Thermal Decomposition of *N*-Nitrosohydroxylamines. III. *N*-Benzoyl-*N*-nitroso-*O*-*tert*-butylhydroxylamine[1]

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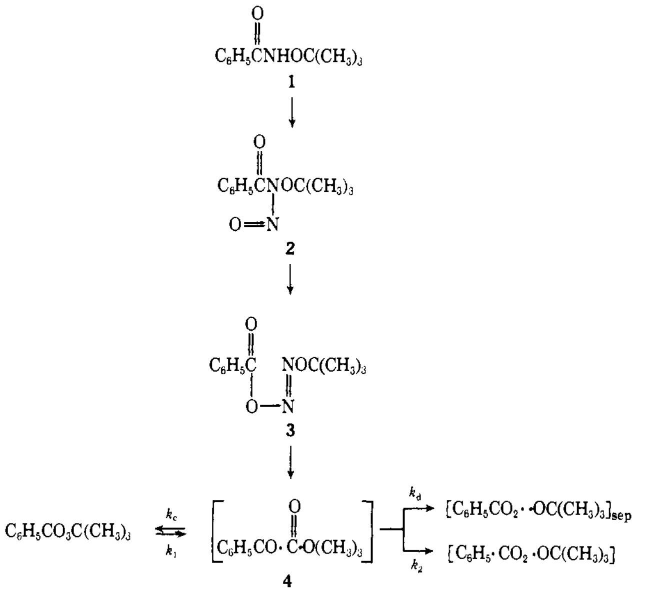
Abstract: The decomposition products of *N*-benzoyl-*N*-nitroso-*O*-*tert*-butylhydroxylamine have been determined in a variety of nonpolar solvents. These products can be ascribed to the intervention of benzoyloxy-*tert*-butoxy radical pairs. *tert*-Butyl perbenzoate is one such product which is formed in yields which increase with increasing viscosity. Oxygen-18 labeling studies show that this product is formed with essentially complete randomization of the benzoyloxy oxygen atoms by a process which does not precede decomposition. Abstraction–fragmentation ratios for the benzoyloxy radicals are nearly the same as those from the decomposition of *tert*-butyl perbenzoate. These ratios, for the butoxy radicals from (1), appear to be anomalously high. The rates of decomposition and oxygen-18 scrambling for the perester in solvents of varying viscosity are also reported.

Studies of organic peroxide[2] molecules have furnished much of the data which constitute the basis of the present understanding of radical formation. Because of the large body of data, already in existence, on the characteristics of radicals formed through O–O bond homolysis and subsequent abstraction or fragmentation reactions, it seemed worthwhile to attempt to find a chemical system which would give rise to the formally identical intermediates (Scheme I) in a deaminative reaction, thus allowing comparison of the overall reactivity of the radicals formed by different routes. A preliminary study[3] of the decomposition of *N*-nitroso-*N*-benzoyl-*O*-*tert*-butylhydroxylamine (2) suggested that this type of compound could be used to generate acyloxy-*tert*-butoxy radical pairs at relatively low temperatures by deaminative decomposition of their expected[4] rearrangement product, the corresponding *O*-acyl-*O*′-alkyl hyponitrite (3). The decomposition of such hyponitrites should be exothermic if the N–O bond strength is less than 60 kcal/mol. The formation of the radical pair (4) which is accompanied by loss of nitrogen is almost certainly more exothermic with respect to the transition state leading to it than in the decomposition of the corresponding perester. Thus, the present system allows a test for differences in overall reactivity which result from energetically different approaches to the "normal" reaction hypersurface in a system where solvation and counterion effects, which must attend the heterolytic counterparts of these comparisons,[5] should be minimal or absent. Previous studies along these lines have been carried out with the azobisnitrile–ketenimine system[6] and with the acetyl member of the present series.[7] Studies of the decomposition of di-*tert*-butyl hyponitrite[8,9] have also been reported during the course of this work.

Scheme I



Results

The *tert*-butoxyamine was prepared by decomposition of ethyl azidoformate in *tert*-butyl alcohol[3,10] followed by basic hydrolysis of the resulting carbamate. The amine was benzoylated with benzoyl chloride in the presence of imidazole. The *N*-benzoyl-*O*-*tert*-butylhydroxylamine was nitrosated using nitrosyl chloride and pyridine in carbon tetrachloride at low temperature. It was found that the work-up procedure after the nitrosation step had to be carried out rapidly and at as low a temperature as possible. If not, then appreciable hydrolysis of the nitroso amide occurs giving nitrous oxide and benzoic anhydride as products. The infrared and nmr spectra of carbon tetrachloride solutions, which were worked up in optimal fashion, indicated the nitroso compound was present in reasonably pure form. The one detectable impurity in these solutions was *tert*-butyl nitrite which was evident from

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(1) Taken in part from the Ph.D. thesis of M. Deinzer, 1969. This work was supported by grants from the National Science Foundation.

(2) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(3) T. Koenig and M. Deinzer, *J. Amer. Chem. Soc.*, **88**, 4518 (1966).

(4) R. Huisgen and G. Horeld, *Justus Leibigs Ann. Chem.*, **562**, 137 (1949); R. Huisgen and L. Krause, *ibid.*, **574**, 157 (1951); D. H. Hey, J. S. Webb, and G. H. Williams, *J. Chem. Soc.*, 4657 (1957); E. H. White, *J. Amer. Chem. Soc.*, **76**, 4497 (1954); E. H. White, *ibid.*, **77**, 6011 (1955).

(5) E. H. White and David J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, Chapter 8; E. H. White, H. P. Tiwari, and M. J. Todd, *J. Amer. Chem. Soc.*, **90**, 4734 (1968); E. I. Snyder, *ibid.*, **91**, 5118 (1969).

