United States Patent [19]

D'Angelo et al.

[11] **3,853,957**

[45] **Dec. 10, 1974**

[54] **OXY SUBSTITUTED PEROXYKETALS**

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[73] Assignee: **Pennwalt Corporation,** Philadelphia, Pa.

[22] Filed: **May 7, 1968**

[21] Appl. No.: **727,336**

[52] **U.S. Cl.** ..... **260/476 R,** 260/610 R, 260/410 R, 260/410.6, 260/410.9, 260/453 R, 260/468 R, 260/469 R, 260/469 C, 260/471 R, 260/484, 260/488 R, 260/488 F, 260/488 J, 260/75 NB, 260/94.9 GA, 260/94.9 C

[51] **Int. Cl.** **C07c 69/76,** C07c 69/02

[58] **Field of Search** ..... 260/610 R, 453 RZ, 488 R, 260/476 R, 468 R, 469 R, 410, 410.9, 410.6, 476 C, 488 F, 488 J, 484, 485 R, 486 R, 471 R, 488 CD, 514

[56] **References Cited**

UNITED STATES PATENTS

2,455,569	12/1948	Dickey	260/610 R
3,296,184	1/1967	Portolanie et al.	260/610 R

Primary Examiner—Bernard Helfin
Assistant Examiner—W. B. Lone
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[57] **ABSTRACT**

Peroxyketals having two peroxy groups attached to the same carbon atom of an aliphatic group having at least three carbon atoms, and at least one hydroxyl, acyloxy, substituted acyloxy, alkoxycarbonyloxy, carbamoyloxy, or substituted carbamoyloxy group. These peroxyketals are useful chemical intermediates, free radical polymerization initiators and crosslinking agent.

Examples

2,2-Bis(t-butylperoxy)propyl caproate.

3,3-Bis(t-butylperoxy)-1-butanol.

7 Claims, No Drawings

OXY SUBSTITUTED PEROXYKETALS

BACKGROUND OF THE INVENTION

1. The Field of the Invention

This invention relates to substituted peroxyketals. Particularly the invention relates to peroxyketals substituted by hydroxy and/or acyloxy groups. Also the invention relates to the preparation of these peroxyketals.

2. Description of the Prior Art

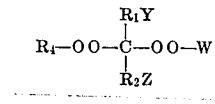
Dickey U.S. Pat. No. 2,455,569, discloses certain peroxyketals.

SUMMARY OF THE INVENTION

These new compounds have two peroxy groups joined to a common carbon of an aliphatic group having at least three carbon atoms and at least one group from the class consisting of hydroxy and acyloxy. The hydroxy group or acyloxy group is joined to a carbon atom which is free of substituent peroxy groups.

The substituted peroxyketals of the invention have the formula:

(I)

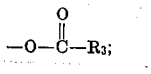


where:

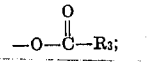
a. R_1 and R_2 are aliphatic or cycloaliphatic biradicals;

b. R_1—C—R_2 together may form a ring;

c. Y is H, OH or



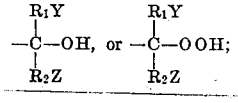
d. Z is OH or



e. R_3 is an aliphatic, cycloaliphatic or aryl radical;

f. R_4 and R_5 are H, aliphatic or cycloaliphatic radicals;

g. W is (i) —R_5, or (ii) when R_4 is H, W can be



and

h. when Y and Z are each —OH, W cannot be —C(R_1Y)(R_2Z)(OH), or —C(R_1Y)(R_2Z)(OOH).

Illustrative compounds of the invention are:

3,3-Dihydroperoxy-2-methylbutyl pivalate.

4,4-Bis(t-butylperoxy)-1-pentanol.

1,3-Diacetyloxy-2,2-bis(t-butylperoxy)propane.

4,4-Bis(pinanylperoxy)pentyl benzoate.

5,8-Dihydroperoxy-5,8-dimethyl-3,6,7,10-tetraoxa-2,11-dodecadione.

UTILITY

The compounds of this invention are useful as sources of free radicals which can be used to initiate the polymerization of monomers; as synergists with organic bromine compounds in flame retardant compositions; as crosslinking or curing agents in unsaturated polyester resin compositions; as crosslinking agents; and as chemical intermediates in the general manner of known peroxyketals.

