The Decomposition of Peresters. I. t-Butyl Esters of Long-chain Aliphatic Percarboxylic Acids in Several Solvents[1]

BY MENDEL TRACHTMAN AND JOHN G. MILLER

The decomposition of a series of t-butyl aliphatic peresters (percaprate, permyristate, perlaurate and perpalmitate) has been studied in various solvents, mostly at 110°. In chlorobenzene, nitrobenzene and diphenyl ether, the decomposition is principally a unimolecular cleavage at the oxygen–oxygen bond, with very little radical-induced reaction. In carboxylic acid solvents there is evidence of acid catalysis accompanied by an inhibitory effect by those acids which have hydrogen atoms on the carbon atom α to the carboxyl group. Quantitative determination has been made of the products of decomposition as well as at the rates at different temperatures.

Study of the decomposition of peresters, $R\text{--}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{--}O\text{--}O\text{--}R'$, has centered about those examples in which R' is t-butyl and R is aromatic or of some other resonance-stabilized nature. The only straight-chain simple aliphatic peresters studied to date have been t-butyl peracetate[2] and performate.[3] Thorough investigation of the decomposition of simple aliphatic peresters would appear to be of fundamental importance to the understanding of the behavior of the more complicated peresters and we have started such an investigation. The t-butyl esters of percapric, permyristic, perlauric and perpalmitic acids have been studied quantitatively in several different solvents, mostly at 110°. As reported below, this first study has uncovered an interesting inhibiting action of certain carboxylic acid solvents.

Experimental

Materials. t-Butyl Hydroperoxide.—Material obtained from the Lucidol Corporation was fractionally distilled under vacuum. The fractions boiling at 42°/(18 mm.) and analyzing 99% or better by iodometric procedure[4] were retained for use.

Chlorobenzene.—Chlorobenzene from the Eastman Kodak Co. was washed six times with sulfuric acid. It was then washed with 10% sodium bicarbonate solution and finally with distilled water until the washings were neutral. After drying over anhydrous calcium chloride and then over phosphorus pentoxide, it was finally fractionally distilled. The fraction used was collected at 130.5–131.0° at 760 mm.

Diphenyl Ether.—Fisher Scientific Co. material was recrystallized twice and then distilled twice under reduced pressure. The fraction used was collected at 93° at 1.25 mm.[5]

Nitrobenzene.—Fisher Scientific Co. material was recrystallized twice. It was then dried over phosphorus pentoxide and finally fractionally distilled. The fraction used was collected at 210.5–211° at 760 mm.

Propionic Acid.—Material obtained from the Fisher Scientific Co. was fractionally distilled over potassium permanganate through a 3-foot Vigreux column. The fraction distilling at 139–141° was collected for refractionation over phosphorus pentoxide. The middle fraction, b.p. 140–140.5° at 760 mm., was then collected for use.

Acetic Acid.—Fisher Scientific Co. material was purified in a manner similar to that for propionic acid. The fraction used distilled at 118–118.5° at 760 mm.

Butyric acid was also Fisher Scientific Co. material and was purified in the way used for propionic acid. The fraction distilling at 164–164.5° at 760 mm. was used.

α-Chloropropionic Acid.—Eastman Kodak Co. material was dried over phosphorus pentoxide and fractionally distilled twice. The final fraction, distilled at 98° at 3 mm., was used.

α-Chloroisobutyric acid was prepared by the City Chemical Corporation of New York. It was dried over anhydrous sodium sulfate and fractionally distilled through a 3-foot glass column packed with glass helices. The first half of the distillate was discarded. The remaining fraction was collected and redistilled, the part distilling at 2.40 mm. being retained for use. The acid was a solid at room temperature, having a melting point of 31°, which is the literature value.[6]

Isobutyric Acid.—Eastman Kodak Co. isobutyric acid was distilled over potassium permanganate and then redistilled over phosphorus pentoxide. The fraction used boiled at 154–154.5° at 760 mm.

Heptafluorobutyric Acid.—Material obtained from the Mathieson, Coleman and Bell Co. was fractionally distilled twice through a 3-foot column packed with glass helices. The part boiling at 120.5–121° at 760 mm. was kept for use.

