A Further Study of the *exo*-
and *endo*-2-Carbo-*t*-butylperoxynorbornanes

Paul D. Bartlett and J. Michael McBride

Contribution from the Converse Memorial Laboratory of Harvard University,
Cambridge, Massachusetts 02138. Received December 28, 1964

New preparations of exo-2-carbo-t-butylperoxynorbornane, m.p. 37.6–39.2°, and its endo isomer, m.p. 33.7–34.5°, have been studied kinetically in cumene and in chlorobenzene. In agreement with previous work from this laboratory the exo isomer decomposes about three times as fast as the endo at the temperatures studied. The results of Martin and DeJongh are explained through isomerization of the corresponding acyl chlorides in thionyl chloride. The unimportance of bridged radicals is reaffirmed.

Introduction

Two years ago a paper from this laboratory[1] described kinetic and product studies of the decomposition of *exo*- and *endo*-2-carbo-*t*-butylperoxynorbornanes in chlorobenzene. The same pair of peresters were studied almost simultaneously by Martin and De-Jongh[2] in cumene and in chlorobenzene, along with a similar study of the corresponding 5-norbornene peresters. Both pairs of authors concluded that there is no evidence for a bridged norbornyl radical analogous to the norbornyl cation.[3] There were, however, the following points of difference between the results from the two laboratories. (1) The peresters of Martin and DeJongh had higher melting points. (2) The carbon dioxide yields of Martin and DeJongh, reported for cumene only,[4] were high (92 and 98%) compared to those of Bartlett and Pincock in chlorobenzene (58 and 76%). (3) Where the same compound was studied under the same conditions, the results in the two papers were mutually consistent for the *exo* perester, but for the *endo* they differed by factors up to 2.6 in rate constant, a discrepancy outside any permissible limits of error. Since the melting points and carbon dioxide yields threw the compounds of Bartlett and Pincock under suspicion, we have made new preparations of *exo*- and *endo*-2-carbo-*t*-butylperoxynorbornanes equal or superior in purity to any past samples and have repeated the kinetic work both in chlorobenzene and in cumene solutions. We have attempted to account for the kinetic discrepancies between the two laboratories.

Results

Table I compares the melting points of the intermediates and final peresters, and the carbon dioxide yields, in the three pieces of work. The melting point of the *exo* perester has been raised by some 10° above the sample of Martin and DeJongh. The difference between carbon dioxide yields of the *endo* perester in

(1) P. D. Bartlett and R. E. Pincock, *J. Am. Chem. Soc.*, **84**, 2445 (1962).
(2) M. M. Martin and D. C. DeJongh, *ibid.*, **84**, 3526 (1962).
(3) H. Hart and F. J. Chloupek, *ibid.*, **85**, 1155 (1963), arrived at the same conclusion through their study of the related diacyl peroxides.
(4) D. C. DeJongh, Thesis, University of Michigan, 1963, reports carbon dioxide yields in *o*-dichlorobenzene of 47 and 75%.

Table I. Criteria of Purity of Intermediates and Peresters

	M.p., °C. (CO₂, % yield)		
	Bartlett and Pincock	Martin and DeJongh	This work
exo-2-Norbornene-5-carboxylic acid	...	42.0–43.5	41.5–43.8
endo Isomer	...	45–46	45–46.6
exo-2-Norbornane-carboxylic acid	54.5–56.5	58	58.5–59.0
endo-2-Norbornane-carboxylic acid	63.5–65.0	65	64.5–65.8
exo-2-Carbo-*t*-butyl-peroxynorbornane	0	27	37.6–39.2
(cumene)	...	(98)	(104)
(chlorobenzene)	(76)	(75)ᵃ	...
endo-2-Carbo-*t*-butylperoxynor-bornane	30–32	34	33.7–34.5
(cumene)	...	(92)	(91, 92, 95)
(chlorobenzene)	(58)	(47)ᵃ	(52, 73)

ᵃ Measured in *o*-dichlorobenzene; ref. 4.

cumene and in chlorobenzene is seen to be real. The *endo* perester gives 91–95% carbon dioxide in cumene, but in chlorobenzene the amount depends upon the perester concentration, varying between 52 and 73%. This result is consistent with the conclusions of both previous sets of authors that induced decomposition becomes important in chlorobenzene, and with the suggestion of Bartlett and Pincock that *endo*-norbornane perester is attacked by the same mechanism as undiluted *t*-butylperoxy isobutyrate, namely[5,6]

$$R_2C-COOC(CH_3)_3 + \cdot OC(CH_3)_3 \longrightarrow$$
$$\underset{H \quad O}{|\quad\;\;||}$$
$$(CH_3)_3COH + R_2\dot{C}COOC(CH_3)_3 \longrightarrow$$
$$\underset{O}{||}$$
$$(CH_3)_3 CO\cdot + (R_2C\!\!-\!\!-\!\!-O) \longrightarrow polyester$$
$$\underset{\underset{O}{||}}{\diagdown C \diagup}$$