DESCRIPTION OF THE INVENTION AND EXAMPLES

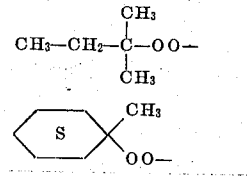
In Formula I, R_1 and R_2 are the same or different aliphatic or cycloaliphatic biradicals. R_1—C—R_2 together may form a ring which is substituted by Y, Z, and two peroxy (—OO—) groups. R_3 is an aliphatic, cycloaliphatic or aryl radical. R_4 and R_5 are the same or different -H, aliphatic or cycloaliphatic radicals.

The aliphatic radical includes substitution by aryl radicals — araliphatic radicals — and cycloaliphatic radicals. The cycloaliphatic radical includes substitution by aliphatic and by aryl radicals. The aryl radicals may be substituted by aliphatic and by cycloaliphatic radicals. Both cycloaliphatic and aryl radicals may be single ring, such as, phenyl and cyclohexyl, or connected rings, such as biphenyl, binaphthyl, bicyclopropyl, bicyclopentyl, or fused rings such as naphthyl, decahydronaphthyl. It is to be understood that the sustituents should not interfere with the desired reaction. In general halogen, oxygen, sulfur and nitrogen substituents or groups containing these do not interfere.

Commonly R_1 and R_2 each have 1–10 carbon atoms in the aliphatic biradical and 3–12 carbon atoms in the cycloaliphatic biradical. Usually R_1 and R_2 are alkylene, phenalkylene, and cycloalkylene and the corresponding halo substituted radicals.

Commonly R_3 has 1–18 carbon atoms in the aliphatic radical, 3–12 carbon atoms in the cycloaliphatic radical, or 6–12 carbon atoms in the aryl radical. Preferably R_3 is alkyl having 1–12 carbon atoms, phenalkyl having 7–12 carbon atoms, cycloalkyl having 4–8 carbon atoms, or phenyl having 6–12 carbon atoms and the corresponding halo substituted radicals.

Commonly R_4 and R_5 are the same or different radicals —H, aliphatic having 4–12 carbon atoms, or cycloaliphatic radicals having 4–12 carbon atoms. Preferably R_4 and R_5 are the same or different radicals —H, aliphatic hydrocarbon having 4–10 carbon atoms, or cycloaliphatic hydrocarbon having 4–10 carbon atoms and each radical affords a tertiary carbon atom which t-carbon atom is joined to a peroxy oxygen atom, for example

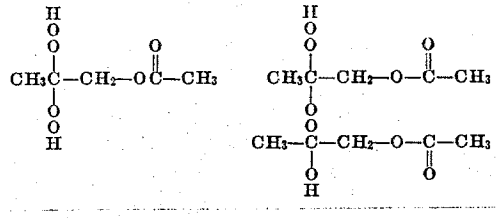


The hydroxy products of this invention can be prepared by the reduction of peroxyketalcarboxylic acids and esters and by the saponification of aceyloxyperoxyketals. The acyloxyperoxyketals are also a new class of peroxy compounds which can be prepared by the reaction of acyloxyketones with hydrogen peroxide or hy-

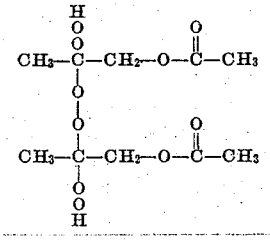
droperoxides in the presence of strong acidic catalysts.

Representative ketones which can be used to prepare the acyloxyperoxyketals of this invention include: acetonyl acetate, acetonyl isobutyrate, acetonyl pivalate, acetonyl chloropivalate, acetonyl 3-chlorobutyrate, acetonyl 4-chlorobutyrate, acetonyl 2-ethylhexoate, acetonyl caproate, acetonyl laurate, acetonyl benzoate, acetonyl 3-chlorobenzoate, acetonyl 4-nitrobenzoate, acetonyl 4-methylbenzoate, acetonyl naphthoate, acetonyl methyl carbonate, acetonyl isopropyl carbonate, acetonyl carbamate, acetonyl dimethylcarbamate, 4-acetoxy-2-butanone, 4-pivaloxy-2-butanone, 4-benzoyloxy-2-butanone, 4-acetoxy-3-methyl-2-butanone, 4-isobutyryloxy-3-methyl-2-butanone, 4-acetoxy-3-n-butyl-2-butanone, 4-acetoxy-1-phenyl-2-butanone, 1,3-bis(acetoxy)acetone, 1,3-bis(isobutyryloxy)acetone, 1,3-bis(benzoyloxy)acetone, 1-acetoxy-2-methyl-3-pentanone, and 2-(3-acetoxypropyl)-1-cyclohexanone.

