current of 30 milliamp. (initial current of 40 milliamp. dropped to 20 milliamp. during the electrolysis) using procedure B. The oily liquid was drawn from the top of the aqueous solution and the solution was extracted several times with ether. The ether extracts and the oil were combined and dried and the ether concentrated through a Vigreux column. Bromine was added directly to this ether concentrate. Evaporation left an orange solid which on crystallization from ethanol gave 740 mg., m.p. 63–65°. Recrystallization from ethanol gave white needles, m.p. 64–65° (literature value[29] for propenylbenzene dibromide, m.p. 65.5–66.5°). (2) A solution of 15 g. of the salt in 200 ml. of water was electrolyzed 20 hr. at 30 milliamp. using procedure B. The workup was as above except that the product was vacuum distilled through a short path still rather than brominated. The water-white product had $n^{24.6}_{\mathrm{D}}$ 1.5397. (A calculation from literature data[29] indicated a mixture of 80% of propenylbenzene and 20% of allylbenzene.) Vapor phase chromatography of a pure sample of allylbenzene[30] and of the above product confirmed the proportions to be 80 and 20%.

Allyldimethylanilinium Iodide.—Procedure B was followed except that the cathode was sometimes a platinum wire. A solution of 5 g. of the salt in 180 ml. of water was electrolyzed for 6.5 hr. with a current of 40 milliamp. A total of 120 ml. of gas was collected which consisted of 32% propylene as shown by vapor phase chromatography. (The same experiment using 15 g. of the salt gave a gas consisting of 47% propylene.) The electrolysis solution was extracted with ether and the ether extracts dried. Addition of an ethanolic solution of picric acid gave 240 mg. of dimethylaniline picrate, m.p. 158–159° dec., mixture m.p. with authentic material prepared from dimethylaniline and picric acid 159–160° dec.

Benzylallyldimethylammonium Iodide.—Using procedure B a solution of 12 g. of the salt in 180 ml. of water was electrolyzed at a current of 40 milliamp. The gas formed consisted of 46% propylene as analyzed by the vapor fractometer. No toluene could be isolated from this electrolysis.

Benzyldimethylanilinium Trifluoroacetate in Water.—A solution of the salt prepared from 15 g. of benzyldimethylanilinium bromide in 200 ml. of water was electrolyzed 4 hr. at an average current of 400 milliamp. (initial current of 700 milliamp. dropped to 100 milliamp. during the electrolysis) according to procedure A. The dark, blue-violet cell contents were extracted three times with ether, the ether extracts washed with water and extracted twice with 50-ml. portions of 1:1 hydrochloric acid. The ether was dried over magnesium sulfate, distilled through a Vigreux column and the residue was distilled through a short path still. A water-white liquid was obtained, n^{20}_{D} 1.4879 (literature value[31] for toluene n^{20}_{D} 1.4961.) No appreciable solid residue was obtained. The infrared spectrum of the liquid was identical to that of toluene. Confirmation was obtained by vapor phase chromatography.

Benzyldimethylanilinium Trifluoroacetate in Dimethylacetamide.—The salt was prepared as above and the water removed *in vacuo*. The white solid was dissolved in 200 ml. of dimethylacetamide and the electrolysis was performed according to procedure A for 7.5 hr. with an average current of 300 milliamp. (initial current of 400 milliamp. dropped to 200 milliamp. during the electrolysis).

The electrolysis mixture was poured into 700 ml. of water and extracted three times with ether. The ether extract was washed once with water and extracted twice with 50-ml. portions of 1:1 hydrochloric acid. After another washing with water the ether was dried over magnesium sulfate and distilled through a Vigreux column. The dark tan residue solidified on scratching. It was taken up in hot ethanol and cooled; white needles were obtained, m.p. 52–53°, 1.1 g. Recrystallization from ethanol gave m.p. 52–53°, mixed m.p. with bibenzyl, prepared according to Miukhailenko[32] was 52–54°. The hydrochloric acid extract was neutralized with sodium hydroxide and extracted with ether. To the concentrated ethereal solution was added an ethanolic solution of picric acid. On standing, yellow crystals were formed. Crystallization of these from alcohol gave 543 mg., m.p. 156–157° dec. On recrystallization the melting point was 157–159° dec., mixture m.p. with authentic dimethylaniline picrate was 157–159° dec.

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(30) C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945, p. 356.

