cyclodecane) was prepared in a similar manner and used without further separation.

Equilibrations.—Glacial acetic acid containing 0.25 g. of *p*-toluenesulfonic acid monohydrate per 100 ml. was transferred into a 10-ml. volumetric flask. The solution was boiled until the vapors just reached the top of the flask which was then capped as quickly as possible with a rubber serum cap. The cap was punctured with a hypodermic needle attached to a nitrogen-filled balloon and the flask was placed in a constant temperature bath at 25° for one hour before adding the olefin (one-tenth the volume of the acetic acid solution). Samples (0.5 ml.) were withdrawn at appropriate intervals with a hypodermic syringe and added to 5 ml. of 25% aqueous potassium carbonate solution. Pentane (0.5 ml.) was added, the flask was agitated and the solution diluted to approximately 10 ml. with water. The pentane layer was analyzed by gas chromatography.

Gas Chromatography.—Gas chromatographic analyses were carried out using 180 × 0.8-cm. Pyrex tubes packed with 48–100 mesh C-22 firebrick (Johns–Manville) which was coated with the appropriate stationary phase. The samples were eluted with helium at 15 p.s.i., and thermal conductivity cells were used as detectors. The stationary phases employed were: (A) 35% (by weight) of a saturated solution (at room temperature) of silver nitrate in diethylene glycol; (B) 30% (by weight) of a 52% solution of silver nitrate in tetraethylene glycol; (C) 30% (by weight) of Silicone oil (Dow–Corning 550) on base-washed firebrick; (D) 30% (by weight) of 4-methyl-4-nitropimelonitrile.[17] Column A was used (column temperature in brackets) to analyze mixtures of methylenecyclopentane and 1-methylcyclopentene (33°). Mixtures of the endocyclic and exocyclic isomers of the six-, seven- and eight-membered cyclic olefins were analyzed using stationary phase B (50–70°); this was also used to separate methylenecyclononane from *cis*-1-methylcyclononene (90°) and to analyze mixtures of methylenecyclodecane and *cis*- and *trans*-1-methylcyclodecene (90°). Stationary phase D was used to separate *cis*-1-methylcyclononene from the *trans* isomer (90°). Mixtures of the 1-methylcycloalkanols, their acetates and of the corresponding olefins (without separation of the isomers) were analyzed using stationary phase C (110–190°). The compositions of the mixtures were computed from the chromatograms by determining the ratios of the individual peak areas.[18]

Isolation and Identification of Products.—The methylenecycloalkanes present in small amounts in the equilibrium mixtures of the five- to eight-membered cyclic olefins were identified by their retention times on gas chromatography. The 1-methylcycloalkenes, 1-methylcycloalkanols and 1-methylcycloalkyl acetates which were the major products of the equilibrations were isolated by gas chromatography and identified by their infrared spectra.

A small amount (0.5%) of an unidentified olefin was formed in the equilibration of methylenecyclooötane; it was not detected in the products from the isomerization of 1-methylcyclooötene. This unknown compound could not have been *trans*-1-methylcyclooötene (which is as yet unknown), since it was found to be stable to acid and to have a retention time in gas chromatography on a silver nitrate column comparable to that of *cis*-1-methylcyclooötene. Judging from the properties of its next higher homolog, *trans*-1-methylcyclooötene would be expected to be extremely sensitive to acid and to be retained on a silver nitrate column much longer than the *cis* isomer.

Authentic samples of 1-methylcyclopentanol,[19] 1-methylcyclohexanol[20] and 1-methylcycloheptanol[21] were prepared from the corresponding ketones and methylmagnesium iodide. The acetates were prepared from the alcohols by the method of Nevitt and Hammond.[22]

1-Methylcyclopentyl acetate was obtained analytically pure in 65% yield, b.p. 66–67° (30 mm.), n^{25}D 1.4291.

1-Methylcyclohexylacetate, obtained in 56% yield, had b.p. 75–76° (17 mm.), n^{25}D 1.4403–1.4414.

1-Methylcycloheptyl acetate, obtained in 83% yield, had b.p. 74–74.5° (8 mm.), n^{25}D 1.4501.