Pyridine.—Fisher Scientific Co. material was refluxed with and distilled from barium oxide, using a 3-foot column packed with glass helices. The middle fraction, boiling at 115° at 760 mm., was used. It was distilled immediately before use to minimize absorption of water.

Methyl Alcohol.—Reagent grade methanol was obtained from the Mallinckrodt Co. and used without further purification.

Thionyl Chloride.—Eastman Kodak Co. material was used without further purification.

Petroleum Ether.—Fisher Scientific Co. petroleum ether was washed with sulfuric acid until there was no discoloration of the acid. The ether was then washed free of acid with distilled water. After drying with anhydrous calcium chloride, the ether was distilled, the part boiling at 42° at 760 mm. being collected for use.

Capric, lauric, myristic and palmitic acids were obtained from the Eastman Kodak Co. and were first purified by conversion to their methyl esters. Esterification was carried out with excess methanol and with sulfuric acid as catalyst. After removal of acid and methanol, the esters were distilled under vacuum through a 3-foot column packed with glass helices.

In addition to the physical constants listed in Table I, the purity of the methyl esters was determined with a model 154-B Perkin-Elmer vapor fractometer and a column of 20% Dow Corning "550" silicone fluid on Chromosorb, the temperature being maintained at 210°. A single peak was observed in each case, indicating the absence of any homologs.

The acids were then obtained from these methyl esters by standard saponification procedures. They were finally converted into their acyl chlorides by reaction with thionyl chloride in benzene.[8] The solution was refluxed for 8

(1) A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Eastern Utilization Research and Development Division of the Agricultural Research Service. Part of this work was presented at the Chicago Meeting of the American Chemical Society, September, 1961.

(2) P. D. Bartlett and R. R. Hiatt, J. Am. Chem. Soc., 80, 1398 (1958).

(3) R. E. Pincock, ibid., 84, 312 (1962).

(4) L. S. Silbert and D. Swern, Anal. Chem., 30, 385 (1958).

(5) P. A. Giguere, B. G. Morisette and A. W. Olmos, Can. J. Chem. Eng., 33, 657 (1955).

(6) P. J. Loder and E. D. Ries, U. S. Patent 2,043,670.

(7) O. S. Privett, E. Breault, J. B. Covell, L. N. Norcia and W. O. Lundberg, J. Am. Oil Chem. Soc., 35, 366 (1958).

(8) L. MacMaster and F. F. Ahmann, J. Am. Chem. Soc., 50, 145 (1928).

TABLE I

PHYSICAL PROPERTIES OF THE METHYL ESTERS OF THE PARENT ACIDS

	B.p.		n_D^t (t, °C.)	
Ester	°C.	Mm.	Observed	Literature[7]
Methyl caprate	114.0	15	1.4233 (25)	1.4239 (25)
Methyl laurate	140.0	15	1.4300 (25)	1.4303 (25)
Methyl myristate	153–154	10	1.4346 (25)	1.4350 (25)
Methyl palmitate	193–194	12	1.4354 (35)	1.4359 (35)

hours and was then freed of benzene, the acyl chlorides being finally distilled *in vacuo* for use as described below.

Synthesis of the *t*-Butyl Peresters.—All of the peresters used in this work were synthesized by reaction of the acyl chlorides with *t*-butyl hydroperoxide following the method developed by Silbert and Swern.[9] The following description of the preparation of *t*-butyl perpalmitate is representative of these preparations.

Palmitoyl chloride (70 g., 0.255 mole) was stirred into *t*-butyl hydroperoxide (36 g., 9.40 mole) dissolved in petroleum ether (120 ml.) and cooled to 10°. Pyridine (28.5 g., 0.37 mole) was then added dropwise with stirring over a period of 20 minutes while the temperature was maintained below 15°. The reaction mixture was then allowed to stand at room temperature for an additional 40 minutes to ensure complete reaction. The mixture was poured into a separatory funnel containing sufficient 10% aqueous hydrochloric acid to remove all the excess pyridine as the pyridine hydrochloride. The reaction mixture was next washed with 10% sodium bicarbonate solution and then distilled water. After drying over anhydrous sodium sulfate, it was filtered and pumped free of solvent and unreacted hydroperoxide. The perpalmitate was then recrystallized from petroleum ether at 0°.