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Peroxides. VI.[2] Preparation of *t*-Butyl Peresters and Diacyl Peroxides of Aliphatic Monobasic Acids[3]

BY LEONARD S. SILBERT AND DANIEL SWERN

RECEIVED OCTOBER 18, 1958

Long chain *t*-butyl peresters and diacyl peroxides were prepared in nearly quantitative yields and in high purity by acylation of pure *t*-butyl hydroperoxide and 50–65% hydrogen peroxide, respectively, in ether–pyridine solutions. These peroxides were accurately analyzed by an improved iodometric procedure employing 0.0005 and 0.002% ferric chloride hexahydrate, respectively, in glacial acetic acid. The diacyl peroxides and *t*-butyl peresters show an alternation in melting points.

Organic peroxides have achieved an important position in organic chemistry. Major emphasis in the past has been on the preparation and properties of aromatic and short-chain aliphatic derivatives. A detailed study of the preparation and properties of high purity long-chain peroxides, comparable to the studies on peracids,[2,4] was needed for clarification of peroxide structure, systematization of their chemical and physical properties, and investigation of the kinetics of their decomposition.

Alkyl Peresters.—Milas and Surgenor[5] described the first synthesis and some of the properties of eight *t*-butyl peresters. *t*-Butyl perstearate was the only long-chain saturated derivative mentioned in their paper. These workers employed the Schotten–Baumann technique which has been the major preparative method in use to date.[6] A

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(1) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) Paper V, THIS JOURNAL, **80**, 323 (1958).

(3) Presented at the Fall Meeting of the American Chemical Society, September 7–12, 1958, Chicago, Ill.

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(6) (a) A. T. Blomquist and I. A. Berstein, *ibid.*, **73**, 5546 (1951); (b) A. G. Davies and K. J. Hunter, *J. Chem. Soc.*, 1808 (1953); and references contained in these papers.

patent[7] describing a process for preparing alkyl peresters by reaction of ketenes with hydroperoxides does not cite the properties of the peresters obtainable by this process. The acylation technique in pyridine, first developed by Deninger[8] and amplified by Ullmann and Nadai,[9] was adapted for the preparation of *trans*-9-decalyl perbenzoate,[10] its substituted derivatives[11] and two esters of peroxycarbonic acids.[6b,12]

The Schotten–Baumann method is inconvenient for the laboratory preparation of peresters of long-chain fatty acids because of formation of emulsions in alkaline media which are difficult to break and hydrolysis of the acyl chlorides which lowers the yield and purity of the products. In a preliminary study we acylated pure *t*-butyl hydroperoxide with stearoyl chloride in a solvent containing pyridine as acid acceptor and the *t*-butyl perstearate obtained melted 25° higher than reported.[5] No pure long-chain *t*-butyl perester had apparently been prepared prior to the present investigation.

Diacyl Peroxides.—Most of the aliphatic diacyl peroxides have been mentioned in the literature, but few properties on pure derivatives have been reported. Aliphatic and aromatic peroxides,[13,14] fluorinated peroxides[15] and numerous aromatic peroxides[16] were obtained by acylation of hydrogen peroxide using the Schotten–Baumann method. We found the same difficulties in the application of this method to the preparation of diacyl peroxides as we observed when it was applied to the preparation of high purity long-chain *t*-butyl peresters.

The development of a homogeneous reaction for the preparation of diacyl peroxides requires an organic solvent for hydrogen peroxide. Ethyl ether[17] has been used for concentrating hydrogen peroxide from aqueous solution while a recent note by Paulsen,[18] in a study of the partition coefficients for aqueous hydrogen peroxide and 41 organic solvents, has shown ethers to be the best solvents. The commercial availability of high concentration hydrogen peroxide and use of diethyl ether permit direct acylation of hydrogen peroxide by a pyridine–acylation method in a homogeneous system (see Experimental.)

Acylation of peracids offers an alternate procedure for the preparation of diacyl peroxides. This method has been described earlier for preparing unsymmetrical aroyl–acyl peroxides by shaking a solution of the appropriate acyl chloride with perbenzoic acid in chloroform in the presence of cold alkali.[13,19] The active oxygen content of the crude products was reported to be 80–90% of theoretical. The relatively simple preparation of aliphatic peracids[4] should permit a convenient preparation of a wide variety of mixed and simple diacyl peroxides in a homogeneous medium by the pyridine modification.