Stability of 1-Methylcycloalkyl Acetates to Hydrolysis.—A sample of 0.1 ml. of 1-methylcyclohexyl acetate was dissolved in 1 ml. of a 0.25% solution of *p*-toluenesulfonic acid monohydrate in glacial acetic acid, and the acetate was immediately re-isolated and analyzed using the methods described above for the equilibrium mixtures. 1-Methylcyclohexanol was found to be completely absent. The same result was obtained with 1-methylcycloheptyl acetate.

---

[17] H. A. Bruson, U. S. Patent 2,361,251; *C. A.*, **39**, 2079 (1945).

[18] E. Cremer and R. Müller, *Z. Elektrochem.*, **55**, 217 (1951); M. Dimbat, P. E. Porter and F. H. Stross, *Anal. Chem.*, **28**, 290 (1956).

[19] N. Zelinski and S. Namjetkin, *Ber.*, **35**, 2683 (1902).

[20] N. Zelinski, *ibid.*, **34**, 2877 (1901).

[21] O. Wallach, *Ann.*, **345**, 139 (1906).

[22] T. D. Nevitt and G. S. Hammond, THIS JOURNAL, **76**, 4124 (1954).

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Peresters. III.[1] *t*-Butyl Phenylperacetate, Trichloroperacetate and Trimethylperacetate

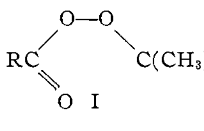
BY PAUL D. BARTLETT AND DONALD M. SIMONS[2]

RECEIVED AUGUST 18, 1959

The decomposition of *t*-butyl trimethylperacetate, *t*-butyl trichloroperacetate and *t*-butyl phenylperacetate has been studied in the temperature range 58–88°. Kinetic studies of all three peresters indicate a first-order concerted cleavage to yield carbon dioxide, *t*-butoxy and *t*-butyl, trichloromethyl or benzyl radicals. There is also a prominent acid-catalyzed ionic decomposition of *t*-butyl trichloroperacetate which can be suppressed by pyridine. Activation parameters are summarized in Table VI. The ΔH^* values suggest near equality for the stabilization energies of *t*-butyl and trichloromethyl radicals, each being about 80% as stable as benzyl. Bond-energy methods[11] lead to values of 12, 12 and 24.5 kcal. for the stabilization energies of these same radicals.

Introduction

Evidence has been presented[1a,3] that a series of peresters of general composition I decompose thermally with concerted rupture of an O–O bond and a C–C bond to produce carbon dioxide and the free radicals $(CH_3)_3CO\cdot$ and $R\cdot$ whenever $R\cdot$ is so constituted as to have a degree of stabilization considerably exceeding that of the methyl or phenyl radical. The three esters described in this paper were the first representatives of this series prepared in



I

---

[1] (a) Part I, P. D. Bartlett and R. R. Hiatt, THIS JOURNAL, **80**, 1398 (1958); (b) part II, P. D. Bartlett and B. T. Storey, *ibid.*, **80**, 4954 (1958).

[2] National Science Foundation Post-doctoral Fellow, 1952–1953.

[3] P. D. Bartlett, *Experientia Suppl.*, **VII**, 275 (1957).

this Laboratory; they provided orientation as to the structural requirements for concerted decomposition to take place.

Experimental

***t*-Butyl Hydroperoxide.**—The product from the Lucidol Co. was distilled twice through a two-foot vacuum jacketed column packed with glass helices. The material used boiled at 41–42° under 25 mm. pressure.

Pyridine was heated under reflux for 16 hours with barium oxide, then distilled through a 14-inch helix-packed column at atmospheric pressure. The material used boiled at 114.2–115.5°.

Chlorobenzene.—Technical chlorobenzene from the Eastman Kodak Co. was purified by shaking four times with concentrated sulfuric acid over a period of two weeks. It was then washed with water and dried over calcium chloride and phosphorus pentoxide. The distilled material used boiled at 131° under 780 mm.