On the basis of reaction order Bartlett and Pincock were inclined to conclude that only the *endo* perester was undergoing such induced decomposition, presumably because of less steric hindrance to attack of *t*-butoxy radicals on its α-hydrogen atom. We have not specifically reinvestigated this point, but the difference between *endo* and *exo* peresters may well be a difference of degree since the carbon dioxide yield from the *exo* perester is also decreased in chlorobenzene. The criterion of induced decomposition which consists in looking for a higher order term in the rate equation for decomposition[7] depends upon a single prevailing

(5) P. D. Bartlett and L. B. Gortler, *J. Am. Chem. Soc.*, **85**, 1864 (1963).
(6) N. A. Milas and A. Golubovic, *ibid.*, **80**, 5994 (1958).
(7) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).

Table II. Thermal Decomposition of exo-Norbornane Perester in Chlorobenzene

Temp., °C.	Initial concn., M	$k \times 10^4$, sec.$^{-1}$	Temp., °C.	Initial concn., M	$k \times 10^4$, sec.$^{-1}$	Temp., °C.	Initial concn., M	$k \times 10^4$, sec.$^{-1}$
Bartlett and Pincock			Martin and DeJongh			Present work[a]		
			94.45	0.24	0.886			
						95.96	0.05	1.43
						96.02	0.06	1.23
						96.11	0.05	1.33
100.10	0.05	1.91						
100.10	0.05	1.88						
100.10	0.52	1.76						
			101.90	0.05	1.43			
			101.90	0.19	2.28			
111.40	0.05	6.79						
111.40	0.52	6.06						
			112.1	0.25	8.85			
120.00	0.05	17.1						
120.00	0.05	15.7						

[a] Decomposition followed by gas evolution.

chain termination step. In the well-known case of benzoyl peroxide decomposition in ethers,[8] the chain terminating step is such that there is no distinction in reaction order between spontaneous and induced decomposition. In most cases, as shown by the product studies in many perester decompositions, several termination reactions are competing, and therefore we cannot generally rely on reaction order alone to tell us whether induced decomposition is playing a role or not.

At each synthetic step following the separation of the isomers of norbornene-2-carboxylic acid the isomeric integrity of the product was established by infrared or n.m.r. spectroscopy or both. The infrared spectra of the two peresters are shown in Figure 1. The isomers are clearly distinguished by the positions, shapes, and relative sizes of the bands in the 7- to 12-μ region. The spectra are identical with those of Pincock[9] except that the latter include shoulders on the low wave length side of the carbonyl peaks. The fact that this shoulder is especially pronounced in the exo isomer, which gave the greatest melting point depression, may indicate that it is due to the impurity which caused the lowered melting point. Infrared spectra of the peresters did not appear in ref. 2 and 4.

In accord with previous findings that the norbornyl acid chlorides do not isomerize when refluxed in chloroform with thionyl chloride,[3,10] we found no interconversion of the exo and endo isomers under our conditions (overnight at room temperature in thionyl chloride as solvent). However, we did find significant isomerization for longer times and higher temperatures. Crude rate measurements with a ninefold excess of thionyl chloride gave for the equilibration
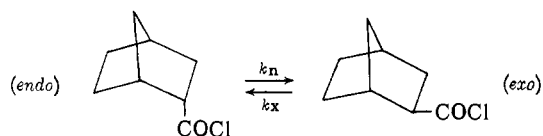
first-order rate constants of k_n = 3.3 × 10^{-7}/sec., k_x = 1.3 × 10^{-7}/sec. at room temperature (about 23°) and k_n = 3.1 × 10^{-4}/sec. and k_x = 1.6 × 10^{-4}/sec.

(8) P. D. Bartlett and K. Nozaki, J. Am. Chem. Soc., 69, 2299 (1947), especially the discussion on p. 2304, column 2.
(9) R. E. Pincock, Thesis, Harvard University, 1959.
(10) W. R. Boehme, E. Schipper, W. G. Scharpf, and J. Nichols, J. Am. Chem. Soc., 80, 5488 (1958).

at 100°. Extrapolation between these points allowed for estimation of the rates at other temperatures. At 100° the same equilibrium mixture (69.4% exo) was obtained from either isomer. In connection with this study we determined the molal ebullioscopic constant for thionyl chloride with dissolved exo acyl chloride to be approximately 5.1 ± 0.9° in the range from 0.16 to 3.5 m.

