638. *Alkylperoxy-radicals. Part I. Reactions with 2 : 4 : 6-Trialkylphenols.*

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(*With an Appendix on the Spectroscopic Determination of the Structure of the Reaction Products.* By C. la Lau.)

Several types of alkylperoxy-radicals (RO·O·) were prepared both by cobalt-catalysed decompositions of the corresponding hydroperoxides (RO·OH) and by addition of alkyl radicals (R·) to oxygen. Their reactions with a number of 2 : 4 : 6-trialkylphenols (AH) have been investigated. The main products appeared to be peroxides (RO·OA) having the structure of alkylperoxy-2 : 4 : 6-trialkyl*cyclo*hexadienones. If a *p*-methyl group was present in the phenol, stilbenequinones were also formed. The results are discussed in relation to the inhibitory activity of phenols in autoxidation.

For most liquid-phase autoxidations of hydrocarbons the propagation sequence generally accepted is :

$$R\cdot + O_2 \longrightarrow RO{\cdot}O\cdot;\quad RO{\cdot}O\cdot + RH \longrightarrow RO{\cdot}OH + R\cdot$$

Termination may occur by interaction of the chain-carrying radicals (R· and RO·O·) or by reaction with an inhibitor (Bolland, *Quart. Reviews*, 1949, **3**, 1). The amounts of inhibitor required to suppress oxygen absorption are generally very small—often as little as 0·01%—probably as a result of the large overall kinetic chain lengths. In consequence, the amounts of products formed from the inhibitor are too small for a detailed study, which seriously handicaps investigations into the mode of action of antioxidants.

Abundant evidence is available (Bolland, *loc. cit.*) as regards the predominating part played by alkylperoxy-radicals (RO·O·) in autoxidation. Since the concentration of alkyl radicals (R·) is generally low as a result of their rapid reaction with oxygen to form alkylperoxy-radicals, it seems plausible to assume the inhibitor to operate mainly by reactions with RO·O·. In order to investigate the latter reactions by isolation of products, methods are required for the preparation of alkylperoxy-radicals on a sufficient scale while avoiding the simultaneous oxidation of an excess of other products. Recent literature has dealt to some extent with methods of this kind. Cosgrove and Waters (*J.*, 1951, 388) investigated the oxidation of phenols with benzoyl peroxide and related their results to the mechanism of inhibition and retardation by alkylphenols. Since the benzoyloxy-radical is not quite comparable to the alkylperoxy-radicals involved in autoxidation of hydrocarbons their conclusions need further support. While the present investigation was in progress, Campbell and Coppinger (*J. Amer. Chem. Soc.*, 1952, **74**, 1469) reported the interaction of *tert.*-butyl hydroperoxide and alkylphenols under the influence of cobalt naphthenate. However, only one product was isolated and its structure was not definitely proved.

The present paper deals with the interactions of a number of 2 : 4 : 6-trialkylphenols with various alkylperoxy-radicals.

Production of Alkylperoxy-radicals and Their Reaction with 2 : 4 : 6-*Trialkylphenols.*—The generation of alkylperoxy-radicals and their reaction with phenolic inhibitors was achieved : (*a*) by decomposition of alkyl hydroperoxides dissolved in benzene by cobalt naphthenate at room temperature in the presence of a 2 : 4 : 6-trialkylphenol, and (*b*) by thermal decomposition in benzene solution of compounds producing alkyl radicals in the presence of oxygen and a 2 : 4 : 6-trialkylphenol.

Reactions of type (*a*) were carried out with *tert.*-butyl, 1-tetralyl, αα-dimethylbenzyl, 1 : 1-diphenylethyl, and triphenylmethyl hydroperoxide. The phenols investigated were 2 : 4 : 6-trimethyl-, 2-*tert.*-butyl-4 : 6-dimethyl-, 4-*tert.*-butyl-2 : 6-dimethyl-, 2 : 4-di-*tert.*-butyl-6-methyl-, 2 : 6-di-*tert.*-butyl-4-methyl-, and 2 : 4 : 6-tri-*tert.*-butyl-phenol.