Phenylacetyl chloride from Eastman Kodak Co. was redistilled, the fraction boiling at 58° (1 mm. pressure) being collected.

Trichloroacetyl chloride was prepared by the procedure of Shirley.[4]

Pivaloyl chloride was prepared by treating pivalic acid with excess thionyl chloride and allowing the mixture to stand until evolution of gas ceased. The solution was heated under reflux for an hour and fractionally distilled through a column. The fraction boiling at 105–106° was collected.

Preparation of Peresters.—The general method of preparation of peresters has been described previously.[1a] *t*-Butyl phenylperacetate and *t*-butyl trimethylperacetate could also be prepared by simultaneously adding the corresponding acid chloride and a 33% solution of potassium hydroxide to a well stirred solution of *t*-butyl hydroperoxide and water at 0°. Purity of the products was judged by their infrared spectra, iodometric analysis and kinetic behavior. *t*-Butyl phenylperacetate is an oil at room temperature but solid at zero, while *t*-butyl trichloroperacetate and *t*-butyl perpivalate are oils solidifying at Dry Ice temperatures. The products were always stored in the refrigerator.

Method of Analysis.—In general, iodometric analysis was no more satisfactory for these peresters than for others of the series. The method used for 9-decalylperbenzoate[5] was entirely unsatisfactory. The method of Blomquist and Ferris[6] gave considerably better results, but even esters appearing to be pure by infrared analysis showed only 70 to 80% purity by iodometric titration. We have suspected that peresters with any tendency to rearrange by an ionic mechanism may be induced to do so in part in the presence of iodine.

Product Studies.—Partial product recoveries were made in the decompositions of *t*-butyl perpivalate and trichloroperacetate, using methods which were the forerunners of those described by Bartlett and Hiatt.[1a] In ease case the liquid perester was weighed into a closed system, dissolved in chlorobenzene, and the gaseous products of decomposition were swept in a stream of nitrogen through a Dry Ice trap and three Ascarite tubes. The solvent and products were subjected to vacuum fractionation and the fractions identified by infrared, derivatives (*e.g.*, acetone 2,4-dinitrophenylhydrazone) and physical properties (*e.g.*, m.p. of *t*-butyl alcohol). The yields of products are reported in the tables on two bases, depending upon whether the starting ester is regarded as pure or as having the degree of purity shown by iodometric assay, using the method of Blomquist and Ferris.[6] The sample of *t*-butyl phenylperacetate used was 80.0% pure, that of *t*-butyl trimethylperacetate was 82.8% pure, by this method. Since this procedure may have sometimes involved the introduction of as much as 20% of unknown material, these product studies are of very limited accuracy compared to those carried out later on related peresters.

Results

Tables I and II summarize the products accounted for. The experiment using Hammond's reagent[7] in Table II was intended to test whether the capture of rapidly decarboxylating benzoate radicals from benzoyl peroxide could be matched in *t*-butyl phenylperacetate. The isolation of 47% of benzoyl iodide and only 5% of phenylacetic acid is consistent with the view that the homolytic decomposition is entirely concerted; however, the experiment is a rough one at best. The product was mostly tar, and it has not yet been shown that iodine is as good an interceptor for aliphatic as for aromatic carboxylate radicals.

TABLE I

PRODUCTS OF DECOMPOSITION OF *t*-BUTYL TRIMETHYLPERACETATE IN CHLOROBENZENE AT 70–80°

	Mole/mole perester	
Product	Based on weight	Based on assay
Carbon dioxide	0.90	1.09
Acetone	.26	0.31
t-Butyl alcohol	.62	.75
Isobutylene and isobutane	.29	.35
Polyisobutylene	.46	.56

TABLE II

PRODUCTS OF DECOMPOSITION OF *t*-BUTYL PHENYLPERACETATE

	Mole/mole perester			
	In chlorobenzene, 90–95°		In CCl_4–H_2O + I_2, 77°	
Product	By weight	By assay	By weight	By assay
Carbon dioxide	0.80	1.00	0.62	0.77
Acetone	.36	0.45		
t-Butyl alcohol	.40	.50		
Stilbene	.10	.12		
Dibenzyl	.11	.14		
Benzyl iodide			.38	.47
Phenylacetic acid	0	0	.04	.05

Rate Measurements.—A number of kinetic experiments with *t*-butyl phenylperacetate and trimethylperacetate yielded first-order plots that were concave upward; many others gave straight lines over three half-lives. Under such conditions the constancy of a rate constant can be a criterion of purity, and only those samples were retained for consideration which met this test.