The results of the kinetic study of the new samples of exo and endo peresters in chlorobenzene are shown in Tables II and III and in Figures 2 and 3. With respect to the exo isomer there is no serious disagreement between the previous results[1,2] of the two laboratories, and the new samples were therefore examined at only one temperature and were found to fall on the same line of ln (k/T) vs. $1/T$ as the other data within the precision of the latter. In the case of the endo perester in chlorobenzene, where the discrepancy between the work of ref. 1 and 2 was serious, new determinations were made of the rate constant of decomposition over a range of temperature somewhat greater than that covered by the previous data. As Figure 3 shows, the new data fall upon the line of Bartlett and Pincock and remain at variance with those of Martin and DeJongh.

To be sure, the endo perester is the one showing the dependence of rate constant upon concentration in chlorobenzene, and it therefore presents a possibility of very different results in comparing reactions carried out at different concentrations. It will be noted, however, from Table III and Figure 3 that the range of concentrations is the same in the new work as in the old, and concentration cannot account for the difference between the results in ref. 1 and 2.

As indicated in the paper of Martin and DeJongh, cumene represents a better choice of solvent for studying the direct decomposition, since it largely eliminates induced decomposition. Table IV and Figure 4 show good agreement between our new rate studies of the exo perester in this solvent and those of Martin and DeJongh. Table V and Figure 5, however, show that for the endo isomer in cumene all our rate constants are lower than the corresponding ones of Martin and DeJongh by factors of 2.2–2.6, and the difference in enthalpies of activation is 1.6 kcal., partly offset by an opposing entropy difference (Table VI). There is no

Table III. Thermal Decomposition of *endo*-Norbornane Perester in Chlorobenzene

Bartlett and Pincock			Martin and DeJongh			Present work[a]		
Temp., °C.	Initial concn., M	$k \times 10^4$, sec.$^{-1}$	Temp., °C.	Initial concn., M	$k \times 10^4$, sec.$^{-1}$	Temp., °C.	Initial concn., M	$k \times 10^4$, sec.$^{-1}$
						93.97	0.032	0.175
			94.45	0.186	0.969			
100.1	0.050	0.461						
100.1	0.520	0.513						
			101.90	0.048	1.33	101.9	0.032	0.620
			101.90	0.052	1.25			
			101.90	0.095	1.96			
			101.90	0.208	1.96[b]			
						109.6	0.034	1.4[c]
						109.6	0.306	1.7
111.4	0.055	1.91				109.8	0.313	1.8
111.4	0.058	2.11						
111.4	0.523	2.59						
			111.90	0.199	6.53			
120.0	0.054	5.21						
120.0	0.051	5.58						
						120.5	0.034	5.72

[a] Decomposition followed by infrared for 1.1 to 6 half-lives. [b] Value from DeJongh thesis, omitted in paper. [c] The 109.6 and 109.8° runs were done on entirely different preparations of the perester.

Table IV. Thermal Decomposition of *exo*-Norbornane Perester in Cumene

Data of Martin and DeJongh			Present study[a]		
Temp., °C.	Initial concn., M	$k \times 10^4$, sec.$^{-1}$	Temp., °C.	Initial concn., M	$k \times 10^4$, sec.$^{-1}$
			84.39	0.038	0.219
94.45	0.047	0.605	94.70	0.047	0.729
94.45	0.235	0.592			
			99.92	0.057	1.34[b]
			100.10	0.044	1.37
101.90	0.050	1.53			
101.90	0.097	1.36			
101.90	0.191	1.28			
			104.98	0.041	2.40
			108.63	0.042	3.62
			108.68	0.086	3.60
			108.70	0.041	3.71
			108.82	0.047	3.37[b]
			109.98	0.035	4.53
112.10	0.061	4.72			
112.10	0.246	4.32			
			113.52	0.033	6.19

[a] Kinetics followed by gas evolution for 3.2 to 5 half-lives. [b] Followed for only 2 half-lives.

Table V. Thermal Decomposition of *endo*-Norbornane Perester in Cumene

Data of Martin and DeJongh			Present study[a]		
Temp., °C.	Initial concn., M	$k \times 10^4$, sec.$^{-1}$	Temp., °C.	Initial concn., M	$k \times 10^4$, sec.$^{-1}$
			93.97	0.033	0.187
94.45	0.0465	0.527			
94.45	0.1983	0.456			
101.90	0.0451	1.17	101.90	0.033	0.530
101.90	0.0510	1.12			
101.90	0.0980	1.16			
101.90	0.1012	1.20			
101.90	0.2085	1.04			
			109.60	0.028	1.13[b]
			109.60	0.236	1.10
			109.80	0.033	1.18
			109.80	0.033	1.19
			109.90	0.052	1.33[c]
			109.90	0.053	1.29[c]
			110.00	0.049	1.32[c]
111.90	0.0499	3.57			
111.90	0.201	3.46			
			120.30	0.033	4.3

[a] Kinetics followed by infrared absorption for 1 to 3.5 half-lives. [b] The 109.6 and 109.8° runs done on entirely different preparations of the perester. [c] These runs were followed by gas evolution for 3 to 5 half-lives.

clear correlation between rate constant and concentration of perester in either set of data.