Two mols. of the hydroperoxide (RO·OH) and one mol. of the phenol (AH) were dissolved in benzene, and small quantities of cobalt naphthenate (Co content 15%) (2—4 g. in all) were added until the reaction was complete (temperature between 20° and 30°). The residue obtained on evaporation *in vacuo* was crystallized or distilled in a high vacuum. In most cases it was possible to obtain pure compounds RO·OA, the reactions involved being:

$$\mathrm{RO{\cdot}OH + Co^{+++} \longrightarrow RO{\cdot}O{\cdot} + H^{+} + Co^{++}} \tag{1}$$

$$\mathrm{RO{\cdot}OH + Co^{++} \longrightarrow RO{\cdot} + OH^{-} + Co^{+++}} \tag{2}$$

$$\mathrm{RO{\cdot}O{\cdot} + AH \longrightarrow (RO{\cdot}OAH){\cdot}} \tag{3}$$

$$\mathrm{(RO{\cdot}OAH){\cdot} + RO{\cdot} \longrightarrow RO{\cdot}OA + ROH} \tag{4}$$

Overall:

$$\mathrm{2RO{\cdot}OH + AH \longrightarrow RO{\cdot}OA + ROH + H_2O} \tag{5}$$

Instead of reactions 3 and 4, hydrogen abstraction from the inhibitor may be the first step, the resulting A· radical then combining with RO·O· to give the same products:

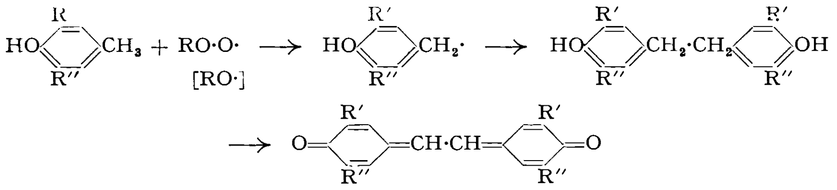
$$\mathrm{RO{\cdot} + AH \longrightarrow ROH + A{\cdot}}$$

$$\mathrm{A{\cdot} + RO{\cdot}O{\cdot} \longrightarrow RO{\cdot}OA}$$

The experimental fact that only catalytic quantities of cobalt naphthenate are necessary for the reaction is expressed by the overall equation (5). Apparently, alkyloxy- and alkylperoxy-radicals are produced in equivalent quantities, the former serving as hydrogen acceptors and yielding an equimolar amount of alcohol. The quantity of alcohol was checked in an experiment with *tert.*-butyl hydroperoxide and an excess of 2 : 6-di-*tert.*-butyl-4-methylphenol; it was proved to be exactly half the amount of the hydroperoxide used.

More than one peroxide may be formed from a 2 : 4 : 6-trialkylphenol; 2 : 4-di-*tert.*-butyl-6-methylphenol and *tert.*-butyl hydroperoxide give a yellow compound of m. p. 70° and a colourless peroxide of m. p. 34°, both having the formula $C_{19}H_{32}O_3$, in yields of 32% and 26% respectively (Table).

Apart from peroxides RO·OA, stilbenequinones are sometimes formed. They must result from an attack of the alkylperoxy- or alkoxy-radical on a *p*-methyl group, followed by dimerization and subsequent dehydrogenation, *e.g.*:



Compounds of this type were isolated when 2 : 4 : 6-trimethyl- and 2-*tert.*-butyl-4 : 6-dimethyl-phenol were treated with hydroperoxides. 2 : 6-Di-*tert.*-butyl-4-methylphenol, though also possessing a *p*-methyl group, did *not* yield a stilbenequinone with most hydroperoxides, but it did so with triphenylmethyl hydroperoxide.

The thermal decomposition (*b*) of compounds producing alkyl radicals, and reaction of the latter with oxygen and inhibitor, were carried out in the following manner: Benzene solutions of 2 : 2′-azo*iso*butyronitrile or 2 : 2 : 3 : 3-tetraphenylbutane and an equimolar quantity of 2 : 4 : 6-trialkylphenol were heated at 60—80° in the presence of a large excess of oxygen until the reaction was complete.* The residue obtained on evaporation was crystallized to yield pure products. When 2 : 6-di-*tert.*-butyl-4-methylphenol was the inhibitor, peroxides could be obtained in the pure state. The reactions are:

$$\mathrm{R{\cdot}N{:}N{\cdot}R \longrightarrow 2R{\cdot} + N_2 \quad [R = Me_2(CN)C{\cdot}]}$$

$$\mathrm{R{\cdot}R \rightleftarrows 2R{\cdot} \quad [R = Ph_2MeC{\cdot}]}$$

$$\mathrm{2R{\cdot} + 2O_2 \longrightarrow 2RO{\cdot}O{\cdot}}$$

$$\mathrm{RO{\cdot}O{\cdot} + AH \longrightarrow (RO{\cdot}OAH){\cdot}}$$

$$\mathrm{(RO{\cdot}OAH){\cdot} + RO{\cdot}O{\cdot} \longrightarrow RO{\cdot}OA + RO{\cdot}OH}$$

Overall:

$$\mathrm{2R{\cdot} + 2O_2 + AH \longrightarrow RO{\cdot}OA + RO{\cdot}OH}$$

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* The time required to obtain a nearly quantitative production of radicals was calculated from the half-life values of azo-compound and hydrocarbon.