Table III lists some kinetic runs on *t*-butyl trimethylperacetate decomposition in chlorobenzene at three temperatures. The insensitivity of the rate constant to a tenfold change of perester concentration (runs 14 and 15) suggests that induced decomposition is not a complication here. However, the presence of the inhibitor sulfur does lower the rate constant by about 17% (run 16 *vs.* runs 12–14); this is a somewhat more reliable criterion for the presence of induced decomposition than is reaction order alone.[8,9]

In the presence of 0.1 *M* trichloroacetic acid (run 17), the rate of decomposition is increased by 12%. From previous experience with peroxide decomposition,[10] this is taken to indicate a susceptibility of this perester to acid-catalyzed decomposition, probably ionic, which would equal the free-radical decomposition in rate at a trichloroacetic acid concentration of 0.85 *M*.

---

[4] D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 286.

[5] P. D. Bartlett and J. L. Kice, THIS JOURNAL, **75**, 5591 (1953).

[6] A. T. Blomquist and A. F. Ferris, *ibid.*, **73**, 3403 (1951).

[7] G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950).

[8] K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).

[9] P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

[10] P. D. Bartlett and J. E. Leffler, *ibid.*, **72**, 3030 (1950).

TABLE III

FIRST-ORDER DECOMPOSITIONS OF *t*-BUTYL TRIMETHYLPERACETATE IN CHLOROBENZENE

Run	[Perester], *M*	Added substance, *M*	*k*, sec.$^{-1}$ × 10^5
		T = 58.6°	
18	0.1	None	3.35
		T = 64.3°	
19	0.1	None	7.37
20	.1	None	6.83
21	.1	None	6.83
		T = 74.8°	
12	0.1	None	28.5
13	.1	None	27.4
14	.2	None	27.7
15	.02	None	25.8
16	.1	S_8, 0.0188	23.1
17	.1	Cl_3CCOOH, 0.1	31.2

Table IV lists the results with *t*-butyl trichloroperacetate. Unlike the other two, this perester decomposed autocatalytically in chlorobenzene, and nearly all of the linear plots were obtained by adding pyridine to the solution. While this eliminated acid-catalyzed decomposition, it apparently introduced a catalysis of its own, as seen by comparing runs 37–38, 43 and 39–40. Carbon dioxide was evolved quantitatively (based on peroxide titer of the perester), but no recognizable compounds were obtained in the product study. For kinetic purposes 0.1 *M* pyridine in chlorobenzene was adopted as a standard medium. The existence of an occasional run, such as 37, in which the decomposition was not autocatalytic, is consistent with the expectation that the autocatalysis should be due to the presence of acid and should produce more acid, whereas a decomposition which begins quite free of acid produces only carbon dioxide and never produces any acid to get the ionic decomposition started.

TABLE IV

FIRST-ORDER DECOMPOSITIONS OF *t*-BUTYL TRICHLOROPERACETATE IN CHLOROBENZENE

Run	[Perester], *M*	Added substance, *M*	*k*, sec.$^{-1}$ × 10^5
		T = 66.8°	
24	0.09	Pyridine 0.1	2.61
27	.1	Pyridine .1	2.75
29	.1	Pyridine .1	2.74
25	.1	Pyridine .2	3.16
28	.1	Pyridine .2 Acetanilide .1	4.71
30	.1	Pyridine .2 Styrene .1	2.71
		T = 77.0°	
39	0.1	Pyridine 0.1	9.9
40	.12	Pyridine .1	10.9
42	.1	Pyridine .1	10.0
32	.1	None[a]	19.0
37	.1	None	6.68
38	.1	Acetanilide 0.1	7.06
43	.01	Pyridine .01	7.58

[a] The solution was acid to congo red after 2 hours.