(6) G. S. Hammond, C. H. S. Wu, O. D. Trapp, J. Wakentin, and R. T. Keys, *J. Amer. Chem. Soc.*, **82**, 5394 (1960).

(7) T. Koenig and M. Deinzer, *ibid.*, **90**, 7014 (1968).

(8) T. Traylor and H. Kiefer, *ibid.*, **89**, 6667 (1967).

(9) C. Walling and J. A. McGuinness, *ibid.*, **91**, 2053 (1969).

(10) W. Lwowski and T. W. Mattingly, Jr., *ibid.*, **87**, 1947 (1965).

Table I. Products[a] from Decomposition of **2** at 32°

Solvent	N_2	CO_2	$C_6H_5CO_2H$	$(CH_3)_2CO$	$(CH_3)_3COH$	Perester	Other
Carbon tetrachloride	0.92	0.79	*b*	0.55	0.22	0.14	*c*
Chlorobenzene[d]	1.03	0.55	0.05	0.11	0.70	0.08	
Cumene	0.89	0.48	0.24	<0.02	0.80	0.10	Bicumyl
Hexane	1.00	0.67	0.29	0	0.84	0.10	Benzene (0.49)
Carbon tetrachloride Hexane (1:4)	0.96	0.64	0.19	0	0.89	0.09	

[a] Moles/mole of **2**. Concentration of **2** estimated by nmr using dioxane as an integration standard. [b] Chlorobenzene (0.74). [c] Methyl chloride (0.55), hexachloroethane, *tert*-butyl nitrite (0.04), isobutylene chlorohydrin (0.15). [d] Containing 0.1 *M* cyclohexane.

the nmr singlet at δ 1.58 and which was isolated as a product. This impurity is most likely a result of some ionic decomposition during the nitrosation procedure.

The rearrangement of **2** is evident by the disappearance of the NN=O band in the infrared at 1545 cm^{-1} [11] and carbonyl band at 1735 cm^{-1} and the simultaneous appearance of a new carbonyl band at 1767 cm^{-1}. The nmr spectra also give evidence of this rearrangement by the shift in the *tert*-butyl singlet from δ 1.29 to 1.45. The visible spectrum also shows the disappearance of the absorption peaks at 407 and 427 mμ. All of these spectral changes occur without the evolution of gas, and the rate of rearrangement ($t_{1/2}$ ~ 2–3 min at room temperature) is such that the rearrangement product is essentially completely formed before any further decomposition takes place. The structure of the rearrangement product is assigned as **3** on the basis of the spectral observations and analogy with other nitroso amide rearrangements.[4]

The products of the decomposition of **2** in several solvents are listed in Table I. Variations in products with viscosity are listed in Table II. Oxygen-18 labeling studies were also carried out with this system. The analysis is summarized in Scheme II.

Table II. Viscosity Variation in Products[a] from **2**

Vol % paraffin oil[b]	η, cP	CO_2[d]	C_6H_5-CO_2H	*tert*-Butyl perbenzoate[c]	Benzene
0	0.33	0.64	0.19	0.09	0.49
33.3	0.93	0.59	0.13	0.13	0.44
58.4	3.37	0.48	0.21	0.23	0.34
83.4	17.0	0.30	0.20	0.38	0.14

[a] Moles/mole of nitrogen evolved. [b] Solvents contain 16.7 vol % carbon tetrachloride and the listed amount of paraffin oil and the remainder is made up by hexane. [c] The numbers listed are by quantitative infrared. Iodometric titrations of product solutions gave consistently higher results which are probably due to the small amount of *tert*-butyl nitrite present initially. [d] The yields of benzoic acid do not appear to be simply related to viscosity which is most likely a result of changing net hydrogen-donating ability of the solvent which accompanies the viscosity change.

The oxygen-18 labeled hydroxylamine was nitrosated in cyclohexane solvent and allowed to rearrange completely. The rearrangement product was then treated with methoxide in methanol giving methyl benzoate (46% yield), nitrous oxide (59% yield), *tert*-butyl alcohol (86% yield), and benzoic acid (38% yield). The benzoic acid may have been formed during the work-up procedure which involved complete removal of solvent which would have subjected the ester to a high concentration of hydroxide ion for a short time. The methyl benzoate and nitrous oxide were analyzed for oxygen-18 (B and C, respectively, Scheme II and Table III). A sample of the same amide was nitrosated in carbon tetrachloride and allowed to decompose completely. The carbon dioxide produced in the direct decomposition was analyzed for oxygen-18 (A in Scheme II and Table III) and this value taken as reflecting the oxygen-18 content of the

Scheme II

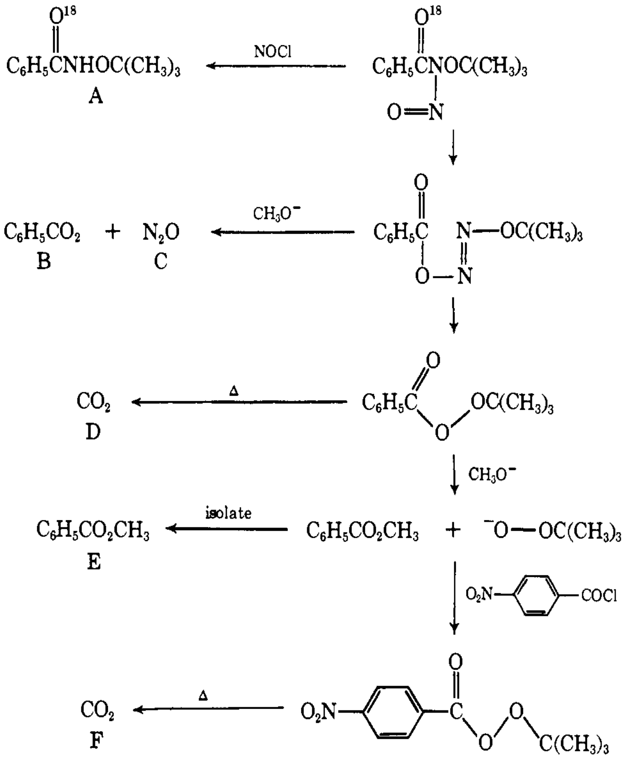

Table III. Oxygen-18 Labeling Studies (Scheme II)