In the reaction of 2 : 6-di-*tert.*-butyl-4-methylphenol with 2 : 2 : 3 : 3-tetraphenylbutane and oxygen both the peroxide and the hydroperoxide could be isolated in yields of over 80%. The same phenol, 2 : 2′-azo*iso*butyronitrile, and oxygen gave a peroxide containing the 1-cyano-1-methylethylperoxy-group, in 54% yield. Peroxides could not be obtained by treating the azo-nitrile with oxygen and other 2 : 4 : 6-trialkylphenols; 2-*tert.*-butyl-4 : 6-dimethylphenol yielded a stilbenequinone which was identical with that obtained in the reaction with *tert.*-butyl hydroperoxide. 2 : 4 : 6-Tri-*tert.*-butylphenol gave 2 : 6-di-*tert.*-butylbenzoquinone among other products.

The above reaction schemes are strongly supported by the finding that the same peroxide $Ph_2MeC{\cdot}O{\cdot}OA$ was obtained from 2 : 6-di-*tert.*-butyl-4-methylphenol and (i) the hydroperoxide $Ph_2MeC{\cdot}O{\cdot}OH$ or (ii) $Ph_2MeC{\cdot} + O_2$.

The yields of the products obtained by methods (*a*) and (*b*) are given in the Table.

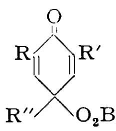
Yields (%) of peroxides from alkyl hydroperoxides and 2 : 4 : 6-trialkylphenols.

	2 : 4 : 6-Trialkylphenols					
Hydroperoxides	2 : 4 : 6-Me_3	2-Bu^t-4 : 6-Me_2	4-Bu^t-2 : 6-Me_2	2 : 4-Bu^t_2-6-Me	2 : 6-Bu^t_2-4-Me	2 : 4 : 6-Bu^t_3
$Bu^tO{\cdot}OH$ ...	7 (3·9 [c]) (52 [a])	25 (3·5 [c]) (20 [a])	46 (1·8 [c]) 13 [d] (3·5 [c])	26 (1·85 [c]) 32 [d] (2·7 [c])	100 (3·85 [c]) —	90 (1·9 [c]) —
1-Tetralyl	—	—	11	33	55	—
$PhMe_2C{\cdot}O{\cdot}OH$...	—	—	—	—	40	48
$Ph_2MeC{\cdot}O{\cdot}OH$...	—	—	—	—	53	—
$Ph_3C{\cdot}O{\cdot}OH$	—	—	—	—	45 [a]	—
$(\colon N{\cdot}CMe_2{\cdot}CN)_2 + O_2$	—	13 [a]	—	—	54	37 [b]
$(CPh_2Me)_2 + O_2$	—	—	—	—	85	—

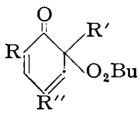
[a] Stilbenequinone. [b] 2 : 6-Di-*tert.*-butylbenzoquinone. [c] Equivs. of hydriodic acid consumed by the peroxides. [d] 2-*tert.*-Butylperoxy-2-methyl-ketones.

Structure of the Peroxidic Products.—The peroxides RO·OA are coloured liquids or colourless crystalline solids, stable at room temperature but often very sensitive to light, which causes a marked discoloration.

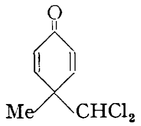
The structure of the products containing a *tert.*-butylperoxy-group has been investigated. The peroxy-group is demonstrated by explosive decomposition at 120—150°. The ultra-violet spectra reveal two types of conjugated double-bond systems, and have been shown to be due to structures (I) and (II) by comparison with the spectra of appropriate model compounds (III) and (IV). The products are all of type (I), except that those covered by footnote *d* in the Table are of type (II). The structure (II) of a yellow peroxide from 2 : 4-di-*tert.*-butyl-6-methylphenol was confirmed by the infra-red spectra in the 6-μ region.



