Peroxy Esters of Dimethylmalonic Acid. α-Lactone Intermediates in Free-Radical Reactions

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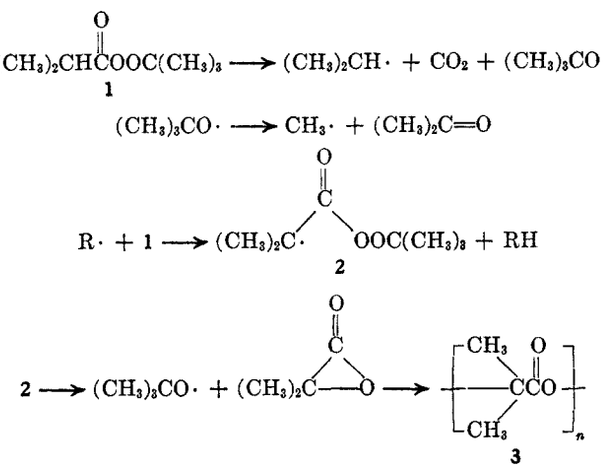
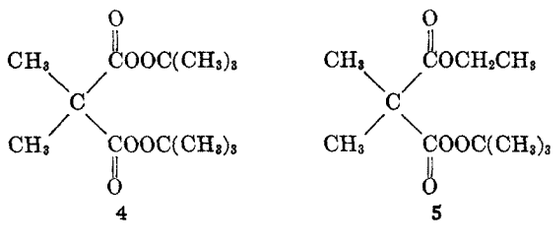
Di-*t*-butylperoxy dimethylmalonate (**4**) and *t*-butylperoxy α-carbethoxyisobutyrate (**5**) have been synthesized. The activation parameters for the decomposition of **4** in cumene are $\Delta H^* = 29.3$ kcal/mole and $\Delta S^* = 5.2$ cal/deg and for **5** are $\Delta H^* = 29.8$ kcal/mole and $\Delta S^* = 6.1$ cal/deg. The major product of the decomposition of **4** in cumene is the polyester of α-hydroxyisobutyric acid. The formation of this product in terms of the intermediacy of an α-lactone is discussed.

In 1958, Milas and Golubović[1] reported the formation of a polyester of α-hydroxyisobutyric acid from the decomposition of *t*-butylperoxy isobutyrate (**1**) in the absence of solvent. Based on their studies of the decomposition of di-*t*-butylperoxy diphenylmalonate in cumene, Bartlett and Gortler[2] proposed a mechanism to account for Milas' results. This mechanism applies



R· = $(CH_3)_2CH$·, $(CH_3)_3CO$·, or CH_3·

only to the decomposition of the isobutyrate in the absence of solvent. Bartlett and Gortler demonstrated that decomposition of **1** in either cumene or chlorobenzene proceeded "normally" and very little polyester was produced. If radical **2** could be generated in solution and polyester **3** obtained as the major product, the above mechanism would be further substantiated. To this end the authors have synthesized and studied the decomposition of di-*t*-butylperoxy dimethylmalonate (**4**) and *t*-butylperoxy α-carbethoxyisobutyrate (**5**).



Results and Discussion

Di-*t*-butylperoxy dimethylmalonate was synthesized by the addition of a solution of dimethylmalonyl chloride in pentane to a solution of *t*-butyl hydroperoxide and pyridine in pentane at 0°. The peroxy ester was obtained as a colorless oil in yields of 45–50%. The rates of decomposition in cumene at various temperatures were determined by following the disappearance of the peroxy ester carbonyl peak at 5.62 μ. The results of these kinetic studies are tabulated in Table I.

TABLE I

RATE CONSTANTS FOR THE DECOMPOSITION OF DI-*t*-BUTYLPEROXY DIMETHYLMALONATE IN CUMENE[a]

Temp, °C	Concn, mole/l.	$k \times 10^5$ sec^{-1}	Half-life, min
79.5	0.0442	6.95	166.2
79.5	0.442	7.32	157.9
89.5	0.0442	23.0	50.2
89.5	0.442	23.4	49.4
100.3	0.0420	74.9	15.4
100.3	0.420	78.6	14.7

[a] $\Delta H^* = 29.3$ kcal/mole. $\Delta S^* = 5.2$ cal/deg.