Compd		Total % excess oxygen-18[a]	%[c]
Hydroxylamine (**2**)			
Direct CO_2	A	0.587	
$C_6H_5CO_2CH_3$[b]	B	0.594	0
N_2O	C	0.001	0
CO_2 (perbenzoate)	D	0.579	
$C_6H_5CO_2CH_3$[b]	E	0.288	98 ± 4
CO_2 (*p*-nitroperbenzoate)	F	0.293, 0.280	98 ± 4

[a] Using 46/44 mass spectral ratio corrected for instrument and carbon-13. [b] As carbon dioxide after combustion. [c] Oxygen-18 equilibration.

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[11] J. H. Cooley, P. T. Jacobs, M. A. Kahn, L. Heasley, and W. D. Goodman, *J. Org. Chem.*, 30, 3062 (1965).

Table IV. Abstraction–Fragmentation Ratios

Initiator	Solvent	Temp, °C	$[C_6H_{12}]$, *M*	$C_6H_5CO_2H/CO_2$	$(CH_3)_3COH/$ $(CH_3)_2CO$
tert-Butyl perbenzoate	Cumene	130.6		0.098	4.5
tert-Butyl perbenzoate	Cumene	110.0		0.126	9.7
tert-Butyl perbenzoate	Cumene	30[a]		~0.45	450
2	Cumene	32		0.5	*b*
tert-Butyl perbenzoate	Chlorobenzene	100	0.19		0.56
tert-Butyl perbenzoate	Chlorobenzene	100	0.40		1.04
tert-Butyl hypochlorite[c]	Chlorobenzene	100	0.40		~1.10
tert-Butyl hypochlorite	Chlorobenzene	40	0.10		2.32
2	Chlorobenzene	32	0.091		6.30
2	Chlorobenzene	32	0.066		5.00
2	Chlorobenzene	32	0.027		2.6

[a] Extrapolated. [b] Acetone was detected but its presence is due to decomposition of the *tert*-butyl perbenzoate product during glpc analysis. [c] Data of ref 9.

starting material (**2**). The perester product was isolated and an aliquot decomposed in cumene. The carbon dioxide thus produced was collected and analyzed for oxygen-18 (D). A second aliquot of this perester was treated with methoxide and the methyl benzoate product isolated and analyzed for oxygen-18 (E). The water-soluble residue from this procedure was treated with *p*-nitrobenzoyl chloride and the resulting *tert*-butyl *p*-nitroperbenzoate isolated and heated in cumene. The oxygen-18 content of the carbon dioxide from this compound was determined (F). These results are summarized in Table III.

Comparison of the abstraction–fragmentation ratios for both the benzoyloxy and *tert*-butoxy radicals generated from **2** and *tert*-butyl perbenzoate were carried out. Two sets of conditions were required since media which give reasonable ratios of benzoic acid to carbon dioxide are such good hydrogen atom donors that essentially all of the *tert*-butoxy radicals result in *tert*-butyl alcohol formation. Thus the product ratios from the perester were studied at two temperatures in cumene to allow extrapolation of the benzoic acid–carbon dioxide ratios down to 32° where study of decomposition of **2** was convenient. The chlorobenzene–cyclohexane solvent system, employed by Walling[9,12] for studies of the abstraction–fragmentation ratios of *tert*-butoxy radicals from several sources, was used to obtain *tert*-butyl alcohol–acetone ratios. As a check, we measured these ratios for *tert*-butyl perbenzoate at 100° in the same solvent system. These results are summarized in Table IV.

The rates of decomposition of the perester in solvents of varying viscosity are listed in Table V. The rates of scrambling, determined from the perester recovered after partial decomposition, are listed in Table VI. The analytical scheme was identical with that used to determine the oxygen-18 distribution of the perester product from the hyponitrite decomposition (Scheme II).

Table V. Rate Constants for Decomposition of *tert*-Butyl Perbenzoate at 130°

Solvent	Viscosity, cP[a]	$k_0 \times 10^4$, sec^{-1}
Hexane	0.140	3.72
Isooctane	0.182	3.36
Dodecane	0.392	3.08
60% hexane oil	0.378	3.39
30% hexane oil	0.820	3.04
Paraffin oil	2.44	2.33

[a] Viscosities are those reported by T. Koenig, R. Cruthoff, and J. Huntington, *J. Amer. Chem. Soc.*, **92**, 5408 (1970).

Table VI. Oxygen-18 Scrambling of *tert*-Butyl Perbenzoate at 130°

Solvent	*t*, min	CO_2 (direct)[a]	CO_2 (p-NO_2)[b]	$k_s \times 10^5$ [c]
Hexane	10	5.478	0.432	
Hexane	40	5.435	0.489	1.6
Isooctane	11	5.481	0.435	
Isooctane	45	5.414	0.534	2.0

[a] 46/44 mass spectral peak intensity ratio × 100 for the carbon dioxide formed directly in the decomposition of *tert*-butyl perbenzoate. [b] 46/44 mass spectral peak intensity ratio × 100 of the carbon dioxide produced from decomposition of the *tert*-butyl *p*-nitroperbenzoate derivative of the recovered perester. [c] First-order rate constant for appearance of scrambled perester. Two point difference not including the origin.