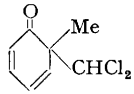
(I)



(II)



(III)



(IV)

The absence of hydroxyl groups was demonstrated by infra-red analysis; this, again, is in agreement with the assigned structures which exclude enolization.

Hydriodic acid reduction revealed interesting differences. Thus, some of the peroxides consume two and others four equivalents of the acid. It appears that those products having a *tert.*-butyl and a *tert.*-butylperoxy-group on the same carbon atom use only two equivalents, whilst the combination of methyl and *tert.*-butylperoxy-groups is connected with a consumption of 3—4 mols. (see Table).

Only some of the reduction products could be isolated. The ketone (I; R = R′ = Me, R″ = Bu^t) gave 2 : 6-dimethylquinol, and (I; R = R′ = Bu^t, R″ = Me) and 2 : 6-di-*tert.*-butyl-4(?)-(1-cyano-1-methylethylperoxy)-4-methyl*cyclo*hexadienone gave 2-*tert.*-butyl-4-methylphenol, all in quantitative yield. A small amount of *tert.*-butylquinol was obtained from (I; R = R′ = R″ = Bu^t). The other peroxy-compounds did not yield pure products.

Reduction of (I; R = R′ = Me, R″ = Bu^t) and of (I; R = R′ = Bu^t, R″ = Me) with octane-1-thiol at 160° regenerated the original phenol.

Differences Between the Various Phenols in Their Reactions with Alkylperoxy-radicals.—Considerable evidence is available with regard to the marked influence of structure on antioxidant efficiencies of alkylphenols (*e.g.*, Wasson and Smith, *Ind. Eng. Chem.*, 1953, **45**, 197; Rosenwald, Hoatson, and Chenicek, *ibid.*, 1950, **42**, 162). However, in inhibited autoxidations of hydrocarbons the antioxidant and the hydrocarbon compete for the alkylperoxy-radicals, whereas the present results are limited to the interaction of the latter radicals and the antioxidants, giving no information on reaction rates.

On the other hand, some interesting differences may be deduced from the Table. Thus, the data presented in the first row (reactions with *tert.*-butyl hydroperoxide and cobalt naphthenate) indicate a decrease in yield of stilbenequinones and an increase in the yield of $Bu^tO{\cdot}OA$ to occur in the series 2 : 4 : 6-Me_3, 2-Bu^t-4 : 6-Me_2, 2 : 6-Bu^t_2-4-Me.

A stilbenequinone is produced in the reaction of triphenylmethyl hydroperoxide and 2 : 6-di-*tert.*-butyl-4-methylphenol, whereas all other hydroperoxides yield peroxides RO·OA with this phenol.

EXPERIMENTAL [With W. ROEST and P. PIET]

Starting Materials.—tert.-*Butyl hydroperoxide.* The crude material, containing about 40% of hydroperoxide, was distilled in a 3-m. Vigreux column, to yield a fraction, b. p. 35—36°/17 mm. (96% of hydroperoxide by iodometric titration).

1-*Tetralyl hydroperoxide.* Tetralin, mixed with 0·02% of cobalt naphthenate, was oxidized with air until at least 20% of the hydroperoxide had been formed. Excess of tetralin was removed in a high vacuum and the residue recrystallized from toluene (m. p. 54—55°; purity >95%).

αα-*Dimethylbenzyl hydroperoxide.* The crude material (75% of hydroperoxide) was purified *via* the sodium salt. Distillation in a high vacuum gave a fraction, b. p. 68—69°/0·08 mm. (97% pure).

1 : 1-*Diphenylethyl hydroperoxide.* This was obtained as a by-product in the reaction of 2 : 6-di-*tert.*-butyl-4-methylphenol with 2 : 2 : 3 : 3-tetraphenylbutane and oxygen. Recrystallization from light petroleum gave a colourless product of m. p. 84°.

Triphenylmethyl hydroperoxide, prepared according to Wieland and Maier (*Ber.*, 1931, **64**, 1205), had m. p. 82°.

2 : 2′-Azo*iso*butyronitrile was synthesized as directed by Bickel and Waters (*Rec. Trav. chim.*, 1950, **69**, 1490).

2 : 2 : 3 : 3-*Tetraphenylbutane.* The directions of Ziegler *et al.* (*Annalen*, 1924, **437**, 227; 1942, **551**, 150) were followed. Slight modifications increased the yield to 80%.

2 : 4 : 6-Trimethylphenol, obtained according to the method of Barclay, Burawoy, and Thomson (*J.*, 1944, 400), had m. p. 72—73°.