The products from the decomposition of **4** in cumene are listed in Table II. The polyester is that of α-hydroxyisobutyric acid. The infrared spectrum of this polymer was identical with the spectrum of polyester obtained from the decomposition of *t*-butylperoxy isobutyrate in the absence of solvent as described by Milas.[1]

TABLE II

PRODUCTS OF THE DECOMPOSITION OF DI-*t*-BUTYLPEROXY DIMETHYLMALONATE IN CUMENE AT 100°[a]

Product	Mg	Mmoles	Moles/mole of peroxy ester
Carbon dioxide	184[b]	3.84	1.02
	195[c]	3.97	1.05
t-Butyl alcohol	455	6.06	1.61
Acetone	195	0.70	0.16
Dicumyl	461	1.98	0.53
Polyester	350	4.07[d]	1.07

[a] Peroxy ester (1.0435 g, 3.77 mmoles) in 10 ml of cumene. [b] Absorbed on Indicarb. [c] By volume. [d] Based on molecular weight of monomer unit, 86.

The quantitative yield of polyester provides further proof for the Bartlett α-lactone mechanism. Peroxy ester **4** undergoes an initial two-bond cleavage yielding a molecule of carbon dioxide, a *t*-butoxy radical and the *t*-butylperoxy isobutyryl radical (**2**). Radical **2**, although now in solution, has the same fate as it did in the absence of solvent, *i.e.*, expulsion of a *t*-butoxy radical and formation of an α-lactone which then polymerizes.

There remained the question of the effect of the second peroxide grouping on the initial bond cleavage. Was the initial two-bond cleavage independent of the

(1) N. A. Milas and A. Golubović, *J. Am. Chem. Soc.*, **80**, 5994 (1958).
(2) P. D. Bartlett and L. B. Gortler, *ibid.*, **85**, 1864 (1963).

second peroxide group or was the mechanism somehow concerted (two-bond cleavage and α-lactone formation in one step) with the rate of decomposition dependent on the presence of two peroxide groups? We attempted to answer this question by comparing the rates and activation parameters of the decomposition of *t*-butylperoxy α-carbethoxyisobutyrate (**5**) in cumene with those of **4**.

Preparation of *t*-butylperoxy α-carbethoxyisobutyrate was accomplished by the dropwise addition of a solution of α-carbethoxyisobutyryl chloride in petroleum ether (bp 30–60°) to a suspension of potassium *t*-butylperoxide. The peroxy ester was obtained in approximately 20% yield after purification by chromatography. The rate constants for the decomposition in cumene are reported in Table III. These rate constants were determined from the rates of disappearance of the peroxy ester carbonyl band at 5.62 μ.

TABLE III

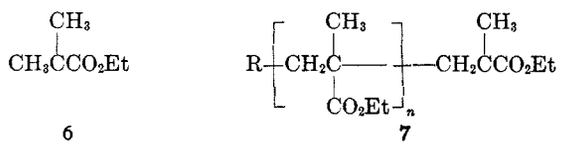
RATE CONSTANTS FOR THE DECOMPOSITION OF *t*-BUTYLPEROXY α-CARBETHOXYISOBUTYRATE IN CUMENE[a]

Temp, °C	Concn, mole/l.	$k \times 10^5$ sec^{-1}	Half-life, min
79.5	0.143	5.40	214
79.5	1.430	5.45	212
89.5	0.143	17.85	64.7
89.5	1.430	18.35	63.0
100.3	0.143	60.38	19.2
100.3	1.430	58.73	19.7

[a] $\Delta H^* = 29.8$ kcal/mole. $\Delta S^* = 6.1$ cal/deg.