The few first-order kinetic runs with *t*-butyl phenylperacetate are listed in Table V. Neither radical-induced nor acid-catalyzed decomposition is evident here, and the non-linear runs are apparently due to difficulties with purity.

TABLE V

FIRST-ORDER DECOMPOSITIONS OF *t*-BUTYL PHENYLPERACETATE IN CHLOROBENZENE

Run	Perester, *M*	Added substance, *M*	*k*, sec.$^{-1}$ × 10^5
		T = 77.0°	
37	0.1	None	6.67
38	.1	Acetanilide, 0.1	7.06
41	.1	None	7.02
		T = 88.6°	
44	0.1	Styrene, 0.2	24.5

Table VI lists the enthalpy and entropy of activation as estimated for decomposition of these three peresters. In each case all determined rate constants from first-order decompositions at 0.1 *M* concentration of perester at a given temperature in chlorobenzene were averaged, and such values for two temperatures 10° apart introduced into the Eyring equation.

TABLE VI

ACTIVATION PARAMETERS OF PERESTERS

Compound	ΔH^*	ΔS^*
t-Butyl trimethylperacetate	30.0	11.1
t-Butyl trichloroperacetate + 0.1 *M* pyridine	30.3	9.4
t-Butyl phenylperacetate	28.1	2.2

Discussion

These three peresters were the first investigated in our current study of the concerted elimination of carbon dioxide from such structures. It has been shown[1a,3] that the kinetic properties of the trimethyl- and phenylperacetates fall fairly smoothly in line with those of compounds differing from them by systematic structural changes. The trichloroperacetate, which needs further study, is of special interest in two connections.

The high yield of carbon dioxide from both the trimethylperacetate and the trichloroperacetate, and the similarity of their rate constants and activation parameters, indicate that both the *t*-butyl and trichloromethyl radicals are stabilized in comparison to the methyl or phenyl radical. This is in agreement with the assignment[11] of a "resonance energy" of 12 kcal. to each of these radicals relative to methyl, on the basis of thermochemical data. As far as the concerted decomposition into free radicals is concerned, the process evidently can proceed well with formation of a strong electron acceptor or a strong electron donor radical. In the former case, however, the competition is greater from an ionic mechanism of decomposition.

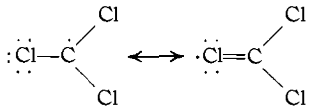
The resonance energies of *t*-butyl, trichloromethyl and benzyl radicals[11] are 12, 12 and 24.5 kcal., respectively. Neither the rate constants nor the enthalpies of activation for decomposition of the peracetates reflects this greatly increased stabilization of the benzyl radical, although ΔH^* for the decomposition of the phenylperacetate is 10 kcal. below

---

[11] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 50.

that of peracetate and 2 kcal. below trimethyl- and trichloroperacetate. The unfavorable entropy of activation in phenylperacetate is reasonable on grounds already discussed[12]; there are conformations of the reacting ester which are unfavorable for producing the stabilized benzyl radical itself, but this is not true of the cleavage of the trimethyl- or trichloroperacetate. It remains to be explained why so much less of the stabilization energy of benzyl than of *t*-butyl or trichloromethyl appears to be available at the transition state.

The contrast in behavior between trichloro- and trifluoroperacetate has been commented upon previously.[1a] The failure of $CF_3\cdot$ to be formed under conditions where $CCl_3\cdot$ is favored emphasizes that the stabilization of the latter radical must depend upon interactions peculiar to elements beyond the first row of the periodic table.



The type of interaction shown puts nine electrons in the valence shell of chlorine, which would not be possible for a fluorine atom.

Acknowledgment.—We thank the National Science Foundation for a fellowship to one of us, and for support of this work.

CAMBRIDGE 38, MASS.

