metal and the ring may allow rapid and reversible intramolecular charge transfer to occur.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Peresters. VII. *t*-Butylperoxyesters of *exo*- and *endo*-2-Norbornanecarboxylic Acids

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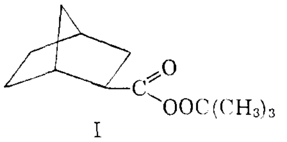
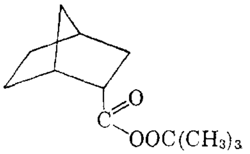
The relative rates of decomposition at 100° in chlorobenzene of the *t*-butylperoxyesters of cyclohexanecarboxylic acid, of *exo*- and of *endo*-2-norbornanecarboxylic acids are 6.0, 4.1 and 1.0, respectively. These peresters give 75, 76 and 58%, respectively, of a mole of carbon dioxide per mole of perester. Decomposition of the *exo*-perester in moist carbon tetrachloride in the presence of iodine decreased the yield of carbon dioxide to 56%. These results show that not more than 56% of the decomposition of the *exo*-perester is of the concerted two-bond type, and it is not certain whether any of these three peresters reacts by this mechanism. This, and the *exo/endo* rate difference of only fourfold, means that carbon 6 of the norbornane ring provides insufficient anchimeric assistance to make the formation of a 2-norbornyl radical comparable in ease to that of *t*-butyl, trichloromethyl or benzyl.

Introduction

Previous studies in this Laboratory[1] have shown that the rates of thermal decomposition of *t*-butylperoxyesters are related (1) to the stability of the alkyl radicals formed and (2) to substitution favoring the cationic character of these radicals in the transition state. Accordingly, the *t*-butylperoxy esters of *exo*- and *endo*-norbornane-2-carboxylic acids (I and II) possess a double interest.


I


II

If the 2-norbornyl free radical were stabilized by a bridged structure like that of the norbornyl cation,[2] we might expect a large excess of k_{exo} over k_{endo} in any reaction in which the 2-norbornyl radical was formed in the rate-determining step. Even if, in accord with a number of indications, there is no favored bridged structure for the radical, it would be of interest to learn whether in the polar contributing structure III[1b] of the transition state

$$R^+CO_2\ ^-OC(CH_3)_3 \quad \text{(III)}$$

anchimeric assistance of the known cationic type in the norbornyl group is able to facilitate homolytic bond fission. Free radical rearrangement of phenyl groups does not occur by direct participation of the migrating group as the original bond breaks, but by rearrangement of the group after initial formation of the radical.[3] This fact, together with the general lack of examples of free radical alkyl rearrangements,[4,5] suggests that neighboring group interaction with the radical center does not occur.

Results

The norbornyl peroxyesters were prepared by reaction of the *exo*- or *endo*-norbornanecarbonyl chlorides with *t*-butyl hydroperoxide in the presence of pyridine in pentane at 0°. The perester derived from cyclohexanecarboxylic acid was also prepared in order to compare it with the bicyclic peresters. The compounds obtained were oils, characterized by their infrared spectra, peroxide titers and elementary analyses.

The kinetic and product studies were carried out in chlorobenzene since relatively high temperatures (100–120°) were required to cause decomposition of these peresters at conveniently measurable rates. The rates were followed by the decline in intensity of the perester carbonyl band at about 5.63 μ. All the runs gave good first-order plots with some increase in rate constant with concentration in the case of the *endo*-norbornyl and of the cyclohexyl peresters. The results of the kinetic runs are shown in Table I and the products of decomposition are shown in Table II.

To investigate the possibility that only the peroxide bond of the *exo*-perester was breaking in the rate-determining step, an attempt was made to trap with iodine in moist carbon tetrachloride the acyloxy radicals which would then be formed.[6] Table III shows the results of decomposing *exo*-2-carbo-*t*-butylperoxynorbornane in carbon tetrachloride in the presence of iodine and water. A control run was carried out without the iodine present.

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(1) (a) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958); (b) P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1756 (1960); (c) P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960).

(2) S. Winstein and D. Trifan, *ibid.*, **71**, 2953 (1949); **74**, 1147, 1154 (1952).

(3) (a) F. H. Seubold, *ibid.*, **75**, 2532 (1953); S. Winstein, R. Heck, S. Lapporte and R. Baird, *Experientia*, **12**, 138 (1956); J. Weinstock and S. N. Lewis, *J. Am. Chem. Soc.*, **79**, 6243 (1957); (b) C. G. Overberger and H. Gainer, *ibid.*, **80**, 4561 (1958).

(4) J. A. Berson, C. J. Olsen and J. S. Walia, *ibid.*, **82**, 5000 (1960); S. J. Cristol and G. D. Brindell, *ibid.*, **76**, 5699 (1954); S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 6039 (1957); J. A. Berson and W. M. Jones, *ibid.*, **78**, 6045 (1956).