The rates of decomposition of **5** were of the same order of magnitude as those of **4** (no more than 35% difference at any of the temperatures) and the activation parameters were quite similar. This result would indicate that the initial two-bond cleavage was independent of the presence of the second peroxide grouping and that formation of α-lactone occurs in a second fast step.

The fate of the ethyl isobutyryl radical generated from the decomposition of *t*-butylperoxy α-carbethoxyisobutyrate is of considerable interest. This radical (**6**) is a simple structural analog of the terminal radical **7** in the polymerization of ethyl methacrylate. The fate



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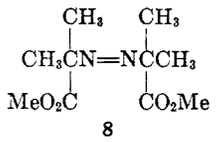

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of this radical should give us information concerning the termination step in the polymerization of ethyl methacrylate. A similar experiment has been reported by Bickel and Waters,[3] who made a study of the thermal decomposition products of dimethyl 2,2′-azobisisobutyrate (**8**). In this case, however, two methyl isobutyryl radicals are produced quite close to one another, a situation not realistic with respect to the terminal radicals in the polymerization of ethyl methacrylate. Our work on this problem continues and our results will be published in another communication.

(3) A. F. Bickel and W. A. Waters, *Rec. Trav. Chim.*, **69**, 312 (1950).

Experimental Section[4]

Materials. *t*-Butyl Hydroperoxide.—Most of the water present in *t*-butyl hydroperoxide obtained from the Lucidol Corp. was removed by refluxing the hydroperoxide in an azeotrope separation apparatus at 20 mm. After this preliminary drying the hydroperoxide was distilled through a 25-cm Vigreux column keeping the pot temperature below 45°. The fraction distilling at 33.5° (16 mm) was used for synthesis of the peroxy esters.

Pyridine.—The pyridine was refluxed overnight over barium oxide and then distilled from the oxide through a 25-cm Vigreux column. The fraction boiling at 114–115° was stored over potassium hydroxide pellets until used.

Pentane.—Technical grade pentane was shaken with concentrated sulfuric acid until the pentane gave no reaction with acidified potassium permanganate. The pentane was washed several times with water and dried over anhydrous calcium chloride. The fraction boiling at 45–55° was collected for use. No residue was obtained when the pentane was evaporated under aspirator pressure.

Cumene.—Eastman Kodak Co. White Label cumene was shaken with portions of concentrated sulfuric acid until the acid layer became only light yellow on prolonged shaking. The cumene was then washed with water, 10% sodium carbonate, and again with water. It was dried with calcium chloride and distilled from sodium through a 25-cm Vigreux column. The fraction boiling at 152–153° was collected for use and stored under nitrogen. The cumene was periodically run over a column of alumina to remove hydroperoxide.

Synthesis of Peroxy Esters.—Diethyl dimethylmalonate was prepared by the methylation of diethyl malonate according to the method of Thorne.[5] The dimethylmalonate was obtained in 67% yield, bp 190–193°, lit.[5] bp 190–195°.

Dimethylmalonic Acid.—The hydrolysis of diethyl dimethylmalonate was carried out as described by Thorne.[5] Dimethylmalonic acid was obtained in 70% yield, mp 186°, lit.[5] 186°.

Dimethylmalonyl Chloride.[6]—Thionyl chloride, 10.5 g (0.09 mole), was added to 5 g (0.037 mole) of dimethylmalonic acid and the mixture was refluxed for approximately 3 hr. Vacuum distillation yielded 1.9 g (31%) of the diacid chloride, bp 45–55° (22 mm); dianilide mp 202–204°, lit.[6] 202.5–203°.

Di-*t*-butylperoxy Dimethylmalonate.—A solution of 0.5 g (2.98 mmoles) of dimethylmalonyl chloride in 15 ml of pentane was added dropwise to a stirred solution of 1.26 g (14 mmoles) of *t*-butyl hydroperoxide and 1.11 g (14 mmoles) of pyridine in 20 ml of pentane maintained at 0°. The rate of addition was controlled to keep the temperature at 0°. The solution was stirred for 1 hr at 0° after addition was complete.