Discussion

The present work confirms the earlier results from this laboratory for both isomers of the perester in chlorobenzene and those of Martin and DeJongh for the *exo* isomer in chlorobenzene and in cumene. Having established this agreement on the rate of decomposition of the *exo* perester, we were perplexed by the uniform disagreement, by a factor of about 2.5, in the rate constants for decomposition of the *endo* perester in both chlorobenzene and cumene between the two laboratories. The comparison is made at similar concentrations, and hence cannot be due to induced decomposition. It is unlikely that inhibition of induced decomposition by atmospheric oxygen in only

one of the laboratories could account for the differences. None of the investigators degassed the samples for kinetic study in the infrared. Degassed samples followed by means of carbon dioxide evolution in this work gave results almost identical with those of the present infrared runs, confirming the finding of Martin and DeJongh that air had no effect on the rates.

The difference factor of 2.5 is close to the 2.3 factor for conversion from common to natural logarithms, but a recalculation of the original data from both laboratories showed that this was not the source of the discrepancy.

The present work has shown that the different results of ref. 1 and 2 did not result from lower purity

Table VI. Activation Parameters[a]

	Bartlett and Pincock	Martin and DeJongh	This work
exo Perester			
cumene ΔH^*		31.4 (31.5 ± 1.1)	30.9 ± 0.4
ΔS^*		7 (7 ± 3)	6 ± 1
chlorobenzene ΔH^*	30.9 (31.1 ± 0.7)	(37 ± 7)[b]	
ΔS^*	6.7 (7 ± 2)	(21 ± 18)	
endo Perester			
cumene ΔH^*		31.1 (31.0 ± 0.9)	32.8 ± 0.9
ΔS^*		6 (6 ± 3)	9 ± 3
chlorobenzene ΔH^*	35.6 (34.6 ± 1.8)	(30.9 ± 6.5)[c]	36.8 ± 1.7
ΔS^*	16.4 (14 ± 5)	(6 ± 18)	20 ± 5

[a] The values in parentheses have been recalculated according to the treatment used in this work. [b] Omitting the least concentrated run gives $\Delta H^* = 36.0 \pm 1.0$, $\Delta S^* = 20 \pm 3$. [c] Omitting the two least concentrated runs gives $\Delta H^* = 30.3 \pm 2.1$, $\Delta S^* = 5 \pm 6$.

of the former's samples. The greatest improvement in the present work was in the melting point 'of the *exo* isomer, and the kinetic results in this case are in

Figure 1. Infrared spectra of 2-carbo-*t*-butylperoxynorbornanes: (A) *exo* isomer, 20 mg./ml. in CCl_4, Perkin-Elmer Model 21 infrared spectrometer; (B) *endo* isomer, 64.6 mg./ml. in CCl_4, copied from tracing of a Perkin-Elmer Model 237 infrared spectrophotometer.

former and the melting points of the latter. Although one would expect an isomeric mixture to give a concave plot of the natural logarithm (perester) *vs.* time, the

Figure 2. Rate of decomposition as a function of temperature for *exo*-2-carbo-*t*-butylperoxynorbornane in chlorobenzene: O (Bartlett and Pincock)[1] in the groups of points from left to right the initial perester concentrations (from top to bottom) are 0.05, 0.05, 0.05, 0.525, 0.05, 0.05, and 0.5 M; △ (Martin and DeJongh) 0.25, 0.19, 0.048, and 0.24 M; □ (this work) 0.05, 0.05, and 0.06 M.

good agreement in all three determinations. Such lack of dependence of rate constant upon quality of sample is possible (though not predictable) because (1) norbornane derivatives tend to have high cryoscopic constants and may melt low with very slight contaminations, and (2) an *inert* impurity will be without effect on a first-order rate constant based upon relative optical densities. The purity of the perester is, of course, of critical importance for product studies of its decomposition.

Although the cryoscopic impurity was not the source of the discrepancy, the fact that the rates of Martin and DeJongh fall between the rates for the two isomers determined in this laboratory suggested a reinvestigation of the isomeric purity of the samples. Evidence for the isomeric purity of the present compounds is mentioned above. In the other work in this laboratory the isomeric purity was established by the infrared spectra of the acyl chlorides and of the peresters. No determination of the isomeric purity of the acyl chlorides or of the peresters was reported for the work of Martin and DeJongh beyond the boiling points of the

straightness of the kinetic plots of ref. 2 (reported correlation coefficients from 0.992 to 1.000) does not preclude the possibility of isomeric impurity in the *endo* perester, for the decomposition of this isomer in cumene was followed to only 68 to 76% completion. The points in Figure 6 were calculated using our rate constants for a hypothetical mixture of 64% *exo* and 36% *endo* perester followed to the same stage of completion. Although curvature is evident here, it is small as attested by the correlation coefficient of 0.999, and the randomness of experimental points could easily have concealed such curvature.