---

[12] Reference 2, p. 1402; ref. 3, pp. 286–288.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Peresters. IV. Substituent Effects upon the Concerted Decomposition of *t*-Butyl Phenylperacetates[1]

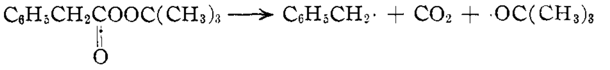
BY PAUL D. BARTLETT AND CHRISTOPH RÜCHARDT[1c]

RECEIVED AUGUST 18, 1959

The thermal decomposition of *t*-butyl phenylperacetate yields benzyl and *t*-butoxy radicals as primary products. The decomposition rates of this ester and its *p*- and *m*-methoxy, *p*-methyl, *p*- and *m*-chloro, and *p*-nitro derivatives have been measured at a series of temperatures by infrared spectrophotometry and at 56° by the use of iodine in toluene as scavenger. The reaction is entirely homolytic in character and the rate constants fit the Hammett equation with the use of σ^+ rather than σ, the observed value of ρ varying from -1.04 at 100° to -1.20 at 56°. The "efficiency" of radical production by the *p*-methoxy ester measured by iodine in toluene varies from 44 to 72% with changes in iodine concentration and in temperature.

Introduction

It has been observed[1b] that the benzyl radical possesses sufficient stability to cause the decomposition of *t*-butyl phenylperacetate to take place with concerted rupture of an O–O and a C–C bond producing carbon dioxide and the benzyl and *t*-butoxy radicals.



$$C_6H_5CH_2\underset{\underset{O}{\|}}{C}OOC(CH_3)_3 \longrightarrow C_6H_5CH_2\cdot + CO_2 + \cdot OC(CH_3)_3$$

From the general behavior of a number of diverse peresters, it has been suggested[2] that the rate and activation enthalpy of the concerted decomposition is determined essentially by the stabilization energy of the carbon radical generated. In some previous instances[3–5] the cleavage of substituted benzoyl peroxides and *t*-butyl perbenzoates into free radicals has been found to obey the Hammett equation, responding to electron withdrawing and releasing character of the substituent groups in the opposite manner to the ionization constants of the benzoic acids (*i.e.*, with ρ being negative). The explanation which has been offered for this behavior[3] is an electrostatic one based upon the strengthening or weaking of the O–O bond in the perester itself by a systematic variation in the residual charge upon one or both of the oxygens. Such a mechanism, if it operated in the *t*-butyl phenylperacetates, should operate more weakly because of the greater remoteness of the substituent from the O–O bond. On the other hand, if the effect of substituents were exclusively on the resonance energy of the benzyl radical, the Hammett equation might not be followed at all. To investigate this point, we have determined the rates of decomposition of the unsubstituted and six *p*- or *m*- substituted *t*-butyl phenylperacetates.

Results and Discussion

The Rates.—The kinetic results are shown in Table I. The first-order rate constant of *t*-butyl *p*-methoxyphenylperacetate varies by 28% over a tenfold range of concentration, suggesting some induced decomposition at a concentration of 0.5 *M*. For comparisons of the substituted peresters, concentrations in chlorobenzene were used of the order of 0.05 *M* and temperatures, depending upon the perester, from 56 to 100°. There is a clear rate-enhancing effect of the methyl and methoxy groups and a rate-depressing effect of the chloro and nitro substituents. As in the recently reported case of *t*-butyl N-phenylperoxycarbamates,[5] the logarithm of the rate constant is a better linear function of σ^{+6} than of σ (see Fig. 1).

Significance of the Hammett Relation.—The only huge difference between the σ and σ^+ scales

---

[1] (a) Presented at the 16th National Organic Symposium, Seattle, Wash., June 17, 1959; (b) part III, P. D. Bartlett and D. M. Simons, THIS JOURNAL, **82**, 1753 (1960); (c) Chemical Institute, University of Munich.

[2] P. D. Bartlett and R. R. Hiatt, THIS JOURNAL, **80**, 1398 (1958).

[3] C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

[4] A. T. Blomquist and I. A. Berstein, *ibid.*, **73**, 5546 (1951).

[5] Compare also E. L. O'Brien, F. M. Beringer and R. B. Mesrobian, *ibid.*, **81**, 1506 (1959).

[6] H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).