by isolation and weighing or by treatment of the product mixture with CH_2N_2 followed by measurement of the GLC peak of the methyl ester. The 2,4-di-*tert*-butylphenol and phenyl 3,5-di-*tert*-butyl-2-hydroxybenzoate[13] were identified by MS and their retention times on columns of different polarity. Biphenyl was determined by isotope dilution.

Kinetics. Rates of disappearance of **3a** and **3b** were measured using samples in individual degassed ampules, either by following the decrease in the perester ir carbonyl absorption or by titration of I_2 liberated by reaction with KI in acetic acid.

References and Notes

(1) Supported by NSF Grants GP 15991 and GP 39990X is gratefully acknowledged.

(2) A. M. Hucek, J. T. Barbas, and J. E. Leffler, *J. Am. Chem. Soc.*, **95**, 4698 (1973).

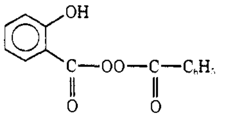
(3) The carboxylic acid and ether formed in the base-initiated decomposition of **1** gave CIDNP signals corresponding either to (a) a triplet radical pair formed from **2** and the THF solvent or (b) a pair formed by diffusion of the two radicals. The latter possibility is less likely because the phenols present in the reaction product are rather good radical scavengers. It was therefore suggested that the ground state of **2** is a triplet.[2]

(4) K. Nakanishi, "Infrared Absorption Spectroscopy", Holden-Day, San Francisco, Calif., 1962.

(5) D. Y. Curtin and S. R. Byrn, *J. Am. Chem. Soc.*, **91**, 6102 (1969).

(6) (a) In the abstraction of H from phenol by 2,4,6-tri-*tert*-butylphenoxyl radical, the rate decreases by a factor of 33 in going from pure CCl_4 as solvent to a mixture containing 0.82 mol fraction of the hydrogen bond accepting component, CH_3CN [L. R. Mahoney and M. A. DaRooge, *J. Am. Chem. Soc.*, **94**, 7002 (1972)]. (b) Similar large decreases are noted in the reaction of phenol with benzoyl peroxide when the solvent contains carbonyl groups capable of acting as H-bond acceptors [C. Walling and R. B. Hodgdon, Jr., *Ibid.*, **80**, 228 (1958)].

(7) Another probable example of anchimeric participation by an *o*-hydroxy substituent is the rapid decomposition of the peroxide **5** obtained in crude form by Y. Ogata, S. Sawaki, and M. Furuta, *J. Org. Chem.*, **39**, 216 (1974). The half-life of **5** was ca. 3 hr at 25° in $CHCl_3–C_2H_5OH$ solution.



5

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

(9) T. H. Fisher and J. C. Martin, *J. Am. Chem. Soc.*, **88**, 3382 (1966).

(10) D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 1938 (1963).

(11) In the intermolecular reaction of phenols with benzoyl peroxide, the k_H/k_D rate is also about 1.30, but this may be merely coincidental.[6b]

(12) (a) G. S. Hammond and L. M. Soffer, *J. Am. Chem. Soc.*, **72**, 4711 (1950).

(13) A. R. Bader and A. D. Kontowicz, *J. Am. Chem. Soc.*, **75**, 5416 (1953).