Discussion

Products and Oxygen-18 Distribution. The general disposition of products isolated in all solvents examined suggests radical decomposition of **2**. Solvent-derived dimers such as hexachloroethane in carbon tetrachloride and bicumyl from runs in cumene are particularly indicative of radical formation. The nmr spectra recorded during the decomposition of **2** also showed emission peaks from the methyl chloride and chlorobenzene products due to chemically induced nuclear polarization.[13] The *tert*-butyl perbenzoate product can be ascribed to geminate combination of the benzoyloxy–*tert*-butoxy radical pair which must be formed initially. The increase in the yield of this product with increasing viscosity of the medium (Table II) also supports this suggestion.

The randomization of the oxygen atoms of the benzoyloxy fragment is also consistent with radical pair combination. However, this equilibration might have occurred before the actual decomposition of the rearrangement product by reversible ion pair or radical pair formation from the hyponitrite (**3**). The results from the methoxide cleavage of the rearrangement

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(12) C. Walling and P. J. Wagner, *J. Amer. Chem. Soc.*, **86**, 3368 (1964).

(13) H. Fischer and J. Bargon, *Z. Naturforsch.*, **229**, 1556 (1967); R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5519 (1967); R. Kaptein, *Chem. Phys. Lett.*, **2**, 261 (1968); T. Koenig and W. R. Mabey, *J. Amer. Chem. Soc.*, **92**, 3804 (1970).

product rule out any path for this randomization which precedes the actual decomposition of **3**.

The oxygen-18 distribution of the perbenzoate product **3** is nearer to complete randomization than was observed in our earlier[7] studies with the peracetate. The low oxygen-18 enrichment lowers the accuracy of the finally calculated fractions randomization. The analytical schemes are rather extended in both cases and these deviations from 100% equilibration could be ascribed to the accumulative errors which are expected from such a scheme. However, it is possible that these differences are real. If so, then the larger fraction randomization for the perbenzoate could be ascribed to a larger activation potential for the benzoyloxy–*tert*-butoxy pair. Such a difference could be inferred from the difference in the rates of decarboxylation of the two acyloxy radicals.

Alternatively, the difference in fraction randomization could be due to an increase in the combination *rate constant* for the acetoxy–*tert*-butoxy pair which is a result of the higher viscosity of the medium in which the pair was generated (paraffin oil compared to carbon tetrachloride for the present case). A careful study of the oxygen-18 distribution of one perester system as a function of viscosity will be necessary before an answer to these questions is possible.

Abstraction–Fragmentation Competition. While the rate of decomposition of *tert*-butyl perbenzoate has been measured by several groups,[14] no quantitative analyses of the products of its decomposition have been reported. The data of Table IV show the *tert*-butyl alcohol–acetone and benzoic acid–carbon dioxide ratios in cumene at two temperatures. These products account for over 92% of the two radical fragments at both temperatures. Extrapolation of these ratios to 30° gives an estimated benzoic acid–carbon dioxide ratio which is slightly smaller than that observed for the decomposition of **2** under comparable conditions. The benzoyloxy radicals formed from this deaminative route do not show any increased tendency to decarboxylate as might be expected if they were formed as vibrationally excited species. This argues against the possibility that the larger fraction decarboxylation of the acetoxy–*tert*-butoxy pairs generated from the nitrosohydroxylamine[7,15] (compared with *tert*-butyl peracetate) is a consequence of an unusually large rate constant for decarboxylation.

The extrapolated value of the *tert*-butyl alcohol–acetone ratio from the perbenzoate in cumene at 30° is too large to be reliably estimated. Some acetone was detected by glpc of the decomposition products of **2** in cumene at 30° but this was probably due to decomposition of *tert*-butyl perbenzoate product during analysis. Conditions comparable to the detailed studies by Walling[9,12] on the abstraction–fragmentation ratios of *tert*-butoxy radicals from other sources were thus chosen for the competition in the present case. The data of Table IV include the *tert*-butyl alcohol–acetone ratios for **2** and *tert*-butyl perbenzoate in chlorobenzene at several cyclohexane concentrations. Results of the hypochlorite reaction are included for comparison.

The ratios for **2** at 32° are higher than the hypochlorite at all cyclohexane concentrations but the extrapolated values at zero cyclohexane are comparable. In contrast, the behavior from the *tert*-butyl perbenzoate is quite comparable to the hypochlorite in both cyclohexane sensitivity and intercept. This could be interpreted as indicating that the radicals generated from **2** have a greater tendency to abstract than to undergo β-scission. However, a more likely explanation is the presence of the cyclohexyl radicals which, in the absence of *tert*-butyl hypochlorite, end up as hydrogen donors. Recent results,[9] reported during revision of this manuscript, on a variety of *tert*-butoxy radical sources have also led to this conclusion. It is worth noting that the *tert*-butoxy radicals appear to have a sufficient lifetime in carbon tetrachloride to react with whatever hydrogen donors are available since an appreciable amount of isobutylene chlorohydrin is formed in that solvent (Table I). The major conclusion from this part of the study is that both the benzoyloxy and *tert*-butoxy radical fragments have reactivities which are essentially independent of their modes of formation when adjustments to common temperature are made.

Combination Efficiency Comparisons. The rates of decomposition of *tert*-butyl perbenzoate decrease with increasing viscosity as expected if the initial radical pair is formed reversibly. Equation 1 has been suggested by Pryor and Smith[16] as a method of estimating k_1 (Scheme I), the unimolecular rate constant for O–O bond homolysis

$$\frac{1}{k_0} = \frac{1}{k_1} + \frac{k_c}{k_1}\sqrt{\frac{\eta}{A}} \tag{1}$$

where the rate constants refer to Scheme I, A is the preexponential term in the Arrhenius equation for macroscopic viscosity, and η is viscosity. Figure 1 shows a plot of $1/k_0$ *vs.* $\eta^{1/2}$ which should give $1/k_1$ as an intercept.