In the preparation of the peresters the greatest difference in procedure among the investigators occurred in the temperature and time chosen for the conversion of the acids to the acyl chlorides in thionyl chloride. In the present work the reaction was allowed to proceed overnight at room temperature. In the earlier work in this laboratory the reaction solution was left at room temperature for 4 hr., then heated on the steam bath for 15 min. The other workers refluxed the mixture gently for 2 hr. We have shown that
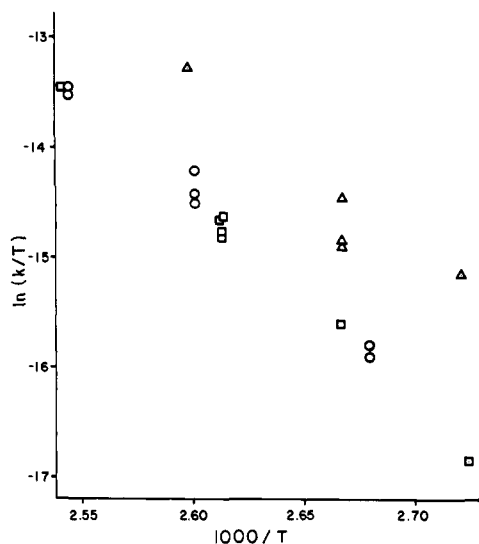
Figure 3. Rate of decomposition as a function of temperature for *endo*-2-carbo-*t*-butylperoxynorbornane in chlorobenzene: ○ (Bartlett and Pincock) in the groups of points from left to right the initial perester concentrations (from top to bottom) are 0.05, 0.05, 0.5, 0.06, 0.05, 0.5, and 0.05 *M*; △ (Martin and DeJongh) 0.2, 0.2, 0.1 (same point), 0.05, 0.05, and 0.2 *M*; □ (this work) 0.03, 0.3, 0.3, 0.03, 0.03, 0.03, and 0.03 *M*.
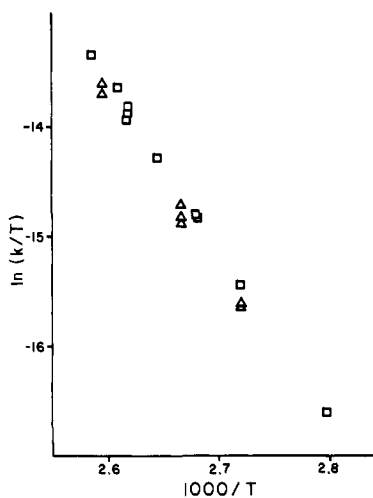

Figure 4. Rate of decomposition as a function of temperature for *exo*-2-carbo-*t*-butylperoxynorbornane in cumene: △, Martin and DeJongh; □, this work.

Figure 5. Rate of decomposition as a function of temperature for *endo*-2-carbo-*t*-butylperoxynorbornane in cumene: △, Martin and DeJongh; □, this work.
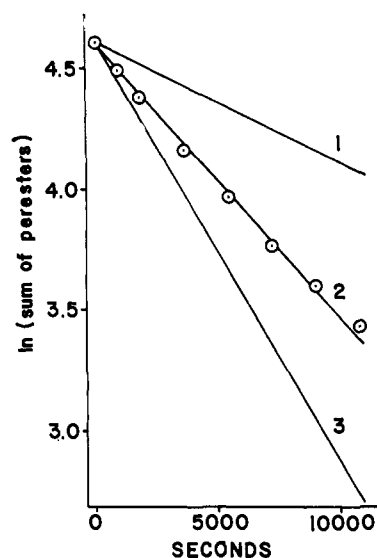
Figure 6. This disappearance of perester with time for thermal decomposition in cumene at 101.9°: solid lines are (1) calculated for the pure *endo* isomer from the present work, (2) *endo* isomer from the work of Martin and DeJongh, and (3) calculated for the *exo* isomer from the present work; the points are calculated for a mixture of 64% *exo* and 36% *endo* from the present work; the radius of the circles corresponds to the point standard deviation of the data of Martin and DeJongh.

under the last conditions considerable isomerization of the acyl chloride is to be expected.