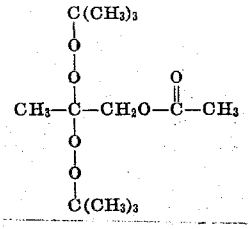
To illustrate the type of products available from the ketones of the representative list above, the reaction of acetonyl acetate with hydrogen peroxide in the presence of acidic catalysts gives a mixture of compounds commonly known as ketone peroxides. Among the components of this mixture, structures such as



and



are to be expected. If, on the other hand, the reaction is carried out with t-butyl hydroperoxide, the simple structure

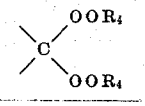


can be obtained.

Representative perketalesters (and perketalacids) which can be reduced to the hydroxyperketals of this invention include methyl 3,3-bis(t-butylperoxy)butyrate, ethyl 3,3-bis(t-butylperoxy)butyrate, n-butyl 4,4-bis-(t-butylperoxy)valerate, n-butyl 5,5-bis(t-butylperoxy)-hexoate, n-butyl 6,6-bis(t-butylperoxy)-heptanoate, diethyl 4,4-bis(t-butylperoxy)heptanedioate, n-butyl 4,4-bis(t-amylperoxy)valerate, n-butyl 4,4-bis(pinanylperoxy)valerate, ethyl 3-{ 2-[1,1-bis(t-butylperoxy)cyclohexyl]} propionate, n-butyl 4,4-bis(cumylperoxy)valerate, 2,2-bis(t-butylperoxy)-propyl acetate, 2,2-bis(t-butylperoxy)propyl caproate, 1,3-bisacetoxy-2,2-bis(t-butylperoxy)propane, 2,2-bis(chloro-t-butylperoxy)propyl acetate, 2,2-bis(t-butylperoxy)propyl 4,4-bis(t-butylperoxy)valerate, 9-acetoxymethyl-3,3,6,6,9-pentamethyl-1,2,7,8-tetraoxayclononane.

By the reduction of diethyl 4,4-bis(t-butylperoxy)-heptanedioate, 4,4-bis(t-butylperoxy)-1,7-heptanediol is obtained. By the reduction of butyl 4,4-bis(t-amylperoxy)-valerate, 4,4-bis(t-amylperoxy)-1-pentanol is obtained. By the reduction of butyl 4,4-bis(pinanylperoxy)valerate, 4,4-bis-pinanylperoxy-1-pentanol is obtained. By the reduction of 2,2-bis-(t-butylperoxy)propyl acetate, 2,2-bis(t-butylperoxy)-1-propanol is obtained. By the saponification of 2,2-bis(chloro-t-butylperoxy)propyl acetate, 2,2-bis(chloro-t-butylperoxy)-1-propanol is obtained. By the reduction of ethyl 3-[2-[1,1-bis(t-butylperoxy)cyclohexyl]]propionate, 3-[2-[1,1-bis(t-butylperoxy)cyclohexyl]]-1-propanol is obtained. By the reduction of 2,2-bis(t-butylperoxy)propyl 4,4-bis(t-butylperoxy)- valerate, a mixture of 2,2-bis(t-butylperoxy)-1-propanol and 4,4-bis(t-butylperoxy)-1-pentanol is obtained. By the saponification of 4-pivaloxy-3-methyl-2,2-bis(t-butylperoxy)butane, 3-methyl-2,2-bis(t-butylperoxy)-4-butanol is obtained. By the reduction of butyl 4,4-bis(cumylperoxy)valerate, 4,4-bis(cumylperoxy)-1-pentanol is obtained.

Acidic catalysts typical of those useful in preparing the peroxyketalesters include: sulfuric acid, phosphoric acid, p-toluenesulfonic acid, methanesulfonic acid, perchloric acid and strong acid ion exchange resins such as Amberlite 200 and Amberlyst 15. When the peroxyketals are prepared using hydroperoxides they can be reacted further to produce the alcoholic products of this invention where Y=H or OH, Z=OH. If the peroxyketal



group is formed in the part of the peroxyketalester directly attached to the carbon atome bearing the carbonyl oxygen, the hydroxyperoxyketal can be obtained by treating the peroxyketalester with a reducing agent of the complex metal hydride type such as lighium aluminum hydride and its chemical equivalents (Reduction With Complex Metal Hydrides, Norman G. Gaylord, Interscience Publishers Inc., N.Y., 1956) which are known to reduce esters to alcohols under mild conditions. If, however, the peroxyketal group is in the part of the ester linked to the carbonyl carbon atome thru an oxygen atom, then the hydroxyperketal can be obtained either by simple hydrolysis or saponification or if desired, by reductive cleavage of the ester with the reducing agents indicated above.