The relationships which we[17] have proposed are summarized as eq 2

$$\frac{1}{y} - 1 = \frac{k_0}{k_s} = \frac{1}{(k_1/k_0) - 1} = \frac{k_1}{k_s} - 1 = \frac{k_2}{k_c} + \frac{k_d}{k_c} \tag{2}$$

where the constants k_1, k_2, k_d, k_c refer to Scheme I, k_0 is the overall rate constant for destruction of the perester, k_s is the rate constant for scrambling of oxygen-18 in labeled perester, and y is the yield of combination product. Our treatment requires a value of k_1 in order to treat the viscosity dependence of k_0 alone. Figure 2 contains a plot of the $1/(k_1/k_0 - 1)$ values *vs.* $(1/\eta)^{1/2}$ using the k_1 estimated using the Pryor relationship (eq 1). The plots show more scatter than other cases which we have examined but are reasonably linear with square root fluidity (viscosity). Both of the treatments have the inherent assumption of a single constant k_1 which is applicable to all solvents.

An alternative way of estimating k_1 is to *assume* it to be the sum of k_0 and k_s, *i.e.*, that all recombinations occur with scrambling of the label. The present results on the essentially random oxygen-18 distribution of the perester product from **3** support this assumption. The values of k_1, obtained in this way (Table VII), are

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[14] A. T. Blomquist and I. A. Bernstein, *J. Amer. Chem. Soc.*, **73**, 5546 (1951); P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

[15] See Table V, footnote *r*.

[16] W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970).

[17] T. Koenig, *ibid.*, **91**, 2558 (1969).

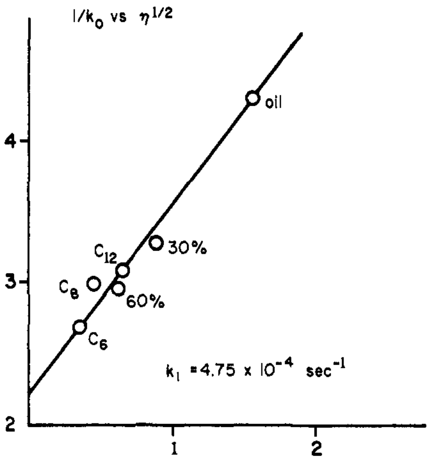

Figure 1. $1/k_0$ *vs.* $\eta^{1/2}$, *tert*-butyl perbenzoate, 130°.

not equal to the one obtained from Figure 1 and are not constant on going from hexane to isooctane (or paraffin oil). Figure 2 shows the discrepancy which is not large in terms of the difference in rate constants but very significant in terms of estimated fraction return. The fraction of recombination using the k_0 data alone is *ca.* 20% in hexane while the $k_0 + k_s$ data give an estimate of only 4%. This complication with respect to a single constant value of k_1 is very similar to the situation recently observed for *tert*-butyl peracetate decomposition.[15] To the extent that the *assumption* of complete scrambling in all recombinations is valid, the k_0/k_s ratios are the best method of estimating fraction return since they are independent of k_1. Figure 2 has included the values of the $(1/Y) - 1$ function for the benzoyl hyponitrite (**3**). The k_0/k_s observed for the perester ratios are not far from the line extrapolated to the same viscosity (with no temperature corrections). This is in strong contrast to the behavior of the acetyl perester and hyponitrite.

Table VII. Resolution of Figure 2

$k_1 \times 10^4$, sec^{-1}	Method	Solvent	f_s[a]
4.75	Pryor[c]	All	0.172
3.88	$k_0 + k_s$	Hexane	0.16
3.56	$k_0 + k_s$	Isooctane	0.15
(2.85)	Calcd[b]	Paraffin oil	0.21

[a] Fraction recombination with scrambling. [b] Assuming linear $(1/\eta)^{1/2}$ behavior for both k_0/k_s and $1/[(k_1/k_0) - 1]$. [c] See ref 16.

An alternative basis for rationalizing the discrepancy of Figure 2 is to suppose that some of the recombination events in the pairs from the perester decomposition occur without randomization of the label. If both the k_0/k_s and k_1/k_0 relationships are linear with $1/\eta^{1/2}$ then a constant fraction return with retention is implied. This amounts to about 84%. The column of Table VII, labeled f_s, represents the pointwise fractions scrambled which are required to rationalize the two lines. This interpretation means the k_1/k_0 relationship is the better method for estimating fraction return and the effect of the nitrogen molecule intervening in the deaminative pair formation is again appreciable as in the acetyl case.[15] It does require that the complete randomization of oxygen-18 in the hyponitrite case not be applicable to the perester generated pair. The difference in the slopes of the k_1/k_0 and deamination yield plots is consistent, in a qualitative sense, with that demand.

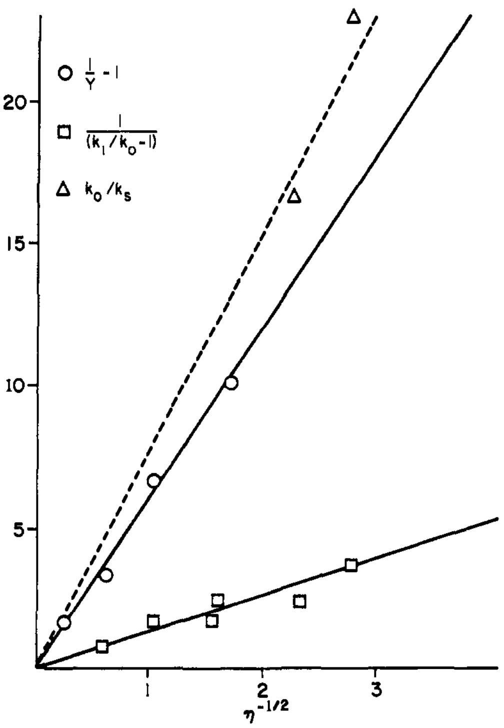

Figure 2. ⊙, $1/y - 1$, benzoyl *tert*-butyl hyponitrite; ⊡, $1/[(k_1/k_0) - 1]$, $k_1 = 4.75 \times 10^{-4}$ sec^{-1}, *tert*-butyl perbenzoate; ◬, k_0/k_s, *tert*-butyl perbenzoate.