The reaction mixture was poured over ice and the organic layer was separated. The pentane solution was washed successively with 10% sodium carbonate solution, 10% sulfuric acid, and finally with cold water until neutral. After drying over anhydrous magnesium sulfate, the pentane was removed *in vacuo* at room temperature. The crude product was a colorless oil that was purified by passing it through a short column of Florosil.

The infrared spectrum showed no extraneous bands and had characteristic strong absorption at 5.62 for the carbonyl group of a peroxy ester. Peroxide content by iodometric titration was 96%, yield 0.730 g (89%).

Anal. Calcd for $C_{13}H_{24}O_6$: C, 56.50; H, 8.76. Found: C, 56.98; H, 8.83.

α-Carbethoxyisobutyric Acid.—This acid was prepared by the half-hydrolysis of diethyl dimethylmalonate according to the method of Robertson and Sandrock.[7] The monoacid was obtained in 49% yield, bp 114–116° (6 mm), lit.[7] 114–116° (6 mm).

α-Carbethoxyisobutyryl Chloride.—This compound was prepared by addition of phosphorus pentachloride to the acid as

(4) A Perkin-Elmer Model 21 spectrophotometer and a Perkin-Elmer Infracord were used for infrared spectra. The Model 21 was used for all rate determinations and Beer's law studies. Analyses were by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

(5) R. Thorne, *J. Chem. Soc.*, **39**, 543 (1881).

(6) M. Freund and K. F. Fleischer, *Ann.*, **399**, 197 (1913).

(7) A. Robertson and W. F. Sandrock, *J. Chem. Soc.*, 1617 (1933).

described by Robertson and Sandrock.[7] The acid chloride was obtained in 84% yield, bp 74–78° (19 mm), lit.[7] 74–78° (19 mm).

t-Butylperoxy α-Carbethoxyisobutyrate.—A solution of 1.3 g (7.3 mmoles) of α-carbethoxyisobutyryl chloride in 15 ml of petroleum ether was added slowly to a suspension of 1.4 g (11 mmoles) of potassium *t*-butyl peroxide[8] in 20 ml of petroleum ether at room temperature. After stirring for 3 more hr at room temperature, 10 ml of water was added and stirring was resumed for 15 min. The organic layer was removed and washed successively with 10% sulfuric acid, 10% sodium carbonate solution, and cold water until neutral. The petroleum ether solution was dried over anhydrous magnesium sulfate and evaporated *in vacuo* at room temperature. The product, an oil, was purified by passing it through a column of Florosil. Infrared analysis showed absorption at 5.62 and 5.75 μ characteristic of the peroxy ester carbonyl group and the ester carbonyl group, respectively. Peroxide content by iodometric titration was 93%, yield 0.40 g (1.7 mmoles), 24%.

Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 57.07; H, 8.77.

Kinetic Measurements.—The procedure used in the kinetic measurements was that described by Bartlett, Benzing, and Pincock.[9]

(8) N. Kornblum and P. de la Mare, *J. Am. Chem. Soc.*, **74**, 3081 (1952).

The peroxy esters were shown to obey Beer's law at the concentrations used in the kinetic measurements.

Product Studies.—The methods used for the study of the products of the thermal decomposition of the peroxy ester in cumene were modeled after those described by Bartlett and co-workers.[9]

The nonvolatile residue was separated into dicumyl and a carbonyl-containing material by chromatography on silica gel. The carbonyl-containing material could not be further divided or purified by chromatography. Solution of this material in benzene followed by evaporation of the benzene left a clear lacquer, whereas similar treatment with pentane left a white solid. Neither the solid nor the lacquer had a distinct melting point. These properties, similar to those observed for previously isolated polyesters,[2] suggested the carbonyl containing material was a polyester.

t-Butylperoxy isobutyrate[2] was carefully decomposed at 85° in the absence of solvent and the solid residue, the polyester described and characterized by Milas,[1] was recrystallized from ethanol. The infrared spectrum of this polyester of α-hydroxyisobutyric acid ($CHCl_3$) was identical in all its features with that of the carbonyl-containing material described above.