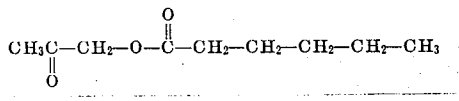
Typical hydroperoxides which can be used to prepare the products of this invention include t-butyl hydroperoxide, t-amyl hydroperoxide, chloro-t-butyl hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, cumyl hydroperoxide, p-menthanyl hydroperoxide, pinanyl

hydroperoxide, diisopropylbenzene hydroperoxide, 2-methyl-2-hydroperoxy-4-hydroxypentane.

To illustrate some of the general methods of preparing and using the new products of this invention, the following examples are included.

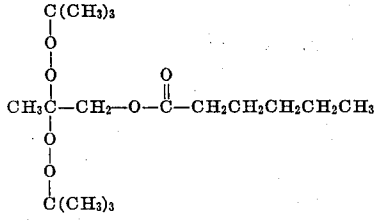
EXAMPLE I

A. PREPARATION OF ACETONYL CAPROATE



A mixture of 30.2g. (0.22 mole) of sodium caproate, 25 ml. of caproic acid and 18.5g. (0.20 mole) of chloroacetone was stirred and heated at 110°–120°C for 5 hours. After cooling to 30°C, 25 ml. of pentane was added, the pentane layer decanted and washed with water and 5% sodium hydroxide solution. After drying over anhydrous magnesium sulfate, the pentane was removed under reduced pressure. The product weighing 16.7g. was obtained in 48.5% yield.

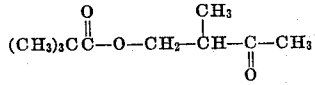
B. Preparation of 2,2-Bist(t-butylperoxy)propyl Caproate



A mixture of 12.9g. (0.075 mole) of acetonyl caproate, and 19.7g. (0.20 mole) of 90% t-butyl hydroperoxide was stirred at 0°C, while 9.8g. of 77% sulfuric acid was added slowly. The reaction mixture was then stirred at 0°C for 4 hours, and the organic layer separated. The produce was washed with water, 5% sodium hydroxide solution and finally with water and then dried over anhydrous magnesium sulfate. The separated product weighed 22.2g. (89% recovery). Iodometric assay indicated that the product contained 98% of the desired compound.

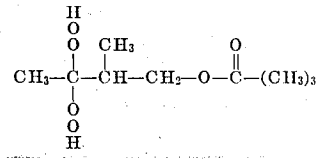
EXAMPLE II

A. Preparation of 4-Pivalyloxy-3-methyl-2-butanone



A mixture of 60g. (0.6 mole) of 4-hydroxy-3-methyl-2-butanone and 70g. (0.7 mole) of triethylamine dissolved in 225 ml. of ether was stirred at 25°–30°C, while 72g. (0.6 mole) of 95% pivalyl chloride dissolved in 75 ml. of ether was added slowly. After the addition was complete, the reaction mixture was stirred at 30°C for 16 hours, the precipitated triethylamine hydrochloride separated by filtration and the ether solution washed with 200 ml. of tartaric acid solution, sodium bicarbonate solution and water and then dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure and 109g. (98% yield) of product recovered.

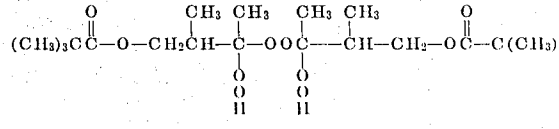
B. Preparation of 3,3-Dihydroperoxy-2-methylbutyl Pivalate



A mixture of 7.35g. (0.04 mole) of 3-oxo-2-methylbutyl pivalate, (4-pivalyloxy-3-methyl-2-butanone) 5.64g. (0.08 mole) of 50% hydrogen peroxide solution and 30 ml. of ether was stirred at 0°C while 0.98g. (0.01 mole) of 95% sulfuric acid was added. After stirring at 0°C for 4 hours, the organic layer was separated, washed with saturated ammonium sulfate solution, and water to neutrality. The ether solution was dried over anhydrous magnesium sulfate, and the ether removed under reduced pressure.