6-*tert.*-Butyl-2 : 4-dimethylphenol was purified by extraction with 10% potassium hydroxide solution, distillation *in vacuo* (b. p. 122—128°/14 mm.), and several crystallizations from light petroleum (b. p. 60—80°). The m. p. of the colourless material was 22·5°.

4-*tert.*-Butyl-2 : 6-dimethyl-, 2 : 4-di-*tert.*-butyl-6-methyl,- and 2 : 4 : 6-tri-*tert.*-butyl-phenol were prepared by alkylation of 2 : 6-dimethylphenol, *o*-cresol, and phenol respectively with *tert.*-butanol and sulphuric acid at 70°. M. p.s of the recrystallized products were 82·5°, 52·5°, and 129—130° respectively.

2 : 6-Di-*tert.*-butyl-4-methylphenol of technical quality, when distilled with steam and recrystallized from methanol, had m. p. 71·0°.

Reactions of hydroperoxides with 2 : 4 : 6-trialkylphenols.

General Procedure.—The phenol (0·1 mole) and the hydroperoxide (0·2 mole) were dissolved in 100 ml. of dry, thiophen-free benzene in a brown bottle. Addition of cobalt naphthenate in 200-mg. portions was continued until the temperature, which was held between 20° and 30°, remained constant. At this stage the residual hydroperoxide content was measured by iodometric titration of a sample; it was usually lower than 0·01 mole. The mixture was filtered and the solvent and volatile products were evaporated *in vacuo* (40°/0·25 mm.). The residue was recrystallized or distilled in a high vacuum.

Reactions of tert.-*Butyl Hydroperoxide.*—(a) *With 2 : 4 : 6-trimethylphenol.* The dark-red insoluble crystals of 3 : 5 : 3′ : 5′-tetramethylstilbene-4 : 4′-quinone, filtered and washed with benzene, had m. p. 220° (decomp.) (Found : C, 81·0; H, 6·9. Calc. for $C_{18}H_{18}O_2$: C, 81·2; H, 6·8%). Distillation of the mother-liquor yielded an oil boiling at 60—80°/1·2 mm. It crystallized from methanol at −70°, producing 4-tert.-*butylperoxy*-2 : 4 : 6-*trimethyl*cyclo*hexa*-2 : 5-*dienone*, m. p. 74° (Found : C, 69·4; H, 9·3. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0%).

(b) *With* 2-tert.-*butyl*-4 : 6-*dimethylphenol.* The red, liquid residue was treated with methanol, and the brick-red crystals of 3 : 3′-*dimethyl*-5 : 5′-*di*-tert.-*butylstilbene*-4 : 4′-*quinone* were filtered off and washed with the same solvent; they had m. p. 230° (decomp.) (Found : C, 82·7; H, 8·7. $C_{24}H_{30}O_2$ requires C, 82·3; H, 8·6%). The mother-liquor was distilled in a high vacuum, yielding a yellow-orange fraction, b. p. 62—63°/0·2 mm. The analysis indicates a tert.-*butyl*-tert.-*butylperoxy-dimethyl*cyclo*hexadienone* (Found : C, 72·3; H, 9·5. $C_{16}H_{26}O_3$ requires C, 72·1; H, 9·8%), but the ultra-violet absorption spectrum indicates unknown impurities in addition to the 4-*tert.*-butylperoxy-compound, whereas the 2-*tert.*-butylperoxy-structure is not likely to be present.

(c) *With* 4-tert.-*butyl*-2 : 6-*dimethylphenol.* The partly crystalline residue was recrystallized from ethanol at −70°, yielding 4-tert.-*butyl*-4-tert.-*butylperoxy*-2 : 6-*dimethyl*cyclo*hexa*-2 : 5-*dienone*, m. p. 78° (Found : C, 71·7; H, 9·8%). A second crop was obtained by distilling the mother-liquor in a high vacuum. The partly crystalline distillate, b. p. 94°/1 mm., was again recrystallized from ethanol; the crystals also melted at 78°. Distillation of the final mother-liquor gave an orange liquid, b. p. 83°/0·5 mm. Its analysis is correct for a tert.-*butyl*-tert.-*butylperoxy-dimethyl*cyclo*hexadienone* (Found : C, 71·5; H, 9·7%). According to the ultra-violet spectrum it may have the 2-*tert.*-butylperoxy-structure, whilst the 4-*tert.*-butylperoxy-derivative is absent.