Table II shows the purity of the peresters, the active-oxygen assays being determined by the modified iodometric procedure of Silbert and Swern.[4]

TABLE II

THE PURITY OF THE *t*-BUTYL PERESTERS

Perester	$n^{20}D$ Observed	$n^{20}D$ Literature[9]	—Oxygen, %— Calcd.	Found
Percaprate	1.4294	1.4293	6.55	6.50
Perlaurate	1.4333	1.4333	5.87	5.81
Permyristate	1.4367	1.4368	5.32	5.30
Perpalmitate	1.4363 (40°)	1.4365 (40°)	4.87	4.85

Rate Measurements.—The perester solution was prepared in a 100-ml. volumetric flask from which 5 or 10 ml. of the solution was pipetted into a 20-ml. glass ampoule, frozen in liquid nitrogen and pumped for 15 minutes at 10^{-3}–10^{-4} mm. The ampoule was then allowed to come to room temperature and degas, the time for degassing varying with the solvent used. This pumping and degassing was repeated twice and then the ampoule was sealed under vacuum. Controls containing solvent alone were also prepared using the same procedure. All the ampoules were then immersed in the constant-temperature bath, the first samples being removed at about 15 minutes to determine the starting concentration for the run. The removal of this sample marked the zero-time for the subsequent samples. Upon removal from the bath, each sample was quenched in Dry Ice–acetone and then allowed to come to room temperature to be opened and analyzed.[4]

The constant-temperature bath was filled with Ucon (polyalkylene glycol containing an oxidation inhibitor) which is stable up to 160°. Each temperature was kept constant within ±0.05°, and the absolute value of the temperature was determined with a platinum resistance thermometer (N.B.S. certificate No, S-153) and a Leeds and Northrup G-2 Mueller Bridge.

Analysis of End Products.—The products of complete decomposition of *t*-butyl percaprate in chlorobenzene and in butyric acid at 110° were determined by gas chromatography, using the model 154-B Perkin–Elmer vapor fractometer. The solutions were decomposed at constant temperature for 24 hours to ensure complete reaction. The analyses were made with 0.2- to 0.5-ml. samples of the solu-

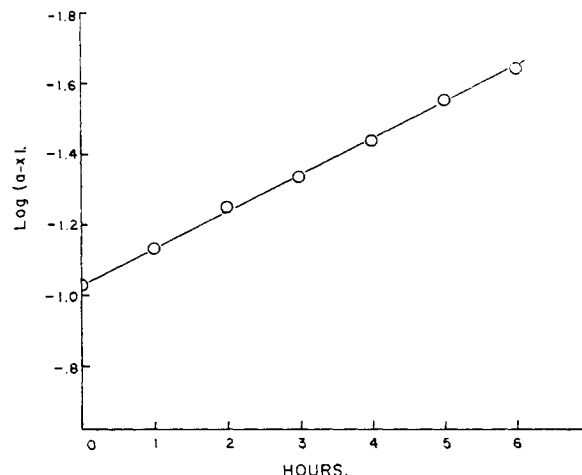(9) L. S. Silbert and D. Swern, *J. Am. Chem. Soc.*, **81**, 2364 (1959).

Fig. 1.—Decomposition of permyristate in diphenyl ether at 110°.

tions. Ampoules with break-off seals and the columns and procedures described by Verderame and McNeill[10] were used.

Especial care was used in the analysis for propane and ethane when it was discovered that only the former of the two was produced. The column used for both of these gases was capable of distinguishing definitely between the two by the difference of their retention times which was checked with mixtures. This column was a 13.7 cm. length of coiled 4 mm. i.d. copper tubing containing 20% by weight dimethyl sulfolane on Johns–Manville Chromosorb and was maintained at 0° in an ice-bath. The retention time for ethane was 9.5 minutes and that of propane was 11.5 minutes. Each was checked by using different tanks of gas and in the analysis of the decomposition products of the peresters duplicate determinations were made with different samples for each run. At a later time a confirmatory test was made by carrying out the decompositions again in both solvents and analyzing for propane and ethane.