Comparison of the k_0/k_s values for the peracetate and perbenzoate at 130° shows the perbenzoate values to be larger than the peracetate by almost the same factor (~5) as was found[18] for the corresponding pair of peroxides. The k_1/k_0 relationships for the two are closer together. These results illustrate the importance of knowing which method to use to estimate fraction return. On the one hand, the present results are inconclusive, but on the other, they serve to define the types of problems which are inherent in treating the diffusion-combination competition. Further studies presently under way in these laboratories will hopefully allow a choice between the possibilities discussed here.

Experimental Section

Proton nuclear magnetic resonance spectra were determined on a Varian A-60 spectrometer. Infrared measurements were made using a Beckman IR-7 instrument. Ultraviolet and visible spectral measurements were made on a Cary 15 recording spectrophotometer. Mass spectra were determined using a modified Consolidated Electrodynamic 26-614 residual gas analyzer. Gas-liquid partition chromatography was carried out on either an Aerograph Autoprep instrument or an Aerograph Hi-Fy Model 600-D instrument equipped with a Disc-Chart integrator, Model 201-B.

Materials. Dioxane was purified by reflux over sodium for 2 days and distillation. *tert*-Butyl alcohol was distilled from calcium oxide. Cumene was purified by shaking with concentrated sulfuric acid, separating, washing with water, and distilling. The first fraction was discarded, and the remainder, bp 152°, was stored for short periods in a dark tightly stoppered flask. Before using, it was checked for peroxides. *tert*-Butyl hydroperoxide was purified by

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[18] J. C. Martin and J. H. Hargis, *J. Amer. Chem. Soc.*, 91, 5399 (1969).

distillation. Methanol, carbon tetrachloride, isooctane, *n*-hexane, and toluene were all Spectroquality reagent grade from either Matheson Coleman and Bell or Mallinckrodt Chemical Works. Paraffin oil, from Allied Chemical, was used without further purification. Benzoyl-^{18}O chloride was prepared from benzotrichloride hydrolysis.[19]

***tert*-Butylhydroxylamine Hydrochloride.** The azide decomposition, described previously,[3] was used in this preparation. A significant improvement of the yield is obtained if the hydrolysis of the carbamate is carried out in 10% sodium hydroxide solution until the mixture becomes homogeneous. The *tert*-butoxyamine can then be distilled directly from the mixture (bp 78°), isolated, and purified as the hydrochloride. The overall yield from ethyl chloroformate is 60%.[20]

***N*-Benzoyl-*O*-*tert*-butylhydroxylamine.** A solution of 10.9 g (0.16 mol) of imidazole, 10 g (0.08 mol) of *tert*-butylhydroxylamine hydrochloride, and 60 ml of anhydrous ethanol was added to a 500-ml round-bottomed flask. The flask was fitted with a dropping funnel and protected from atmospheric moisture with potassium hydroxide. The reaction mixture was stirred with a magnetic stirrer. The reaction flask was immersed in an ice bath and after the solution reached 0°, a chilled solution of 11.21 g (0.08 mol) of benzoyl chloride in 10 ml of anhydrous ethanol was added from the dropping funnel. The period of addition was 30 min, and the mixture was then stirred at 0° for 12 hr.

The solvent was stripped off under reduced pressure (aspirator). To the solid residue was added 250 ml of chloroform. The solution was then washed with two 50-ml portions of water, one 50-ml portion of 3 *M* HCl, and finally one 50-ml portion of water. The chloroform layer was dried over anhydrous magnesium sulfate for 24 hr. The chloroform solution was filtered, and the chloroform then removed by distilling under reduced pressure (aspirator). The residue, 12.5 g (80.5%), was recrystallized from 100 ml of Skellysolve B and 95% ethanol, 85:15, to give the product, mp 134–135°.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.30; H, 7.77; N, 7.24. Found: C, 68.38; H, 8.00; N, 7.47.

The infrared spectrum showed $\nu_{max}^{CCl_4}$ 1695 (s) (amide $>C=O$), and 3200, 3500 cm^{-1} (weak) (NH).

Nitrosation Procedure. The nitrosations were carried out using nitrosyl chloride and pyridine in carbon tetrachloride at −20°.[7] However, it was found that the washing of the product solutions must be carried out below 0° and as quickly as possible to avoid hydrolytic destruction of the nitroso compound. In one case, washing the product solution at 10° with dilute HCl gave rise to large amounts of nitrous oxide and benzoic anhydride after a few minutes. This problem is not apparent at the lower temperature.

Product Studies. The solution of nitrosated amide was added to break-seal flasks together with the solvent or hexane and paraffin oil to effect the proper viscosity of the reaction medium. The flasks were evacuated and after several freeze–thaw cycles were sealed off at reduced pressure. Decompositions of the reactants were carried out in constant-temperature baths. Yields of gaseous products were determined utilizing a calibrated vacuum line and mass spectrometry. Peresters were determined using the carbonyl absorption $\nu_{max}^{CCl_4}$ 1767 cm^{-1} in the infrared. All other liquids were determined by glpc. Calibration curves were made by plotting injected volumes of solution of known concentration *vs.* area. Product identification was by comparison of nmr, infrared, and mass spectra of isolated materials with authentic samples.