The product weighed 6.46g. contained 21.6% of the calculated amount of active oxygen by iodometric assay, and was obtained in 15.1% yield.

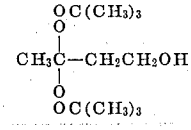
By further reaction of the 3,3-dihydroperoxy-2-methylbutyl pivalate with 3-oxo-2-methylbutyl pivalate and hydrogen peroxide in the presence of the acidic catalyst, more complex ketone peroxide structures such as 2,2,6,7,10,11,15,15-octamethyl-7,10-dihydroperoxy-4,8,9,13-tetraoxa-3,14-hexadecanedione



are possible components of the product mixture.

EXAMPLE III

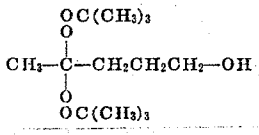
Preparation of 3,3-Bis(t-butylperoxy)-1-butanol



A solution of 3.08g. (0.082 mole) of lithium aluminum-hydride dissolved in 250 ml. of ether was stirred at 5°–10°C, while 28.3g. (0.1 mole) of methyl 3,3-bis(t-butylperoxy)-butyrate dissolved in 50 ml. of ether was slowly added. After stirring for 2 hours at 10°C, 75 ml. of wet ether was added slowly followed by 40ml. of water and then 20g. of sodium tartarate. The mixture was allowed to stir overnight. The ether layer was separated after 300 ml. of water was added to complete the solution of the inorganic salts. The ether layer was washed, dried over anhydrous magnesium sulfate and the ether removed under reduced pressure. The product weighing 24.2g (97% recovery) was found to contain 12.5% active [O] [Calculated active [O], 12.8%] corresponding to 97.5% assay.

EXAMPLE IV

Preparation of 4,4-Bis(t-butylperoxy)-1-pentanol

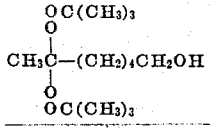


A solution of 3.08 g. (0.082 mole) of lithium aluminum-hydride dissolved in 250 ml. of ether was stirred at 0°–5°C while a solution of 34.5 g. (0.1 mole) of n-butyl 4,4-bis-(t-butylperoxy)-valerate dissolved in 50 ml. of ether was slowly added followed by 30 ml. of water, and 25g. of sodium tartrate. The mixture was allowed to stir overnight.

The ether layer was separated, washed with water, dried over anhydrous magnesium sulfate, and the ether removed under reduced pressure (25°C, 15 Torr). The residue, 30.2g., was taken up in 200 ml. of pentane and redried. The pentane was removed under reduced pressure, leaving 29.7g. of product in more than 100% yield (n-butyl alcohol is present as is evidenced by its odor). Calculated: active [O], 11.25%. Found: active [O], 9.69% corresponding to an assay of 86%.

EXAMPLE V

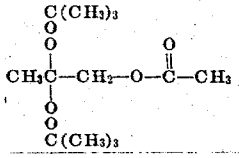
Preparation of 6,6-Bis(t-butylperoxy)-1-heptanol



A solution of 1.0g. (0.026 mole) of lithium aluminum-hydride dissolved in 35 ml. of ether was stirred and maintained at 20°–25°C, while 4.2g. of n-butyl 6,6-bis(t-butylperoxy)-heptanoate (recovered from an incomplete reaction of the ester with an insufficient amount of $LiAlH_4$) dissolved in 25 ml. of ether was added slowly. After stirring for 2 hours, 50 ml. of wet ether was added to hydrolyze unreacted $LiAlH_4$ followed by the slow addition of 50 ml. of water to ensure complete hydrolysis. Approximately 15g. of sodium tartrate was then added and the mixture stirred to dissolve the inorganic salts. The ether solution of the product was separated, washed, dried over anhydrous magnesium sulfate and the ether removed under reduced pressure, leaving 2.7g. of product (93% recovery). Calculated: Active [O], 10.95%. Found: Active [O], 9.35%: 86% assay. Some of the n-butyl alcohol formed during the reduction of the ester is left in the product and is easily detected by its odor.