Present Investigation.—Highly pure *t*-butyl peresters (Table I) and diacyl peroxides (Table II) of the normal aliphatic monobasic acids have been prepared in virtually quantitative yields by rapid acylation of *t*-butyl hydroperoxide and hydrogen peroxide, respectively, in homogeneous solution in the presence of pyridine[20] as the acid acceptor. The simple, rapid and accurate iodometric procedure developed for the analysis of *t*-butyl peresters[21] was adapted to the analysis of pure diacyl peroxides. A plot of melting points against carbon content (Fig. 1) shows alternation for the diacyl peroxides and *t*-butyl peresters. X-Ray and polarographic data obtained for these peroxides will be reported in a subsequent publication.

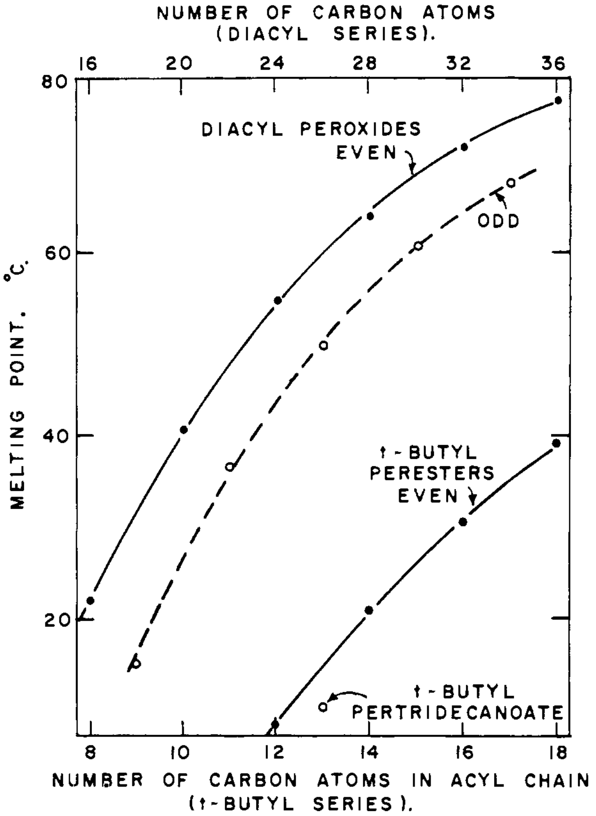

Fig. 1.

Purity Determinations.—Purity of the *t*-butyl peresters was determined by a modified iodometric procedure in which the glacial acetic acid contained an optimum concentration of 0.002% ferric chloride hexahydrate.[21] Purity determinations of these

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TABLE I

CONVERSIONS AND CHARACTERISTICS OF LONG CHAIN *t*-BUTYL PERESTERS

	Conversion, %	M.p.,[a] °C.	d^{30}_4	n^{30}_D	$(-dn \times 10^5/dt)$	Peroxide oyxgen, %[21] Calcd.	Found
Perpelargonate	99	[b]	0.8868	1.4271	40 (30–50°)	6.95	6.93
Percaprate	95	−6.5	.88325	1.4293	39 (30–50°)	6.55	6.58
Perlaurate	99	8.0–8.6	.8784	1.4333	38 (30–50°)	5.87	5.87
Pertridecanoate	..	10.0–10.4	....	....	....	5.59	5.43
Permyristate	99	20.5–21.0	.8751	1.4368	38 (30–50°)	5.32	5.34
Perpalmitate	98	30.3–30.6	....	1.4365[c]	38 (35–60°)	4.87	4.83
Perstearate	96	38.7–39.3[d]	....	1.4386[c]	36 (40–60°)	4.49	4.45

[a] Fisher–Johns melting point apparatus. [b] Distilled, 52–55° (10 μ). [c] n^{40}_D. [d] Reference 5 gives m.p. 14–16.5°.

TABLE II

CONVERSIONS AND CHARACTERISTICS OF LONG CHAIN DIACYL PEROXIDES

	Conversions, %	M.p., °C. Found[a]	Reported[b]	Peroxide oxygen, %[c] Calcd.	Found
Octanoyl[d]	..	21.8–22.4	23	5.59	5.54
Pelargonyl[e]	96	13.0–13.5[f]	...	5.09	5.05
Decanoyl	..	40.5–41.0	...	4.67	4.64
Lauroyl	100	54.7–55.0	41–42	4.01	4.01
Tridecanoyl	..	48.3–48.8	...	3.75	3.73
Myristoyl	98	63.9–64.4	59	3.52	3.50
Palmitoyl	98	71.4–71.9	67–68	3.13	3.12
Stearoyl	..	76.5–76.9	...	2.82	2.81