***N*-Benzoyl-*O*-*tert*-butylhydroxylamine-^{18}O.** The procedure already described for the unlabeled compound was used except that benzoyl-^{18}O chloride was used.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.30; H, 7.77; N, 7.24. Found: C, 68.35; H, 7.76; N, 7.24.

Oxygen-18 Studies Using *N*-Benzoyl-*N*-nitroso-*O*-*tert*-butylhydroxylamine. To a mixture of 4 g (20.7 mmol) of *N*-benzoyl-*O*-*tert*-butylhydroxylamine-^{18}O, 3 ml of pyridine, and 30 ml of carbon tetrachloride at −10°, there was added under stirring 100 ml of carbon tetrachloride solution saturated with nitrosyl chloride. The generalized procedure already described for the preparation of *N*-benzoyl-*N*-nitroso-*O*-*tert*-butylhydroxyalmine was continued, except that work-up required a fivefold volume increase of solutions. The solution (adjusted to 150 ml), which was about 0.17 *M*, was added to a 1-l. break-seal flask together with an extra 100 ml of carbon tetrachloride. The flask was evacuated and sealed off as previously described. After complete decomposition of the nitrosated compound at 32°, the 46/44 mass ratio for carbon dioxide was determined (A, Table III). The carbon tetrachloride was removed from the reaction mixture by bulb-to-bulb distillation on the vacuum line, and the *tert*-butyl perbenzoate remained in the residue containing, in addition, large amounts of hexachloroethane, and benzoic anhydride. The residue in 5 ml of *n*-hexane was chromatographed on a 1 in. × 15 in. column of silica gel at −10° using first 500 ml of *n*-hexane to elute the hexachloroethane, and then 500 ml of anhydrous ether to elute the perester. After removal of the ether on a rotary evaporator, 397 mg of material was obtained which was identical in its spectral properties with authentic *tert*-butyl perbenzoate. Two 20-mg portions of the perester were dissolved in 5-ml portions each of isooctane and added to 10-ml break-seal flasks. These were evacuated and sealed off as previously described, and the perester then thermally decomposed at 100° for 24 hr. The carbon dioxide from this reaction was collected from a vacuum line, and the oxygen-18 content determined (D, Table III). One equivalent, 110 mg (2.05 mmol) of sodium methoxide in 25 ml of anhydrous methanol, was added to the remaining 90% *tert*-butyl perbenzoate and this solution was stirred at room temperature for 24 hr. The products were distilled by a bulb-to-bulb technique on the vacuum line giving methyl benzoate and methanol as distillate and leaving a solid residue of sodium *tert*-butyl peroxide. The residue was washed with three 15-ml portions of anhydrous ether, and the combined washings were added to the methanol solution. This was then distilled leaving methyl benzoate which was collected by preparative glpc using a 0.25 in. × 5 ft column packed with 5% SE 30 on Chromosorb W at a settiing of 65°. The pure methyl benzoate was combusted, and the 46/44 mass ratio for the carbon dioxide determined by mass spectrometry (E, Table III).

The residue containing the sodium *tert*-butyl peroxide was dissolved in 35 ml of water and cooled to 0°. To this was added, under stirring, 379 mg (2.05 mmol) of *p*-nitrobenzoyl chloride in 25 ml of methylene chloride. Vigorous stirring was continued for 5 hr. The organic layer was separated and washed three times with 25-ml portions of 10% sodium carbonate, and then several times with 25-ml portions of water. The organic solution was dried over anhydrous calcium chloride and, after filtration, the solvent was removed. The crystalline *p*-nitro-*tert*-butyl perbenzoate was obtained with an approximately equal amount of *p*-nitrobenzoic anhydride as determined by infrared. Total weight was 545.7 mg.

The mixture (320 mg) was chromatographed over $^3/_8$ in. × 1.5 in. column of basic Woelm alumina, using anhydrous ether as eluting solvent at −10°. Several cuts were made in an attempt to separate the perester from the impurity. However, by washing the mixture which was in methylene chloride with a 10% solution of potassium hydroxide, pure perester was obtained that was identical with *p*-nitroperbenzoate in its infrared absorptions, $\nu_{max}^{CCl_4}$ 1765 cm^{-1} (s) (perester $>C=O$). A solution of 27 mg (0.119 mmol) of this *p*-nitrobenzoyl perester and 5 ml of cumene in an evacuated 10-ml break-seal flask was immersed in a bath at 145° for 4 hr (8 half-lives). The carbon dioxide was collected from a vacuum line and the 46/44 mass ratio determined (F, Table III) by mass spectrometry. Approximately 200 mg of the unpurified perester was dissolved in cumene and decomposed in the same manner. The 46/44 mass ratio was measured and found to be about 4% lower than the same ratio for carbon dioxide from purified *p*-nitro-*tert*-butyl perbenzoate.

Methanolysis of *O*-Benzoyl-*O*-*tert*-butyl Hyponitrite-^{18}O. To a mixture of 594.4 mg (3.08 mmol) of *N*-benzoyl-*O*-*tert*-butylhydroxylamine-^{18}O (used in the above sequence), 0.48 ml of pyridine, and 10 ml of *n*-hexane at −10°, there was added under stirring 10 ml of *n*-hexane saturated with nitrosyl chloride. The procedure for preparation of a solution of *N*-benzoyl-*N*-nitroso-*O*-*tert*-butylhydroxylamine was followed. After the work-up procedure the nitroso compound in the hexane was allowed to rearrange completely at 0° to the hyponitrite. An aliquot of the solution (10 ml, *ca.* 0.15 *M*) was then added to one chamber of a double-chambered break-seal flask. The other chamber contained 150.3 mg (2.77 mmol) of sodium methoxide in 30 ml of dry methanol. The flask was evacuated and sealed off after two freeze–pump–thaw cycles. While still at 0° the solutions were mixed together. An orange color appeared that persisted throughout the remainder of the experiment. After the solution had been at 0° for 2 hr, it was kept at room temperature overnight. The gas, which was shown to be nitrous oxide (0.69 mmol) by mass spectrometry, was collected from the vacuum line, and the 46/44 mass ratio (C, Table III) was determined. The volatile material in the

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(19) L. Pouticorro and D. R. Henburg, *J. Amer. Chem. Soc.*, **76**, 1705 (1954).