Results

Figure 1 shows a typical run, the decomposition of *t*-butyl permyristate in diphenyl ether at 110°, the $(a - x)$ values being in moles per liter. Table III shows the lack of effect of initial perester concentration on the rate in chlorobenzene. The rate constants and their standard errors were always calculated by least-squares treatment of the data. The runs gave excellent linear behavior over their full course.

TABLE III

THE FIRST-ORDER RATE CONSTANT FOR DIFFERENT INITIAL CONCENTRATIONS IN CHLOROBENZENE AT 110°

	Approx. init. concn., M	10^5k, sec.$^{-1}$
Perlaurate	0.02	9.02 ± 0.44
	.10	8.88 ± .38
	.20	9.02 ± .32
Perpalmitate	.02	8.81 ± .13
	.10	8.37 ± .19
	.20	8.56 ± .26

The influence of solvent is shown by the results given in Table IV. In addition, heptafluorobutyric acid was tried as solvent with the percaprate but the rate at 110° was too rapid to measure. Upon analyzing the first sample which was removed fifteen minutes after immersion in the bath,

(10) F. D. Verderame and W. McNeill, *J. Org. Chem.*, **27**, 122 (1962).

TABLE IV

THE DECOMPOSITION OF *t*-BUTYL PERESTERS IN VARIOUS
SOLVENTS AT 0.01 *M* INITIAL CONCENTRATION AT 110°

Perester	Solvent	$10^5 k$, sec.$^{-1}$
Percaprate	α-Chloroisobutyric acid	45.6 ± 2.5
Permyristate		44.7 ± 2.1
Percaprate	Acetic acid	10.09 ± 0.45
Permyristate		10.03 ± .45
Percaprate	α-Chloropropionic acid	8.11 ± .13
Permyristate		7.86 ± .26
Percaprate	Chlorobenzene	8.30 ± .19
Permyristate		8.69 ± .06
Percaprate	Nitrobenzene	6.58 ± .06
Permyristate		6.38 ± .06
Percaprate	Diphenyl ether	6.39 ± .13
Permyristate		6.46 ± .06
Percaprate	Propionic acid	5.41 ± .06
Permyristate		5.48 ± .06
Percaprate	*n*-Butyric acid	5.35 ± .06
Permyristate		5.22 ± .13

it was found that 90% decomposition had already occurred.

Tables V and VI give the results of determination of the effect of temperature in different solvents. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were obtained by least-squares treatment of the data.

TABLE V

THE EFFECT OF TEMPERATURE ON THE DECOMPOSITION IN NITROBENZENE

Perester	Temp., °C.	$10^5 k$, sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal. mole^{-1}	$\Delta S^{\ddagger}$, e.u.
Percaprate	100	1.90 ± 0.00	35.3 ± 0.4	14.0 ± 1.0
	110	6.58 ± .06		
	120	23.13 ± .32		
	130	69.6 ± 2.3		
Permyristate	100	1.83 ± 0.00	35.0 ± 0.1	13.1 ± 0.2
	110	6.38 ± .06		
	120	21.10 ± .32		
	130	66.2 ± 1.3		

TABLE VI

THE EFFECT OF TEMPERATURE ON THE DECOMPOSITION OF
t-BUTYL PERMYRISTATE IN DIFFERENT SOLVENTS

Solvent	Temp., °C.	$10^5 k$, sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal. mole^{-1}	$\Delta S^{\ddagger}$, e.u.
Butyric acid	110	5.22 ± 0.13	34.4 ± 0.8	11.2 ± 2.5
	120	17.95 ± 0.26		
	130	52.0 ± 1.1		
α-Chloropropionic acid	110	7.86 ± 0.26	31.5 ± 0.4	4.3 ± 1.2
	120	23.77 ± 0.32		
	130	64.5 ± 2.3		

Table VII is a summary of the products obtained from the decomposition of *t*-butyl percaprate in two different solvents at 110°. Capric acid was not determined in the case of the decomposition in butyric acid because of its similarity to the solvent.