[a] Fisher–Johns melting point apparatus. [b] Reference 13. [c] Method of reference 21 but using 0.0005% $FeCl_3 \cdot 6H_2O$ in glacial acetic acid. [d] d^{30}_4 0.9275, n^{30}_D 1.4363; $-dn/dt$ 0.00027 (30–50°). [e] d^{30}_4 0.9182: n^{30}_D 1.4388; $-dn/dt$, 0.00029 (30–50°). [f] Heating curve, 13.0°, and cooling curve, 13.0–13.2°, agrees with Fisher–Johns fusion method.

derivatives by carbon and hydrogen analysis are of little value, for the presence of as much as 5% *t*-butyl ester will pass undetected as impurity in the corresponding perester.

Purity of the diacyl peroxides was also determined iodometrically. A brief discussion of the analysis is warranted in view of certain problems associated with iodometric methods of analysis of diacyl peroxides. Analysis of diacyl peroxides by a frequently used iodometric method[22h] yields peroxide oxygen values from 1–2%, and on occasion up to 5%, above calculated values. Many variations of the iodometric procedures, stated to be applicable to diacyl and diaroyl peroxides, employ modifications in solvent[16b,22] and in oxygen exclusion.[22f,g] These methods are inconvenient and lack the accuracy and precision desired for pure derivatives.

The use of ferric chloride hexahydrate in the analysis of *t*-butyl peresters gave such excellent results that its application to the analysis of diacyl peroxides was investigated. The results obtained on three diacyl peroxides, and one diaroyl peroxide, included to show the generality of the method, are reported in Table III. The table shows the results obtained, expressed in percentage difference from calculated, for the iodometric method,[22h] this method modified by addition of 10 and 20 ml. of acetone, respectively, and the improved method developed for *t*-butyl peresters at varying iron chloride concentrations. The reactions were conducted in the manner reported for analysis of *t*-butyl peresters.[21] The maximum blank observed was 0.02 ml. of 0.1 *N* sodium thiosulfate.

TABLE III

COMPARISON OF PEROXIDE OXYGEN DETERMINED BY VARIOUS IODOMETRIC METHODS

	Peroxide oxygen content, % difference from calcd.					
Peroxide	Iodometric method[22h]	Acetone method[22g] 10 ml.	20 ml.	$FeCl_3.6H_2O$ in acetic acid,[21] % 0.002	0.001	0.0005[a]
Dipalmitoyl	+2.0	+2.2	−0.10	−0.86	−1.0	−0.44
Dimyristoyl	+1.5	+0.51	+ .40	− .74	....	− .45
Dilauroyl	+0.50	+ .65	− .95	− .62	− .70	.0
Dibenzoyl	−1.0	−1.6	− .80	− .27	....	− .33

[a] Preferred concentration.

A comparison of the results in Table III clearly demonstrates that the improved method using ferric chloride in acetic acid gives results superior to the normal and acetone procedures. An optimum concentration of 0.0005% ferric chloride hexahydrate in acetic acid for diacyl peroxides, compared to an optimum concentration of 0.002% for *t*-butyl peresters, gives results paralleling the accuracy and precision reported for the peresters (average percentage deviation 0.29%; standard deviation 0.42%).

Additional evidence of high purity was supplied by X-ray diffraction spectra (see subsequent paper) which had sharp diffraction lines and showed no evidence of a second phase.

Experimental

Starting Materials.—*t*-Butyl hydroperoxide obtained from the Lucidol Corporation, Division of Wallace and Tiernan Co.,[23] was fractionally distilled *in vacuo* and the fractions, b.p. 42° (18 mm.), analyzing 99% or better by the iodometric procedure,[22h] were retained for use. Hydrogen peroxide (50–65%) grades were generously furnished by Becco Chemical Division of Food Machinery and Chemical Corporation and E. I. du Pont de Nemours and Co. *t*-Butyl alcohol, Eastman Kodak White Label, was fractionally distilled, combining fractions of constant refractive index and boiling point, 82.1°. Olefin-free petroleum naphtha was obtained by treatment of the commercial petroleum naphtha, boiling range 35–60°, with concentrated sulfuric acid. The naphtha was water-washed until acid-free and distilled from anhydrous calcium chloride.