Figure 6 shows that a 64% *exo*, 36% *endo* isomeric mixture would give a good approximation of the rate of Martin and DeJongh for the decomposition of the *endo* isomer at 101.9°. In fact these hypothetical data give a least-squares rate constant of 1.09 × 10^{-4}/sec. compared to Martin and DeJongh's values of 1.04 to 1.20 × 10^{-4}/sec. In order to get this amount of conversion from *endo* to *exo* acid chloride in 2 hr. (ignoring any concentration dependence of our isomerization rate constants) a reaction temperature of about 96° would be needed. The boiling point of pure thionyl chloride is 78.8°. Using our rough molal ebullioscopic constant of 5.1° we calculate that a solution about 3.4 *m* (0.4 mole of acyl chloride per mole of thionyl chloride) would give this boiling point.

DeJongh reports that an excess of thionyl chloride was used. If this excess were about 2.5-fold the discrepancy in kinetic data for the *endo* isomers of the different laboratories could be explained by the above chain of events.

Although in general the present work supports the activation parameters as well as the rates of Bartlett and Pincock, the extension of the study to cumene has shown a smaller difference (1.8 kcal.) in the activation enthalpies between *endo* and *exo* than in chlorobenzene (possibly as much as 5–6 kcal.). It is likely, therefore, that most of the large difference in chlorobenzene results from the greater susceptibility of the *endo* isomer to induced decomposition in that solvent, the attack of *t*-butoxy radical upon perester having a higher ΔH^* than the spontaneous perester decomposition.

Cumene largely or wholly eliminates this induced decomposition. The difference that remains in rate between the isomers is small.

Experimental

Materials. Cumene.[11] Eastman Kodak Co. White Label cumene was purified by the method of Bartlett, Benzing, and Pincock.[12] A middle fraction boiling at 152.1–152.4° was collected and stored in the dark under nitrogen.

Chlorobenzene from the Fisher Scientific Co. was purified by the method of Martin and DeJongh[2] and stored over Fisher Type 5A molecular sieve, b.p. 130–130.2°.

t-Butyl hydroperoxide from the Borden Chemical Co. was purified by extraction into cold 15% aqueous potassium hydroxide followed by regeneration of the free hydroperoxide upon neutralization with solid ammonium chloride and distillation under reduced pressure. A center fraction, boiling at 35–36° at 8.5 mm. having $n^{23.5}D$ 1.3994 and assaying 98.4% by the iodometric procedure of Wagner, Smith, and Peters,[13] was used.

Sodium t-butyl peroxide was prepared by adding a 10% excess of purified *t*-butyl hydroperoxide to a stirred suspension of sodium hydride in a large volume of anhydrous diethyl ether (50 ml. of ether per gram of sodium *t*-butyl peroxide). The reaction mixture was protected from moisture and stirred vigorously at room temperature for 24 hr. The sodium salt was collected by filtration, washed repeatedly with fresh portions of diethyl ether, and dried *in vacuo*. The yield of white powder was 99.6%. The sodium salt assayed 99.2% by titration against hydrochloric acid and 97.1% by iodometric titration. It showed no loss of active oxygen content on storing for 1 year at 0°.

Preparation of Peresters. exo- and endo-5-carboxyl-2-norbornenes were prepared by the addition of cyclopentadiene to acrylic acid. The distilled acids were separated through iodolactonization according to the method of Rondestvedt and Ver Nooy[14] used also by DeJongh.[4] Recrystallization from 30–60° petroleum ether gave the pure isomeric acids, *endo*, m.p. 45–46.6° (lit.[4,10,14] m.p. 45–46°) and *exo*, m.p. 41.5–43.8° (lit. m.p. 42.0–43.5°[4] and 44–45°[10,14]). The absence of infrared peaks at 7.77, 8.06, and 14 μ in the spectrum of the *endo* isomer showed that it was free of the *exo*.

Norbornane-2-endo-carboxylic acid and norbornane-2-exo-carboxylic acid were prepared from the corresponding unsaturated acids by hydrogenation in aqueous alkaline solution under 3.5 atm. of hydrogen with platinum oxide catalyst until no more gas was taken up. The *endo* isomer, recrystallized from 30–60° petroleum ether, had m.p. 64.5–65.8° (lit. m.p. 65°,[4] 63.5–65.0°,[1] and 65°[15]). That this acid was free of its *exo* isomer was verified by the absence of an n.m.r. signal upfield of δ 1.15, in which region the signal from the *exo*

isomer attains one half of its maximum amplitude. Its freedom from unsaturated isomers was demonstrated by the absence of any n.m.r. signal between δ 3 and 12.2. The *exo* isomer recrystallized from ligroin had m.p. 58.5–59.0° (lit. m.p. 54.5–56.5°,[1] 58°,[4] 58–58.5°,[15] and 56–57°[16]). That this acid was free of its *endo* isomer was shown by its lack of n.m.r. absorption in the δ 2.7–3 region where the *endo* isomer has four peaks attaining 0.16 of its maximum peak height. Norbornene derivatives were excluded by the absence of peaks in the δ 2.7–12.1 region.