(5) For a kinetic and product study of the effect of neighboring sulfur and of iodine see J. C. Martin and W. G. Bentrude, *Chemistry & Industry*, 192 (1959), and J. E. Leffler, R. D. Faulkner and C. C. Petropoulos, *J. Am. Chem. Soc.*, **80**, 5435 (1958).

(6) (a) G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950); (b) H. J. Shine and D. M. Hoffmann, *ibid.*, **83**, 2783 (1961); (c) D. F. DeTar and R. C. Lamb, *ibid.*, **81**, 122 (1959).

TABLE I

RATES OF DECOMPOSITION OF PERESTERS, R–CO$_2$–OC(CH$_3$)$_3$, IN CHLOROBENZENE

R	Initial concn., M	T, °C.	$k \times 10^4$, sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
Cyclohexyl	0.0577	100.1	2.77	31.3	8.6
	.0662	100.1	2.72		
	.0515	111.4	9.77		
	.0556	111.4	9.52		
	.650	111.4	9.86		
	.0523	120.0	24.1		
	.0614	120.0	23.7		
endo-Norbornyl	.0502	100.1	0.461	35.6	16.4
	.520	100.1	0.513		
	.0546	111.4	1.91		
	.0584	111.4	2.11		
	.523	111.4	2.59		
	.0537	120.0	5.21		
	.0514	120.0	5.58		
exo-Norbornyl	.0515	100.1	1.91	30.9	6.7
	.0518	100.1	1.88		
	.521	100.1	1.76		
	.0487	111.4	6.79		
	.525	111.4	6.06		
	.0547	120.0	17.1		
	.0526	120.0	15.7		

TABLE II

PRODUCTS OF DECOMPOSITION OF *exo* AND *endo*-2-CARBO-*t*-BUTYLPEROXYNORBORNANES AND CARBO-*t*-BUTYLPEROXYCYCLOHEXANE IN CHLOROBENZENE AT 100°

Perester	*exo*-Perester	*endo*-Perester	Cyclohexyl perester
Decomposed in 10 ml. of chlorobenzene, g.	0.725	1.01	0.844
Products, moles/mole of perester			
Gas (CO and CH$_4$)	.03	0.06	.08
Carbon dioxide	.76	.58	.75
t-Butyl alcohol	.22	.32	.43
Acetone	.40	.36	.32
Undistilled residue[a]	.40	.48	.45

[a] The undistilled residue in each case consisted of three fractions: biphenyl derivatives, unknown esters (carbonyl absorption *ca.* 5.77 μ) and the carboxylic acid derived from the parent ester. Gas chromatography of the product solutions showed the presence of norbornane or cyclohexane.

TABLE III

RADICAL TRAPPING EXPERIMENTS OF *exo*-2-CARBO-*t*-BUTYLPEROXYNORBORNANE

Conditions	Trapping run	Control run
Perester, mmoles	2.38	2.49
Iodine, mmoles	2.32	None
Water, ml.	0.3	0.3
CCl$_4$, ml.	10	10
Hours at 78–80°	70	70
Prod., moles/mole of perester		
Carbon dioxide	0.56	0.67
exo-Norbornanecarboxylic acid	.26	.16
Neut. undistilled prod.	.120	.135

Discussion

The activation energy for perester decomposition is large relative to that of the radical chain reactions previously used in investigations of participation in free radicals[3] and the perester decomposition should therefore be more sensitive to effects (such as participation) which might reduce the activation energy. However, as shown in Table I, at 100° the rate of decomposition of the *exo*-perester was only 4.1 times greater than that of the *endo*-perester. Even if this difference in rate were all due to the formation of a bridged radical, it would be a very unimpressive phenomenon compared to the *exo*/*endo* rate factors observed in the ionization of norbornyl sulfonate esters. It is impossible to assign such a small factor with confidence to any special cause. The close similarity in yields of carbon dioxide and of residue in the *endo*, *exo* and monocyclic peresters is not in accord with any considerable change in mechanism from one compound to the next.

Actually, there would seem to be good reason why the bridged norbornyl radical should be inferior in stability to the cation. The latter has a pair of electrons in a bonding orbital made up by overlap of atomic orbitals from C-1, C-2 and C-6. The radical would have to use a second MO of higher energy to accommodate the odd electron. If cations with localized and delocalized charge are not very different in energy, as is the case, then the free radical with conventional bonds and a localized odd electron is likely to be preferred over its bridged valence tautomer. These results also mean that special stability of the norbornyl cation alone is not enough to favor a concerted decomposition of *t*-butyl peroxynorbornane-2-carboxylate by a radical mechanism. This situation is in contrast to the behavior of ethers toward free radicals. The reactivity of α-hydrogen in an ether, which is manifest only in abstraction by strongly electron-acceptor radicals, reflects the stability of the α-alkoxyalkyl *cation* and not of the corresponding radical.