The preparation of pure capric, lauric, myristic, palmitic and stearic acids has been described.[24] Pure pelargonic acid (99%) was generously supplied by Emery Industries, Inc. Acyl chlorides were prepared from the pure acids and

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(23) Reference to commercial products is not intended to be a recommendation of these products by the U. S. Department of Agriculture over others not mentioned.

(24) D. Swern and E. F. Jordan, Jr., THIS JOURNAL, **70**, 2334 (1948).

thionyl chloride,[25] distilled *in vacuo* and sealed in glass ampules until used.

t-Butyl Peresters. **Preparation of *t*-Butyl Perpalmitate by Schotten–Baumann Method.**—To a solution of 7.3 g. (0.081 mole) of *t*-butyl hydroperoxide and 4.9 g. (0.27 mole) of water maintained below 20°, 20.1 g. (0.073 mole) of palmitoyl chloride and 17.7 g. of 30% aqueous potassium hydroxide solution were simultaneously added with stirring. The reaction mixture was stirred overnight, then poured into 50 ml. of ethyl ether. The emulsion was broken by neutralizing the soap and excess alkali with cold 10% hydrochloric acid solution. The ether solution was washed with three 50-ml. volumes of water, dried over anhydrous sodium sulfate, filtered and evaporated to dryness *in vacuo*. The crude product was analyzed for peroxide oxygen content by the improved iodometric method[21] and for acid number; peroxide oxygen, found 2.96%, calcd. 4.87%; acid number, found 89.6, equivalent to 41% palmitic acid. These analyses corresponded to 60% conversion to *t*-butyl perpalmitate based on palmitoyl chloride.

Preparation of *t*-Butyl Perstearate by Pyridine Acylation Method.—Stearoyl chloride (50 g., 0.165 mole) was stirred into *t*-butyl hydroperoxide (18.0 g., 0.20 mole) dissolved in petroleum naphtha (120 ml.) and cooled to 10°. Pyridine (15.8 g., 0.20 mole) was then added dropwise with stirring over a period of 20 minutes while the temperature was maintained below 15°. The reaction mixture was 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% hydrochloric acid solution to remove excess pyridine and pyridine hydrochloride. (Conversion and yield were determined by diluting the naphtha solution to a known volume, pipetting a sample for iodometric analysis and drying the sample under vacuum to remove solvent and unreacted hydroperoxide.) The petroleum naphtha solution was washed with 5% potassium bicarbonate solution, water-washed, and dried over anhydrous sodium sulfate. After filtration, *t*-butyl perstearate crystallized at 2° in long, hard needles (Table I).

Other *t*-Butyl Peresters.—The other *t*-butyl peresters listed in Table I were prepared by the pyridine acylation procedure described for *t*-butyl perstearate, with the quantities of reactants as shown (recrystallization temperature is given in parentheses): *t*-butyl perpelargonate: 44.3 g. (0.25 mole) of pelargonyl chloride, 27.0 g. (0.30 mole) of *t*-butyl hydroperoxide, 23.7 g. (0.30 mole) of pyridine (perester distilled from alembic apparatus, head temperature 55–58°/10 μ); *t*-butyl percaprate: 50 g. (0.262 mole) of capryl chloride, 28.3 g. (0.314 mole) of *t*-butyl hydroperoxide, 24.8 g. (0.314 mole) of pyridine (−40°); *t*-butyl perlaurate: 34.2 g. (0.156 mole) of lauroyl chloride, 17.0 g. (0.188 mole) of *t*-butyl hydroperoxide, 14.9 g. (0.188 mole) of pyridine (−35°); *t*-butyl tridecanoate: 2.6 g. (0.011 mole) of tridecanoyl chloride, 1.6 g. (0.018 mole) of *t*-butyl hydroperoxide, 1.2 g. (0.015 mole) of pyridine (−16°); *t*-butyl permyristate: 50 g. (0.203 mole) of myristoyl chloride, 21.9 g. (0.243 mole) of *t*-butyl hydroperoxide, 19.2 g. (0.243 mole) of pyridine (−20°); *t*-butyl perpalmitate: 41.2 g. (0.15 mole) of palmitoyl chloride, 20.3 g. (0.225 mole) of *t*-butyl hydroperoxide, 15.0 g. (0.188 mole) of pyridine (2°).