(20) Unpublished work in these laboratories by W. R. Mabey.

break-seal flask was separated from the residue by bulb-to-bulb distillation on the vacuum line. Glpc analysis of the distillate showed *tert*-butyl alcohol (1.23 mmol) to be present. The residue was washed three times wth 25-ml portions of carbon tetrachloride. The washings were combined with the methanol solution and then distilled to remove the methanol and carbon tetrachloride which left as residue the methyl benzoate. This was collected on a preparative glpc as described before. About 10 mg of the pure methyl benzoate was combusted, and the 46/44 ratio for carbon dioxide was measured by mass spectrometry (B, Table III). Final acidification of the residue (0.57 mmol) and extraction with ether gave benzoic acid on evaporation.

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α-Halo Sulfones. XV. Thermal Rearrangement of the Ketals of 2-Chloro-3-thietanone 1,1-Dioxide[1]

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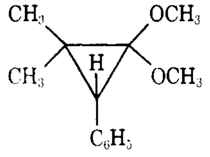
Abstract: The thermolysis of 2-chloro-3,3-diethoxythietane 1,1-dioxide (**24**) at 230–250° affords a 95% yield of ethyl acetate, together with sulfur dioxide and ethyl chloride. Analogously, 2-chloro-3-thietanone 1,1-dioxide ethylene ketal (**13b**) gives rise to 2-chloroethyl acetate (86.5%) and sulfur dioxide. Two isomers of 2-chloro-3-thietanone 1,1-dioxide 1′,2′-propylene ketal (possibly **18** and **20**) have also been prepared; both substances are seen to rearrange to identical mixtures of 2-chloropropyl acetate (**26**) and 3-chloro-2-propyl acetate (**27**). When the thermal decomposition of **13b** is performed in ethanol or *n*-propyl alcohol, the passage to 2-chloroethyl acetate is interrupted and the corresponding esters of (chloromethanesulfonyl)acetic acid (**31**) are produced. The thermal behavior of such α-chloro ketals cannot be reconciled with a concerted $[{}_{\sigma}2_{a} + {}_{\sigma}2_{s} + {}_{\sigma}2_{a}]$ six-electron rearrangement. Rather, the formation of the various esters is interpreted in terms of the initial generation of a dipolar intermediate which suffers sequential intramolecular chlorine and hydrogen shifts to expel sulfur dioxide and elemental carbon.

Although endowed with considerable strain energy, cyclopropanone ketals are quite stable at elevated temperatures. For example, ketal 1 can be recovered quantitatively after being heated at 250° for 1 hr.[3] In marked contrast, ketals of 2-chlorocyclopropanone are sufficiently labile that partial pyrolysis often accompanies attempted distillation. In the case of 2, heating at 195° for 2 hr results in quantitative conversion to methyl α-phenyl-β-methylcrotonate (3) and methyl chloride.[3] This propensity for thermal rearrangement is shared by several ketals of 2-bromocyclobutanone, *e.g.*, 4, which have recently been shown to undergo concomitant ring contraction with the formation of cyclopropylcarboxylates such as 5.[4] Preliminary attempts to extend this ring contraction process to analogous cyclopentyl and cyclohexyl bromo ketals have apparently not given rise to similar phenomena.[4-6] The combination of ring strain and an α-halogenoketal function would therefore appear to be the necessary prerequisite for these unprecedented transformations.



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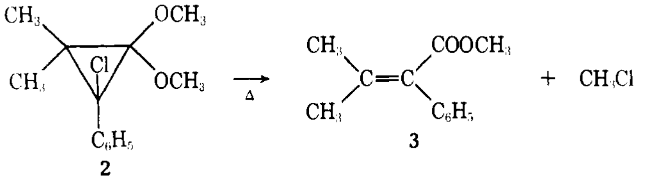

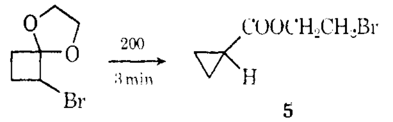

The thermochemical behavior of molecules such as 2 and 4 is of considerable interest in that such isomerizations may be concerted and, as a result, follow well-defined stereochemical specificity. Baldwin and Gano[7] have recently pointed out that the available $[{}_{\sigma}2_{a} + {}_{\sigma}2_{s} + {}_{\sigma}2_{a}]$ pathway unequivocally demands retention at the carbon atom which represents the migration

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[1] Part XIV is L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, 91, 3973 (1969).

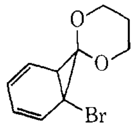
[2] NDEA Fellow, 1967–1970.

[3] S. M. McElvain and P. L. Weyna, *J. Amer. Chem. Soc.*, 81, 2579 (1959).

[4] J. Salaun and J.-M. Conia, *Tetrahedron Lett.*, 4545 (1968).

[5] Acyclic ketals bearing an α-halogen atom also seem to afford a diversity of unspecified thermal degradation products.[4]

[6] The conversion of 2-bromotropone to 3-bromopropyl benzoate upon attempted ketalization with trimethylene glycol has been interpreted in terms of rearrangement *via* norcaradiene valence tautomer i.[7]



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[7] J. E. Baldwin and J. E. Gano, *Tetrahedron Lett.*, 1101 (1969).