Norbornane-2-endo-carbonyl Chloride and Norbornane-2-exo-carbonyl Chloride. Eastman Kodak Co. thionyl chloride (13 ml.) was added to 13.4 g. of norbornane-2-*endo*-carboxylic acid in a 50-ml. flask cooled in an ice bath. The mixture was allowed to react overnight at room temperature, and the solution was distilled under vacuum. Acid chloride (10.1 g.) was collected, b.p. 55–55.5° at 4 mm. (lit. b.p. 63–66° at 1.5 mm.,[1] 90° at 18 mm.[4]). The *exo* isomer was prepared from the corresponding acid by the same method, b.p. 61–62° at 6 mm. (lit. b.p. 61–63° at 1 mm.,[1] 83–84° at 12 mm.,[17] and 90° at 18 mm.[4]). The infrared spectra of the isomers in the 11–13-μ region showed each to be isomerically pure.

endo-2-Carbo-t-butylperoxynorbornane. Sodium *t*-butyl peroxide (10.6 g.) was weighed into a 500-ml. flask in a −6° ice-salt bath, and 250 ml. of methylene chloride which had been dried over magnesium perchlorate was added. With magnetic stirring 10.1 g. of norbornane-2-*endo*-carbonyl chloride in 50 ml. of methylene chloride was added over a period of 1.25 hr. After stirring for another 1.5 hr. in the cold the mixture was filtered and most of the solvent was removed from the filtrate below room temperature. The residue was diluted with ether and washed with two 75-ml. portions of 8% sodium bicarbonate. The organic layer was dried over magnesium sulfate and the solvent was removed. The 12.4 g. of liquid residue was chromatographed on 55 g. of Florisil and eluted with ligroin. The resulting material was recrystallized four times from pentane at −50°. This gave 4 g. of the white, crystalline peroxy ester, m.p. 33.7–34.5° (lit. m.p. 30–32°[1] and 34°[4]). Iodometric titration by the method of Silbert and Swern[18] indicated 94.8% purity. The isomeric purity of the compound was established by the infrared spectrum shown in Figure 1.

exo-2-Carbo-t-butylperoxynorbornane was prepared from the corresponding acid chloride by the same method, m.p. 37.6–39.2° (lit. m.p. 27°[2] and 0°[1]). Iodometric titration indicated 88% purity although later carbon dioxide yields showed the purity to be 100 ±5%. The isomeric purity of this compound was also established by the infrared spectrum in Figure 1.

Kinetic Studies. Most of the decompositions of the *endo*-peroxy ester were followed by the disappearance of the perester carbonyl peak at about 5.6 μ according to the infrared method of Bartlett and Hiatt.[19] Runs were followed to more than 75% completion. Most of the *exo*-peroxy ester decompositions were followed

(11) The authors are indebted to Dr. R. D. Swigert of this laboratory for generously supplying purified cumene and sodium *t*-butyl peroxide.
(12) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).
(13) C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).
(14) C. S. Rondestvedt, Jr., and C. D. Ver Nooy, *J. Am. Chem. Soc.*, **77**, 4878 (1955).
(15) J. A. Berson and D. A. Ben-Efraim, *ibid.*, **81**, 4083 (1959).
(16) K. Alder, K. Heimbach, and R. Reubke, *Ber.*, **91**, 1516 (1958).
(17) K. Alder and G. Stein, *Ann.*, **514**, 211 (1934).
(18) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).
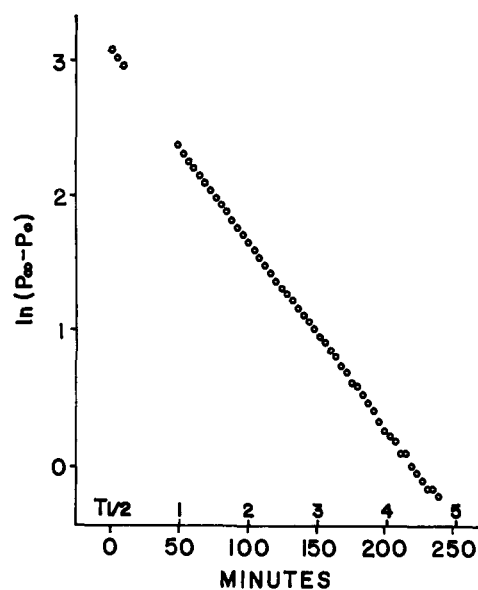(19) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