Diacyl Peroxides. Preparation of Dipalmitoyl Peroxide by Schotten–Baumann Method.—Palmitoyl chloride (20 g., 0.073 mole) was dissolved in chloroform (20 ml.) and cooled to 5°. Hydrogen peroxide (2.5 g. of 50% concentration, 0.037 mole) and sodium hydroxide (11.6 g. of 25% concentration) were simultaneously added dropwise with vigorous stirring, while the temperature was maintained below 15°. The mixture was stirred for one hour after complete addition of reactants and poured into a chloroform–water mixture. The emulsion could not be broken without partial acidification. The chloroform solution was washed with water, dried over anhydrous sodium sulfate, filtered and evaporated. The product, recovered in 77% yield, had a peroxide oxygen content 64% of calculated. This represents a 50% conversion based on palmitoyl chloride. The resulting product was difficult to purify by direct crystallization.

Preparation of Dimyristoyl Peroxide by Pyridine Acylation Method.—Only the preferred procedure will be described in detail: myristoyl chloride (24.7 g., 0.10 mole) was dissolved in ether (175 ml.) and cooled to 0°. Hydrogen peroxide (4.25 g. of 60% concentration, 0.075 mole) was added, followed by the dropwise addition of pyridine (9.5 g., 0.12 mole) while the temperature was maintained at 0–5°. The diacyl peroxide precipitated as it formed. After complete addition of pyridine, the ice-bath was removed and stirring of the slurry was continued for a total time of one hour. A homogeneous solution was obtained at room temperature by addition of more ether. The ether solution was washed with dilute hydrochloric acid, 5% potassium bicarbonate, followed by water and then dried over anhydrous sodium sulfate. The solution was diluted to a known volume and a sample pipetted for iodometric analysis. This procedure was followed for a series of experiments varying the amount of solvent, temperature of reaction, mole ratio of reactants and time as summarized in Table IV. For product isolation, the original ether solution was cooled to 0–2°.

The temperature at which reaction is conducted is the most important factor for attainment of high conversions. Sufficient solvent is used to permit unhindered stirring of the slurry which forms by crystallization of diacyl peroxide during reaction. The reaction is believed to be instantaneous, but an additional time is allowed after complete pyridine addition to permit any acyl chloride occluded by the precipitating peroxide to redissolve and effect quantitative reaction.

TABLE IV

DETERMINATION OF CONDITIONS FOR MAXIMUM CONVERSION OF MYRISTOYL CHLORIDE TO DIMYRISTOYL PEROXIDE

Mole ratio of reactants, RCOCl[a]: pyridine: H_2O_2	Solvent, ml.	Temp., °C.	Time, hours	Conversion, %
1:1.1:0.55	$CHCl_3$, 75	15–20	3	65
1:1.25:0.55	$CHCl_3$–ether 1:2, 112	15–20	1	71
1:1.3:0.75	$CHCl_3$–ether 1:14, 188	15–20	2	90
1:1.1:0.60	Ether, 175	0–5	0.5	84
1:1.2:0.75	Ether, 175	0–5	1	98

[a] 0.10 mole.

Other Diacyl Peroxides.—Chloroform (75 ml.) was used as a cosolvent at the end of the reaction period only for the relatively insoluble dipalmitoyl and distearoyl peroxides. Distearoyl and dipalmitoyl peroxide were crystallized from the chloroform–ether solution. Ditridecanoyl and dilauroyl peroxides were crystallized from ether. Didecanoyl and dipelargonyl peroxides were crystallized from olefin-free petroleum ether.

Acylation of Perlauric Acid.—Perlauric acid (4.80 g., 0.0222 mole) was dissolved in ethyl ether (54 ml.), cooled to 0° and lauroyl chloride (4.87 g., 0.0222 mole) was added. Pyridine (2.1 g., 0.0266 mole) was added dropwise while stirring the mixture at 0–5°. The mixture was stirred for an additional 40 minutes while it was allowed to warm to room temperature. The ether solution was washed with water, dried over anhydrous sodium sulfate, and analyzed iodometrically. Peroxide oxygen was 89.3% of calculated.

The above experiment was repeated at 10–15°. At the higher reaction temperature, the peroxide oxygen content of the product was only 79.4% of calculated. Recrystallization of both crude products from ethyl ether–petroleum naphtha (1:1) yielded pure dilauroyl peroxide.

Melting Points.—Melting points were determined on a Fisher–Johns melting point apparatus. Crystals with melting points between ice and room temperatures were determined on the Fisher–Johns block in a cold room thermostatically controlled at 2°. The compounds melted sharply with controlled heating of the block. The accuracy of the method was checked by comparing the value found for dipelargonyl peroxide crystals with the value determined from its heating and cooling curves using a calibrated N.B.S. thermometer.

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