One pair of observations in Tables I and II does appear to provide a significant contrast between *endo*- and *exo*-esters. The *endo*-perester shows a rate constant which increases with increasing concentration, whereas the *exo*-perester does not. This would be the case if *t*-butoxy radicals were prone to induce decomposition by abstracting available α-hydrogen from the *endo*-ester but not hindered α-hydrogen from the *exo* compound. Such a difference in behavior would account for the fact that the acetone/*t*-butyl alcohol ratio (a measure of the average lifetime of the (CH$_3$)$_3$CO· radical) is 1.8 for the *exo*, 1.1 for the *endo* and 0.7 for the cyclohexane carboxylate. In a later paper[7] we shall report two cases in which the consequences of this kind of hydrogen abstraction from peresters of α-branched acids have been further explored. If the behavior in those cases is general, the unknown esters in our residues may include polyesters of 2-hydroxynorbornane-2-carboxylic acid.

It might be argued that the difference of 4.7 kcal. in $\Delta H^{\ddagger}$ between the *endo*- and *exo*-peresters supports a change in mechanism between the two. This is a substantial difference, and would mean a factor of over a thousand in rate if not counteracted by the attendant difference in entropy. Although we consider these rate measurements re-

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[7] (a) P. D. Bartlett and L. B. Gortler, to be published. (b) See also N. A. Milas and A. Golubović, *J. Am. Chem. Soc.*, **80**, 5994 (1958).

liable, there are at least two reasons for not building a superstructure of interpretation upon the activation parameters alone. As long as there is evidence for a mixture of mechanisms, $\Delta H^\ddagger$ and $\Delta S^\pm$ as determined are purely empirical constants, containing hidden within them the gradual shifts between mechanisms that occur with temperature changes. We have reason to suspect that this is a rather general situation in free radical decompositions, throwing their activation parameters open to more suspicion than the ample amount which should be focused upon activation parameters generally.[8]

From the temperature required for the decomposition of these peresters it would not be surprising if much of the decomposition of the *endo* isomer, at least, were unconcerted O–O bond fission. The Hammond–Soffer reagent has never been as efficient in scavenging aliphatic as aromatic carboxylate radicals.[6] Our results indicate that some such radicals must be formed even in the *exo* case, but from the results of Shine and Hoffmann[6b] it is difficult to judge how much of our decomposition must have gone through the carboxylate radical in order for iodine in this non-quantitative reaction to shift 10–11% of the product from carbon dioxide to norbornanecarboxylic acid. We can summarize our observations by saying that the decomposition of *endo*- and *exo*-norbornanecarboxylic esters of *t*-butyl hydroperoxide shows no counterpart of the behavior of norbornyl sulfonates in solvolysis.

Experimental

Sources and purification of starting materials were as previously described.[9]

Synthesis of Peresters. ***exo*** **and** ***endo*****-5-Carbomethoxy-2-norbornenes.**—Eastman Kodak Co. methyl acrylate, 660 g., and 506 g. of freshly distilled cyclopentadiene were mixed and held at 35° until the reaction heat subsided (about 6 hours). After standing overnight, distillation at 55–60° (4 mm.) gave 720 g. (67%) of *exo*- and *endo*-esters (80–83°/(12 mm.[10])). This mixture[10] contains about 70% of the *endo* isomer, estimated by comparing infrared spectra.

***exo*- and *endo*-2-Carbomethoxynorbornanes.**—The mixture of *exo*- and *endo*-carbomethoxy-2-norbornenes (400 g.) was hydrogenated for 45 hours with 1.0 g. of platinum catalyst at room temperature. After removal of the platinum by filtration the product was distilled at 45–48°(1 mm.). A sample (0.3 g.) of this product showed no further uptake of hydrogen in a quantitative hydrogenation.

Norbornane-2-*endo*-carboxylic Acid.—The mixture of *exo*- and *endo*-2-carbomethoxynorbornane (70 g.) was hydrolyzed by heating under reflux for 8 hours with 50 g. of sodium hydroxide in 100 ml. of water and 175 ml. of methanol. The product was separated by ether extraction after acidification and distilled at 104° (1.5 mm.). After three slow recrystallizations from acetonitrile with great losses, 13.5 g. of *endo*-acid was obtained which melted at 63.5–65.0° (reported[11] 65°). The crystal structure of this acid was distinctly different from that of its *exo* isomer and its infrared spectrum was also characteristically different. The acid recovered from the acetonitrile was converted *via* its methyl ester to the *exo* isomer (see below).