Discussion

The decomposition of the *t*-butyl esters of the long-chain aliphatic peresters in chlorobenzene, nitrobenzene and diphenyl ether appears to be a simple unimolecular fragmentation of these molecules at the oxygen–oxygen bond, similar to the behavior of the short-chain compounds, *t*-butyl peracetate[2] and *t*-butyl performate[3] in chloroben-

TABLE VII

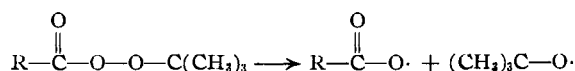PRODUCTS OF DECOMPOSITION OF *t*-BUTYL PERCAPRATE AT
110°

Product	Mole/mole of perester	
	In chlorobenzene	In *n*-butyric acid
Acetone	0.66	1.12
t-Butyl alcohol	.28	0.14
Propane	.58	.48
Methane	.15	.33
Carbon dioxide	.75	.93
Carbon monoxide	Trace	.03
Capric acid	0.31	..
Isobutylene	0.26	0.05

zene. The absence of a large amount of radical-induced reaction in these solvents is indicated by the strict first-order behavior of the reaction throughout practically the entire life of these peresters. This is further confirmed by the studies in chlorobenzene (Table III) which showed that the rate constant is independent of initial concentration.

Additional evidence for the fundamental simplicity of the reaction in these solvents is found in the values of the enthalpy and the entropy of activation compared with those reported for the peracetate and performate. ·In nitrobenzene the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for both the percaprate and permyristate (Table V) are not greatly different from those for the peracetate[2] (38 kcal. mole^{-1} and 17 e.u.) and the performate[3] (38 kcal. mole^{-1} and 15 e.u.) in chlorobenzene. From the correlations made by Bartlett and Hiatt[2] these quantities in the case of our compounds indicate very little lowering of the energy barrier to reaction by resonance developed in the transition state; *i.e.*, "concerted" decomposition is not shown in nitrobenzene.

The dielectric constant of the medium appears to have no important effect in view of the nearly identical rates in nitrobenzene and diphenyl ether (Table IV).

The yields of the products of decomposition in chlorobenzene (Table VII) are also for the great part in accord with a rate-determining homolytic cleavage uncomplicated by competitive reactions involving the parent perester molecules

$$\text{R—}\overset{\displaystyle O}{\overset{\|}{\text{C}}}\text{—O—O—C(CH}_3)_3 \longrightarrow \text{R—}\overset{\displaystyle O}{\overset{\|}{\text{C}}}\text{—O· + (CH}_3)_3\text{C—O·}$$

One would in this case expect the sum of the yields of acetone, *t*-butyl alcohol and isobutylene resulting from the *t*-butoxyl radical to be about 1 mole per mole of perester, which is the result obtained within the probable error of the analyses. Similarly, the carboxylate radical would be expected to produce both carbon dioxide and fatty acid with a combined total of 1 mole per mole of perester which again is the case. Bartlett and Hiatt[2] obtained similar results for *t*-butyl peracetate in chlorobenzene at 140° although, as might be expected from the higher temperature,[11] they found a higher yield of acetone but no *t*-butyl alcohol.

(11) J. H. Raley, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1337 (1948).

It is the behavior in the acid solvents that is most striking. Catalysis by acid as found by Blomquist and Ferris[12] for *t*-butyl perbenzoate in several solvents containing trichloroacetic acid and as suggested by our experiment with heptafluorobutyric acid, is not apparent in most of the acids shown in Table IV. In acetic, α-chloropropionic, propionic and *n*-butyric acids, the rates are not greatly different from those in chlorobenzene, and in the case of the last two are slightly lower. Although α-chloropropionic acid is a much stronger acid than acetic acid, the rate in it is smaller. Examination of the structures of these four acids suggested that their effects may be related to the number and strength of binding of the hydrogen atoms on the carbon atom alpha to the carboxylate group. This further suggested trying an acid with no hydrogen in the α-position, which explains the choice of α-chloroisobutyric acid.