(d) *With* 2 : 4-*di*-tert.-*butyl*-6-*methylphenol.* The partly crystalline residue was treated with methanol at −70° and filtered, yielding yellow 2 : 4-*di*-tert.-*butyl*-6-tert.-*butylperoxy*-6-*methyl*cyclo*hexa*-2 : 4-*dienone*, m. p. 70° (Found : C, 74·0; H, 10·5. $C_{19}H_{32}O_3$ requires C, 74·0; H, 10·5%). The mother-liquor was distilled in a high vacuum, the fraction of b. p. 90°/0·5 mm. yielding colourless 2 : 4-*di*-tert.-*butyl*-4-tert.-*butylperoxy*-6-*methyl*cyclo*hexa*-2 : 5-*dienone*, m. p. 34°, after crystallization from ethanol at −70° (Found : C, 74·1; H, 10·4%).

(e) *With* 2 : 6-*di*-tert.-*butyl*-4-*methylphenol.* Recrystallization of the residue from ethanol gave 2 : 6-di-*tert.*-butyl-4-*tert.*-butylperoxy-4-methyl*cyclo*hexa-2 : 5-dienone, m. p. 87° (Found : C, 74·4; H, 10·6%). Campbell and Coppinger (*J. Amer. Chem. Soc.*, 1952, **74**, 1469) have recorded m. p. 74°. Hydrogenation over Adams catalyst in glacial acetic acid, removal of the solvent *in vacuo*, and crystallization from ethanol produced a *dihydro*-derivative, m. p. 78—79° (Found : C, 73·5; H, 11·2. $C_{19}H_{34}O_3$ requires C, 73·5; H, 11·0%). This product still contains the peroxy-grouping.

The amount of *tert.*-butanol formed was determined in a separate experiment with 0·050 mole each of hydroperoxide and phenol. Benzene and the volatile products were distilled and dried (Na_2SO_4). *tert.*-Butanol was determined spectroscopically (Found : 0·0252 mole).

(f) *With* 2 : 4 : 6-*tri*-tert.-*butylphenol.* The liquid, green-yellow residue was crystallized from methanol at −70°, yielding green-yellow 2 : 4 : 6-*tri*-tert.-*butyl*-4-tert.-*butylperoxy*cyclo*hexa*-2 : 5-*dienone*, m. p. 5° (Found : C, 75·3; H, 11·0. $C_{22}H_{38}O_3$ requires C, 75·4; H, 10·9%). According to the ultra-violet absorption spectrum this preparation may contain some of the 2-*tert.*-butylperoxy-derivative. Distillation of the mixture in a high vacuum gave a brown-green liquid, b. p. 85°/0·15 mm., which gave correct analyses but could not be crystallized. An attempt to hydrogenate this peroxide over Adams catalyst in acetic acid was unsuccessful.

Reactions of 1-*Tetralyl Hydroperoxide.*—(a) *With* 4-tert.-*butyl*-2 : 6-*dimethylphenol.* Treatment of the residue with ethanol produced yellow 4-tert.-*butyl*-2 : 6-*dimethyl*-4(?)-1′-*tetralylperoxy*cyclo*hexadienone*, m. p. 104° (Found: C, 77·8; H, 8·4. $C_{22}H_{28}O_3$ requires C, 77·6; H, 8·3%).

(b) *With* 2 : 4-*di*-tert.-*butyl*-6-*methylphenol.* The residual syrup was diluted with an equal volume of ethanol; the resulting yellow crystals of 2 : 4-*di*-tert.-*butyl*-6-*methyl*-4(?)-1′-*tetralylperoxy*cyclo*hexadienone* had m. p. 91° after recrystallization from methanol (Found : C, 78·7; H, 9·0. $C_{25}H_{34}O_3$ requires C, 78·5; H, 9·0%). The mother-liquor yielded a product, m. p. 95°, which proved to be identical with the peroxide of m. p. 91° (mixed m. p. 93°). The m. p. of the first product could also be raised to 95° by repeated recrystallizations.

(c) *With* 2 : 6-*di*-tert.-*butyl*-4-*methylphenol.* The residue was recrystallized from methanol, yielding 2 : 6-*di*-tert.-*butyl*-4-*methyl*-4(?)-1′-*tetralylperoxy*cyclo*hexadienone*, m. p. 104° (Found : C, 78·7; H, 8·8%).