(9) P. D. Bartlett, F. P. Benzing, and R. E. Pincock, *ibid.*, **82**, 1762 (1960).

Polar, Steric, and Solvent Effects in the Cleavage Reactions of Trichloro- and Tribromoacetates with Primary and Secondary Amines[1,2]

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The reactions of a series of trichloro- and tribromoacetates with primary and secondary amines were investigated both in the absence and in the presence of solvents. All primary amines reacted with ethyl trichloroacetate to give predominantly amides while secondary amines yielded products which resulted from both acyl oxygen and haloform cleavages. The extent of acyl oxygen cleavage was dependent upon the geometry rather than the basicity of the amine. The reactions of *n*-butylamine with various tribromoacetates gave products which resulted from both types of cleavage. Exclusive acyl oxygen was never observed in these reactions. The reactions of piperidine with methyl and ethyl tribromoacetates in the absence or presence of solvents gave predominantly a haloform cleavage. Several side reactions were noted. Possible mechanisms are discussed for the side and main reactions that occur when trihalogenated esters are treated with amines.

Trifluoroacetates[4–6] are known to undergo aminolysis when treated with either primary or secondary amines. Trichloroacetates[4,6,7] react with primary amines to yield predominantly amides but with secondary amines carbamates are the major products. From these studies, it is obvious that the action of amines on trihalogenated esters may cleave these esters in two different ways. These cleavages appeared to be of sufficient interest to warrant further investigation.

The first objective of the present study was to examine the role of the amine. The second objective was to synthesize and examine the reaction of four esters of particular interest: β,β,β-trifluoroethyl, β,β,β-trichloroethyl, and β,β,β-tribromoethyl trichloroacetates and also ethyl dichlorofluoroacetate. The third and last objective was to synthesize a few tribromoacetates and to study their reactions with *n*-butylamine and piperidine. Gas–liquid partition chromatography was used extensively for both the qualitative and quantitative analyses of the reaction mixtures. The reactions of tribromoacetates with amines proved to be more complex than the same reactions with trichloroacetates and the separation and identification of all products was a laborious operation.

(1) Abstracted from the Ph.D. dissertation of R. H. Yocum, University of Pennsylvania, 1965.

(2) Presented before the Division of Organic Chemistry, First Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 3, 1966, p 111.

(3) Recipient of E. F. Smith Memorial Scholarships, 1963–1965.

(4) M. M. Joullié and A. R. Day, *J. Am. Chem. Soc.*, **76**, 2990 (1954).

(5) M. M. Joullié, *ibid.*, **77**, 6662 (1955).

(6) A. C. Pierce and M. M. Joullié, *J. Org. Chem.*, **28**, 658 (1963).

(7) Y. Ursy and M. Paty, *Compt. Rend.*, **252**, 3812 (1961).

Experimental Section[8]

Materials.—All of the compounds used in this investigation were analytically pure. Analytical data was obtained for all new compounds and compounds whose physical constants did not agree with those in the literature. All solvents were purified by standard methods until their physical constants agreed with literature values. Purity of liquids was checked by gas–liquid partition chromatography. Amines were purified by allowing them to stand over potassium hydroxide pellets for 3 days, removing the pellets, and distilling the filtrate through a 30-cm column, 2 cm in diameter, packed with glass helices.

Tribromoacetyl Bromide.—This compound was prepared by an improved method. Tribromoacetic acid (44.6 g, 0.15 mole),

(8) Melting points were determined in a Thomas–Hoover capillary melting point apparatus. Microanalyses were carried out by Galbraith Laboratories, Knoxville, Tenn., and by Dr. A. Bernhardt, Max Planck Institute, 433 Mulheim (Ruhr), West Germany. Infrared spectra were determined on a Perkin-Elmer double-beam Model 521 recording spectrophotometer. All spectra were run as carbon tetrachloride solutions using 0.211-mm matched sodium chloride cells. Refractive indices were recorded on an Abbe 3L refractometer.