Figure 7. Gas evolution, followed by manometric readings at constant volume, in the decomposition of exo-2-carbo-t-butylperoxynorbornane (17.6 mg. in 2 ml. of cumene) at 104.98°.
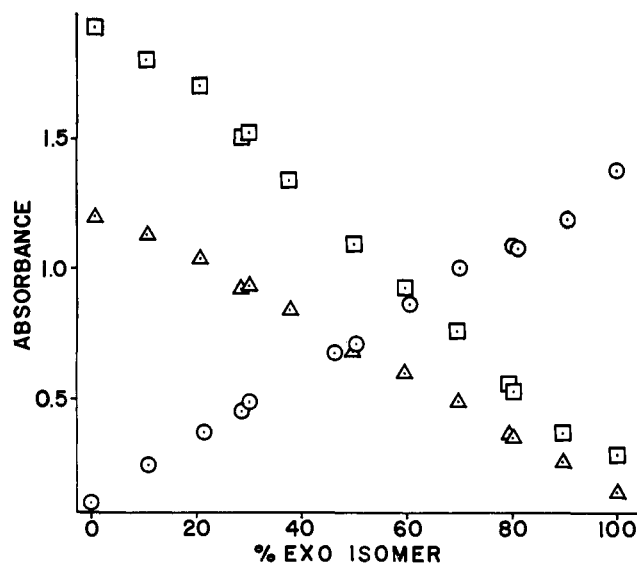

Figure 8. Standard curves for infrared absorbances of 56.6-mg mixtures of endo- and exo-norbornane-2-carbonyl chlorides in 1 ml of CS_2: $\odot$, band at 11.62 μ; $\triangle$, band at 12.11 μ; $\square$, band at 11.95 μ

by gas evolution at constant volume on an apparatus designed and constructed by Berezin[20] in this laboratory. Runs were followed to at least 90% completion. Figure 7 shows the experimental points obtained on this apparatus for the decomposition of 17.6 mg. of exo perester in 2 ml. of cumene at 104.98°, and followed to 96.3% decomposition. The interval after the first three points was due to a temporary valve obstruction. Control experiments with the apparatus showed that the rates observed were independent of variations in the stirring rate used.[21]

Rates of isomerization of the acid chlorides were determined by weighing 50 mg. of an isomerically pure acid into an ampoule, adding about 0.61 g. of Eastman White Label thionyl chloride, sealing the ampoule after 3 hr. at room temperature, and putting it into a constant temperature bath. After the desired reaction time had elapsed the ampoule was cooled and stored in a refrigerator. For analysis the ampoule was opened, the thionyl chloride was removed under vacuum, and 1 ml. of carbon disulfide was added. Analysis was performed on a Cary–White Model 90 infrared spectrometer by measuring the maximum intensity of the peaks of the endo isomer at 11.95 and 12.11 and of the exo isomer at 11.62 μ. Concentrations were determined from these intensities by reference to a plot of absorbance vs. concentration of known mixtures. This plot (Figure 8) shows remarkable linearity over a wide range of concentration in spite of the fact that the peaks interfere slightly. An accuracy of ±3% was obtained in this way; 90% of the acid chloride mixture was recovered even after 15 hr. at 100°.

Ebullioscopic measurements were made by adding weighed increments of the exo acid to 15 ml. of thionyl chloride, warming under reflux until the reaction was complete, and recording the temperature of the magnetically stirred liquid in a 110° bath.

Treatment of the Data. The first-order rate constants for perester decomposition were calculated by the method of least squares. For infrared runs ln (P/P_0) was plotted against time. Some gas evolution runs were also plotted in this fashion and all were treated by the Guggenheim method.[22] The plots showed no long-range curvature although a few runs showed a slight increase in rate after 3 to 4 half-lives. This is probably a reflection of the diminishing sensitivity of the analytical methods at lower concentrations. The infrared and gas evolution runs were each reproducible to within 8%. Under identical conditions the two methods agreed to within 10%. Activation parameters were calculated using $\Delta H^* = -R \times m$ and $\Delta S^* = R(b - \ln (k'/h))$ where m and b are the slope and intercept, respectively, of the least-squares line through the points on a plot of ln (k/T) vs. $1/T$, and R, k', and h are the usual physical constants. The uncertainties for the activation parameters are their sample standard deviations. The assumption of normality in the distribution of the points about the least-squares line gives these as the estimate of uncertainty at a confidence level of about 70% depending on the number of points used. The rate of isomerization of endo and exo acid chlorides in thionyl chloride at 100° was determined from the slope of a plot of ln $(K_{eq} \times endo - exo)$ vs. time. The rate at room temperature was estimated by assuming an equilibrium constant and iterating through the equations $k_1 + k_2 = 1/t \ln ((endo_1 \cdot K_{eq} - exo_1)/(endo_2 \cdot K_{eq} - exo_2))$ for the two samples until self-consistency was reached. All calculations were performed on an IBM 1620 computer.

Carbon dioxide yields were determined as previously described.[12]

(20) I. V. Berezin, work to be published.
(21) P. D. Bartlett and R. H. Jones, J. Am. Chem. Soc., 79, 2154 (1957).

(22) E. A. Guggenheim, Phil. Mag., 2, 538 (1926).