EXAMPLE VI

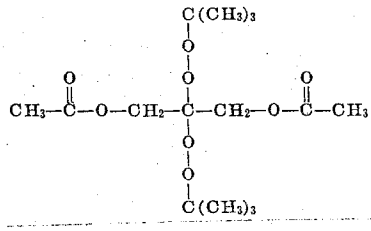
Preparation of 2,2-Bis(t-butylperoxy)propyl Acetate



A mixture of 69.6g. (0.6 mole) of acetonyl acetate and 118.2g. (1.2 mole) of 90% t-butyl hydroperoxide was stirred at 0°C, while 59.1g. of 77% sulfuric acid was slowly added over a period of 50 minutes. The mixture was then stirred at 0°C for 4 hours, the organic layer separated and washed cold with water, 50% sodium hydroxide solution and finally with water and then dried over anhydrous magnesium sulfate. The separated product weighed 128.6g. (77% recovery). Iodometric assay indicated the product contained 95.7% of the desired compound.

EXAMPLE VII

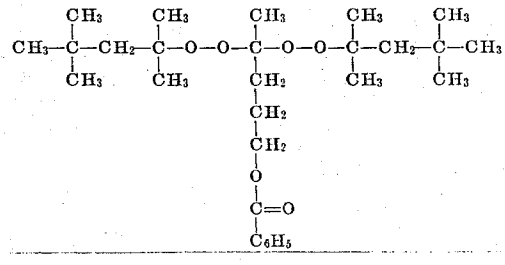
Preparation of 1,3-Diacetoxy-2,2-bis(t-butylperoxy)propane



A reaction mixture containing 17.4g. (0.1 mole) of 1,3-diacetoxyacetone, 21.7g. (0.22 mole) of 90% t-butyl hydroperoxide and 70 ml. of benzene was stirred at 0°C, while 10.8g. 77% sulfuric acid was added slowly. The reaction mixture was then stirred at 0°C for 4 hours, and the organic layer separated. The organic layer was washed with water, 2% sodium hydroxide solution and finally with water, and then dried over anhydrous magnesium sulfate. The product weighed 7.8g. Iodometric assay indicated the product contained 96.5% of the desired compound.

EXAMPLE VIII

Preparation of 4,4-Bis(1,1,3,3-tetramethylbutylperoxy)-pentyl Benzoate

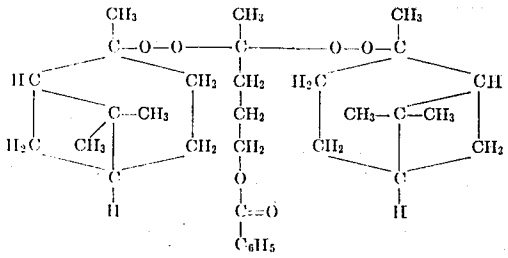


A mixture of 8.24g. (0.04 mole) of 4-oxopentyl benzoate, 18.80g. (0.104 mole) of 1,1,3,3-tetramethylbutyl hydroperoxide (85%) and 25 ml. of ether was stirred at 10°C while 9.0g. of 77% sulfuric acid solution was slowly added. The reaction mixture was then stirred at 0°C for 4 hours, diluted with cold water and the organic layer separated, washed with 5% sodium hydroxide solution and then with water to neutrality. The ether solution was dried over anhydrous magnesium sulfate and the ether removed under reduced pressure.

The product weighed 20.0g. assayed 101.3% of the calculated amount of active oxygen by iodometric assay.

EXAMPLE IX

Preparation of 4,4-Bis(pinanylperoxy)pentyl Benzoate

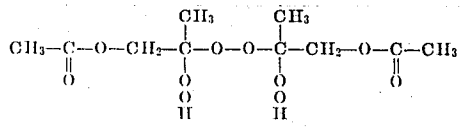


A mixture of 18.0g. (0.08 mole) of pinanyl hydroperoxide 8.24g. (0.04 mole) of 4-oxopentyl benzoate and 50 ml. of ether was stirred at 0°C while 9.0g. of 77% sulfuric acid solution was added slowly. After stirring for 4 hours at 0°C, the organic layer was separated, washed with 5% sodium hydroxide solution and finally with water to neutrality. The solution was dried over anhydrous magnesium sulfate and the ether removed under reduced pressure.

The 18.34g. of product assayed for 98.4% of the calculated amount of active oxygen by iodometric assay for a yield of 85.8% of theory.