Reactions of αα-Dimethylbenzyl Hydroperoxide.—(a) *With* 2 : 6-*di*-tert.-*butyl*-4-*methylphenol.*

The residue, in light petroleum, was extracted with 2N-hydrochloric acid in order to remove cobalt salts. Evaporation of the solvent produced a syrup which was crystallized from methanol at −70°. Recrystallization from ethanol yielded colourless 2 : 6-*di*-tert.-*butyl-αα-dimethylbenzylperoxy-4-methyl*cyclo*hexadienone*, m. p. 42·5° (Found: C, 77·8; H, 9·3. $C_{24}H_{34}O_3$ requires C, 77·8; H, 9·25%).

(b) *With* 2 : 4 : 6-*tri*-tert.-*butylphenol.* Cobalt was removed as previously described. Crystallization from ethanol gave yellow 2 : 4 : 6-*tri*-tert.-*butyl*-4(?)-*αα-dimethylbenzylperoxy*cyclo*hexadienone*, m. p. 35° (Found: C, 78·7; H, 9·8. $C_{27}H_{40}O_3$ requires C, 78·6; H, 9·8%).

Reaction of 1 : 1-*Diphenylethyl Hydroperoxide with* 2 : 6-*Di*-tert.-*butyl-4-methylphenol.*—Cobalt was extracted with hydrochloric acid. Crystallization of the residue from ethanol at −15° gave colourless 2 : 6-*di*-tert.-*butyl*-4(?)-(1 : 1-*diphenylethylperoxy*)-4-*methyl*cyclo*hexadienone*, m. p. 67° (Found: C, 80·4; H, 8·5. $C_{29}H_{36}O_3$ requires C, 80·5; H, 8·4%). The mother-liquor was evaporated and the residue treated with light petroleum. The light brown crystals obtained had m. p. 80·5° (with 1 : 1-diphenylethanol, mixed m. p. 80·5—81°).

Reaction of Triphenylmethyl Hydroperoxide with 2 : 6-*Di*-tert.-*butyl-4-methylphenol.*—The red crystalline residue of 3 : 5 : 3′ : 5′-tetra-*tert.*-butylstilbene-4 : 4′-quinone was washed with ethanol and recrystallized from glacial acetic acid; it had m. p. 303° (decomp.) (Found: C, 82·8; H, 9·7. Calc. for $C_{30}H_{42}O_2$: C, 82·9; H, 9·7%).

Reactions of 2 : 2′-*azo*iso*butyronitrile and* 2 : 2 : 3 : 3-*tetraphenylbutane with oxygen and* 2 : 4 : 6-*trialkylphenols.*

General Procedure.—The phenol (0·1 mole) and the nitrile or butane (0·1 mole) were dissolved in dry, thiophen-free benzene (150 ml.) and a rapid stream of dry oxygen was bubbled through the solution by means of a sintered-glass plate for 6 hr. at 80° or 60°. The reaction mixture was evaporated in *vacuo* (40°/0·25 mm.).

Reactions of the Nitrile.—(a) *With* 2-tert.-*butyl*-4 : 6-*dimethylphenol and oxygen.* Methanol was added to the residue, and the red crystals of 5 : 5′-di-*tert.*-butyl-3 : 3′-dimethylstilbene-4 : 4′-quinone were filtered off. They had m. p. 230° (decomp.) after recrystallization from ethyl methyl ketone.

(b) *With* 2 : 6-*di*-tert.-*butyl-4-methylphenol and oxygen.* The crude material was recrystallized from methanol, yielding colourless 2 : 6-*di*-tert.-*butyl*-4(?)-(1-*cyano*-1-*methylethylperoxy*)-4-*methyl*cyclo*hexadienone*, m. p. 92·5° (Found: C, 71·9; H, 9·6; N, 4·4. $C_{19}H_{29}O_3N$ requires C, 71·5; H, 9·2; N, 4·4%).

(c) *With* 2 : 4 : 6-*tri*-tert.-*butylphenol and oxygen.* Distillation of the residue with steam produced orange-yellow crystals, m. p. 68° after recrystallization from methanol (Found: C, 76·1; H, 9·3. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·15%). Reduction with zinc in boiling 90% acetic acid yielded a *quinol*, m. p. 103° (from light petroleum) (Found: C, 75·7; H, 9·9. $C_{14}H_{22}O_2$ requires C, 75·6; H, 9·9%). The oxidation product of m. p. 68° should therefore be 2 : 6-*di*-tert.-*butylbenzoquinone*, since the derived quinol is not identical with 2 : 5-di-*tert.*-butylquinol, m. p. 216°.