The great effect of the absence of hydrogen atoms on the α-carbon atom is shown by the more than fivefold increase in rate in α-chloroisobutyric acid above that in α-chloropropionic acid. When a mixture of 10 mole-per cent. of isobutyric acid and 90 mole-per cent. of α-chloroisobutyric acid was used as solvent with *t*-butyl permyristate at 110°, the 10^5k value was 29.5 sec.$^{-1}$, showing the inhibitory effect of the presence of the isobutyric acid.

These results show that the acid catalysis expected of a carboxylic acid is diminished greatly if the acid has one or more hydrogen atoms on its α-carbon atom. This stabilizing or inhibitory effect shows a dependence also upon the other atoms attached to the α-carbon atom and in the

case of propionic and butyric acids is great enough to render the net rate of decomposition of the perester lower than in pure chlorobenzene.

Other evidence of combined inhibitory action and acid catalysis by carboxylic acids is found in the observations of Blomquist and Ferris[12] with *t*-butyl perbenzoate. They found that the rate in acetic acid was higher than in aromatic solvents such as chlorobenzene at the same temperature but that while addition of trichloroacetic acid to the ester in *p*-chlorotoluene had a marked catalytic effect, addition of dichloroacetic acid had practically no effect. An effect of the presence and the nature of the hydrogen atoms on the α-carbon of the acid is thus apparent in their work also.

The exact nature of the action of carboxylic acids must be determined by extensive further research and we do not wish to speculate upon it at present. No good clue to that nature is provided by the analysis of the products produced in *n*-butyric acid (Table VII) since that analysis is not sufficiently different from the one obtained for the decomposition in chlorobenzene. On the other hand, the effects of the acids on the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values (Table VI) do not fit well with the correlations found for peresters undergoing simple or "concerted" cleavage free of radical-induced reaction.[2]

(12) A. T. Blomquist and A. F. Ferris, *J. Am. Chem. Soc.*, **73**, 3412 (1951).

Cyclopropanes. XIII. The Absolute Configuration of 1-Methyl-2,2-diphenylcyclopropane[1]

BY H. M. WALBORSKY AND C. G. PITT

The absolute configuration of 1-methyl-2,2-diphenylcyclopropane has been determined by a direct chemical correlation with (+)-R-propylene oxide and with (−)-S-2-methyl-3,3-diphenylpropionic acid. The absolute configuration of the latter was established from the optical rotatory dispersion curves of the corresponding methyl ketone, aldehyde and morpholinothiocarbamide derivatives. The above findings are compared with a previous tentative assignment of absolute configuration to 2,2-diphenylcyclopropanecarboxylic acid, which had been based on the results of partial asymmetric syntheses. The results of the chemical correlation and the asymmetric syntheses are shown to be compatible if one assumes that a "diazo-exchange" reaction has occurred in the addition of diazodiphenylmethane to the menthyl acrylate and methacrylate.

Introduction

Prelog,[2] Cram,[3] and their co-workers have studied the course of asymmetric syntheses in a variety of systems and have found that the configuration of the newly created asymmetric center is dependent on the conformation of the original asymmetric

moiety. The concepts derived from this work have been applied, with much success, to the correlation of configuration. This has been notably true for the atrolactic acid system of Prelog.[2,4] However, certain anomalous results have recently been reported. For example, Collins and co-workers[5]

(1) This study was supported by the U. S. Army Research Office (Durham) and by the National Science Foundation.

(2) V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953).

(3) D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, **74**, 5828 (1952)

(4) For a review of this work, see J. A. Mills and W. Klyne, Ch. 5, in "Progress in Stereochemistry," Vol. I, Academic Press, Inc., New York, N. Y., pp. 198–201; E. Eliel, "Stereochemistry of Carbon Compounds," McGraw–Hill Book Co., Inc., New York, N. Y., 1962.

(5) J. H. Stocker, P. Sidisunthorn, B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **82**, 3913 (1960).