EXAMPLE X

Preparation of 5,8-Dihydroperoxy-5,8-dimethyl-3,6,7,10-tetraoxa-2,11-dodecadione



A mixture of 10.9g. (0.16 mole) of 50% hydrogen peroxide, 0.98g. (0.01 mole) of 95% sulfuric acid and 30 ml. of ether was stirred at −5°C while 18.58g. (0.16 mole) of acetoxyacetone was added over a period of 15 minutes. The reaction mixture was stirred for an additional hour at 0°C, the ether layer separated, washed with cold 40% ammonium sulfate solution and then treated with solid sodium bicarbonate to adjust the pH of the aqueous layer to pH 5. The ether layer was separated, dried over anhydrous magnesium sulfate and the ether removed under reduced pressure, leaving 15.57g. of product assaying 7.01% active oxygen by iodometric titration (43.5% of the calculated active oxygen for the desired product).

EXAMPLE XI

SPI EXOTHERM TESTS

Curing of Basic Polyester Resin

Samples of 1-acetoxy-2,2-bis(t-butylperoxy)-propane (from Example VI) assaying 99.2% (Compound A) and 1-caproxy-2,2-bis(t-butylperoxy)-propane (from Example I) assaying 98% (Compound B) were tested in the SPI Exotherm test in basic polyester resin and compared at equal active oxygen levels with t-butyl peroxybenzoate (tBPD). The bath temperature was 115°C, and the weight percentages used were 1% tBPD, 0.71% Compound A, and 0.85% Compound B.

	tBPD	Compound A	Compound B
Gel (min.)	5.5	5.9	7.0
Cure (min.)	6.7	7.2	8.3
Peak °F	435	438	436
Barcol*	40–45	45–50	40–45

*Barcol Impressor reading (Model GYZj- 934-1)

Tests under comparable conditions were run on samples of the hydroxyperketals, obtained in these examples by the reduction of the perketal esters. Compound D [4,4-bis(t-butylperoxy)-1-pentanol (from Example IV) assaying 80%] and Compound E[3,3-bis(t-butylperoxy)-1butanol (from Example III) assaying 97.5%] were used at levels of Compound D, 0.84% and Compound E, 0.65% in comparison to 1% tBPD at a bath temperature of 115°C.

	tBPD	Compound D	Compound E
Gel (min.)	5.5	4.2	3.0
Cure (min.)	6.7	5.3	4.2
Peak °F	435	440	438
Barcol*	40–45	40–45	40–45

*Barcol Impressor reading (Model GYZj- 934-1)

Polymerization tests were carried out, using the "SPI Procedure for Running Exotherm Curves — Polyester Resins" published in the Preprint of the 16th Annual Conference — Reinforced Plastics Division, Society of Plastics Industry Inc., February 1961.

The tests were run in general purpose "Basic" unsaturated polyester resin, having the following formulation:

Maleic anhydride	1.0 mole
Phthalic anhydride	1.0 mole
Propylene glycol	2.2 mole
Acid Number of alkyl resin	35 - 45
Inhibitor (Hydroquinone) (% of final solution)	0.013
Styrene monomer (% of final solution)	32 - 34

EXAMPLE XII

CURING OF A COBALTED POLYESTER RESIN

A sample of 5.8-dihydroperoxy-5,8-dimethyl-3,6,7,10-tetraoxa-2,11-dodecadione (from Example X) (Compound C) assaying 43.4% was used in the SPI exotherm test to cure a cobalt accelerated polyester resin formulation [basic polyester resin to which 0.2% of 6% cobalt ten-Cem [1] (cobalt salt of a long chain organic acid) solution had been added], and compared in activity to LUPERSOL DDM, a commercial ketone peroxide catalyst. The samples were compared at an equal active oxygen level (1% by weight of LUPERSOL DDM, 1.55% Compound C). The room temperature (approximately 23°C) data and the 30°C gel times (minutes) were recorded. ([1] Mooney Chemicals Inc., Cleveland, Ohio)

	Compound C	LUPERSOL DDM*
30°C gel	9.8	25.5
R.T. Gel	15.5	36.2
R.T. cure	20.4	43.5
Peak °F	308	255
Barcol	40	40

* MEK PEROXIDES in Dimethyl phthalate solution [11% Active Oxygen]

temperatures. The extent of crosslinking was determined by immersing the cured samples in tetrahydrofuran at 25°C for 16–18 hours and determing the amount of undissolved material. In the table the weight of peroxidic compound is given in phr (parts per 100 parts of resin).