Norbornane-2-*exo*-carboxylic Acid.—*exo*- and *endo*-2-carbomethoxynorbornane (75 g.) and 80 g. of anhydrous sodium methoxide in 350 ml. of anhydrous Merck methanol was refluxed 16 hours. After allowing part of the methanol to distil away, 150 ml. of water was slowly added. After refluxing 6 hours, the solvent was evaporated to about two-thirds of its volume and acidified with hydrochloric acid. The product was extracted into ether and distilled at 101–104° (1.5 mm.). Six recrystallizations from acetonitrile, followed each time with a water wash to prevent excessive oiling, brought the melting point from below 40° to an almost constant 54.5–56.5° (reported 48°,[12] 56–57°,[13] 58–58.5°[11]) depending somewhat on the rate of heating. The final yield of pure material was 9.9 g., crystallized in plates. The melting point of either the *exo*- or *endo*-acid was greatly depressed by small amounts of the other isomer. Recovered impure acid was used in similar preparations of the *exo*-acid after esterification.

Norbornane-2-*exo*-carbonyl Chloride.—Norbornane-2-*exo*-carboxylic acid (6.4 g.) was added in small portions to 18 g. of thionyl chloride at room temperature. After standing at room temperature for 4 hours and warming on the steam-bath for 15 minutes, the excess thionyl chloride was removed under vacuum and the product distilled at 61–63° (1 mm.) (reported[12] 83–84° (12 mm.)). The yield was 7.2 g.

Norbornane-2-*endo*-carbonyl Chloride.—Norbornane-2-*endo*-carboxylic acid with thionyl chloride gave its acid chloride distilling at 63–66° (1.5 mm.). The infrared spectra of the two acid chlorides showed very distinct differences.

***exo*-2-Carbo-*t*-butylperoxynorbornane.**—To a solution of 1.14 g. of *t*-butyl hydroperoxide and 1.0 g. of pyridine in 20 ml. of anhydrous pentane at −5° was added dropwise over 1 hour a solution of 2.0 g. of *exo*-acid chloride in 15 ml. of pentane. After stirring at 0° for 1 hour, cold 10% sulfuric was added and the pentane layer was washed with cold solutions of 10% sulfuric acid and 10% sodium bicarbonate and with cold water several times. After drying with magnesium sulfate the pentane was stripped off and 2.4 g. (90%) of *exo*-perester obtained. This perester was a thick oil at room temperature but slowly solidified at 0°. It did not explode when heated quickly in a flame but titrated for 86% peroxide by the iodine–thiosulfate method. Its spectrum had carbonyl absorption at 5.65 μ and showed no peaks other than those normal for this perester.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.69; H, 9.54.

***endo*-2-Carbo-*t*-butylperoxynorbornane** was prepared from the *endo*-acid chloride by the same method used for its *exo* isomer. The *endo* compound was a low melting (about 30–32°) oil which titrated for 89% peroxide. Its infrared spectrum was similar to that of the *exo* isomer except for several distinctive bands in the fingerprint region. It had peaks at 12.03 and 12.25 μ and completely lacked the peak at 9.75 μ which was of medium intensity in the *exo* spectrum.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.00; H, 9.41.

Carbo-*t*-butylperoxycyclohexane.—Cyclohexanecarbonyl chloride (b.p. 83–89° (30–35 mm.)), from cyclohexanecarboxylic acid (Eastman Kodak Co.) and thionyl chloride, was made to react with *t*-butyl hydroperoxide and pyridine in pentane by the usual method. This perester was an oil, 90 and 94% pure by peroxide titration, and had $n^{25.5}$D 1.4482.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.56; H, 9.96. Found: C, 65.96; H, 10.07.

Kinetic Studies.—The kinetic runs were carried out in chlorobenzene using the same procedure as described previously[9] for spontaneous decompositions in benzene. All the decompositions were followed to at least 80% decomposition. The first-order rate constants were calculated by the method of least squares using points to 90% decomposition. No deviations from linearity occurred in the plots of log (P/P_0) against time.

Products Studies.—Product studies were carried out in chlorobenzene using the general procedure previously outlined.[9]

Acknowledgment.—We thank the National Science Foundation for a research grant and a predoctoral fellowship.

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(8) R. C. Petersen, J. H. Markgraf and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3821 (1961), and especially Table VI.

(9) P. D. Bartlett and R. E. Pincock, *ibid.*, **82**, 1769 (1960).

(10) A. C. Cope, E. Ciganek and N. A. LeBel, *ibid.*, **81**, 2799 (1959).

(11) J. A. Berson and D. A. Ben-Efraim, *ibid.*, **81**, 4083 (1959).

(12) K. Alder and G. Stein, *Ann.*, **514**, 211 (1934).

(13) K. Alder, K. Heimbach and R. Reubke, *Ber.*, **91**, 1516 (1958).