*dibasic lead phosphite

	Assay %	phr	uz,24/34 Cure (Min) Temp	°F/Time	% Crosslink
1-Acetoxy-2,2-bis(t-butyl-peroxy)-propane (from Example VI)	95.8	2.1	350	15	74
			375	15	92
1-Caproxy-2,2-bis(t-butyl-peroxy)-propane (from Example I)	57.6	2.5	350	15	85.8
LUPERSOL 230 (commercial) (perketal)					
n-butyl 4,4-bis(t-butylperoxy)-valerate	—	2.5	350	15	46.8
			375	15	80.4

EXAMPLE XIII

A sample of 1-acetoxy-2,2-bis(t-butylperoxy)propane (from Example VI) assaying 99.2% was tested as synergist in a flame retardant formulation for styrene at a concentration of 0.198% (equivalent to 0.4% of dicumyl peroxide) and 0.4% tetrabromoethane.

The formulated styrene was self-extinguishing in 2.4 seconds, showing that the peroxidic product was a good flame retardant synergist.

Flame Retardant Test

In this test ASTM D-635-56T and more completely discussed in U.S. Pat. No. 3,388,864, a sample containing only the 0.4% tetrabromoethane (no peroxide) was not self-extinguishing.

EXAMPLE XIV

Crosslinking of Polyethylene

The peroxide crosslinking of polyethylene (Union Carbide DYNH-1)* was carried out by mixing 0.01 equivalent of peroxide with 100g. of polyethylene on a roll mill and curing the samples in a heated press for 30 minutes to crosslink the polyethylene. The extent of crosslinking was determined by extracting the crosslinked samples with hot xylene, the undissolved fraction being the crosslinked material.

*Density 0.919; melt index 2.0 Bakelite Polyethylene Injection Molding Material

	phr**	Cure °F	% Cross-link
1-acetoxy-2,2-bis(t-butylperoxy) propane (from Example VI)	1.4	320	67.4
		340	67.5
		375	68.2
1-caproxy-2,2-bis(t-butylperoxy) propane (from Example I)	1.7	320	73.5
		340	73.1
		375	73.2

**parts peroxide per 100 parts of resin.

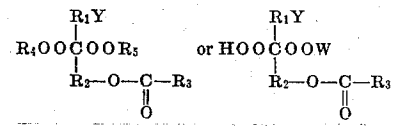
EXAMPLE XV

Crosslinking of Polyvinyl Chloride

The crosslinking of polyvinyl chloride was carried out by incorporating 0.015 moles of the peroxidic compound in 100 parts of Exon 905 polyvinyl chloride resin (Firestone general purpose resin) and 5 parts of Dyphos PG* lead stabilizer (National Lead Co.) and then curing the formulations in a heated press at various

Thus, having described the invention, what is claimed is:

1. A peroxyketal having the formula



in which

R_1 and R_2 are C_1–C_{10} alkylene, C_7–C_{10}-phenalkylene or C_3–C_{12}-cycloalkylene; or

$—R_1—C—R_2—$ is a cyclohexylene ring;

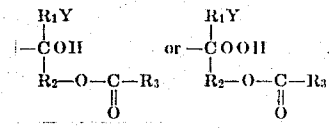
Y is H or

Y is attached to a carbon atom of R_1 which carbon atom also contains an attached hydrogen atom;

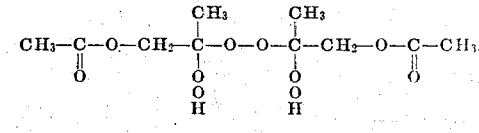
is attached to a carbon atom of R_2 which carbon atom also contains an attached hydrogen atom;

R_3 is C_1–C_{12}-alkyl, C_3–C_{12}-cycloalkyl; C_7–C_{12}-phenylalkyl; phenyl, naphthyl, chlorophenyl or nitrophenyl;

R_4 and R_5 are H, C_4-C_{12}-alkyl or C_4-C_{12}-cycloalkyl; and W is



2. A peroxyketal of claim **1** having the formula



3. 3,3-Dihydroperoxy-2-methylbutyl pivalate.

4. 1,3-Diacetoxy-2,2-bis(t-butylperoxy)propane.

5. 4,4-Bis(pinanylperoxy)pentyl benzoate.

6. A peroxyketal of claim 1, 2,2-bis(t-butylperoxy)-propyl caproate.

7. A peroxyketal of claim 1, 2,2-bis(t-butylperoxy)-propyl acetate.

* * * * *