Reaction of 2 : 2 : 3 : 3-*Tetraphenylbutane with* 2 : 6-*Di*-tert.-*butyl-4-methylphenol and Oxygen.*—Light petroleum was added to the residue, yielding crystals of 1 : 1-diphenylethyl hydroperoxide (93%). Recrystallization from the same solvent raised the m. p. to 84°. The filtrate was evaporated *in vacuo* and the residue treated with ethanol. The colourless crystals of 2 : 6-di-*tert.*-butyl-4(?)-(1 : 1-diphenylethylperoxy)-4-methyl*cyclo*hexadienone had m. p. 67° after recrystallization and were identical with those obtained by reaction of the phenol with 1 : 1-diphenylethyl hydroperoxide.

Reduction of peroxidic products.

General Procedure with Hydriodic Acid.—The peroxide (6·0 g.) was dissolved in acetic acid (200 ml.), mixed with freshly distilled 57% hydriodic acid (60 ml.), kept at 65° for 45 min., and then poured into water. Iodine was removed with concentrated sodium thiosulphate solution, and the excess of hydriodic acid neutralized with sodium hydroxide. Reduction products were extracted with ether.

Reduction of (I; $R = R' = Me$, $R'' = Bu^t$).—The crude product, recrystallized several times from toluene, had m. p. 148—149° (Found: C, 69·5; H, 7·3. Calc. for $C_8H_{10}O_2$: C, 69·5; H, 7·3%), alone or mixed with 2 : 6-dimethylquinol.

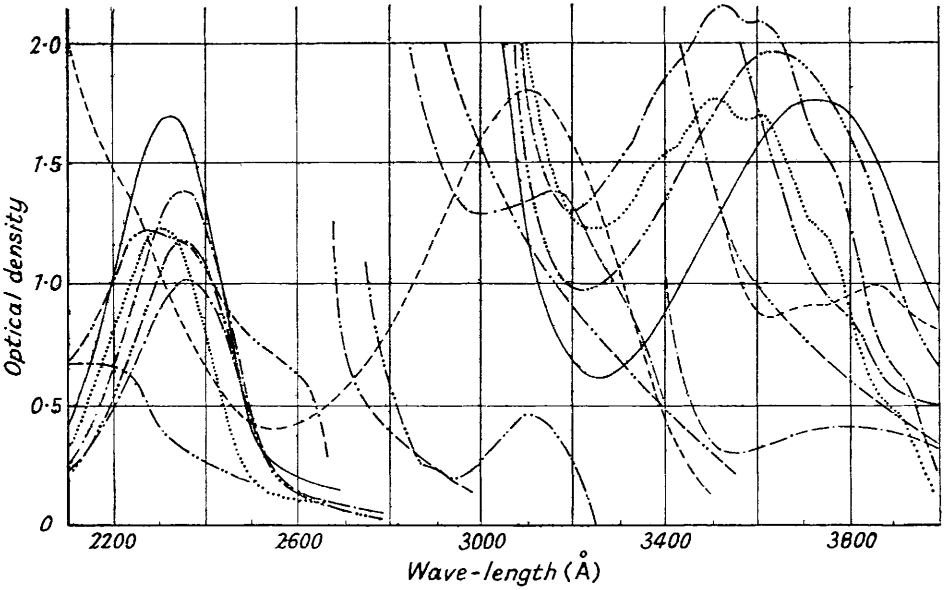
Reduction of (I; $R = R' = Bu^t$, $R'' = Me$).—The residual oil, crystallized from light petroleum, had m. p. 52° (Found: C, 80·2; H, 10·0. Calc. for $C_{11}H_{16}O$: C, 80·4; H, 9·8%). It was 2-*tert.*-butyl-4-methylphenol (mixed m. p.).

Reduction of (I; R = R′ = R″ = Bu^t).—The crude product, *tert.*-butylquinol, recrystallized three times from toluene, had m. p. and mixed m. p. 127—128° (Found: C, 72·4; H, 8·4. Calc. for $C_{10}H_{14}O_2$: C, 72·3; H, 8·5%).

Reduction of 2 : 6-*Di*-tert.-*butyl*-4(?)-(1-*cyano*-1-*methylethylperoxy*)-4-*methyl*cyclo*hexadienone*.—2-*tert*.-Butyl-4-methylphenol was isolated as described above.

Reductions with Octane-1-*thiol*.—Octane-1-thiol (150 g.) was kept at 160—170° and 0·05 mole of the peroxide was added in small portions. The excess of thiol was removed at 20 mm. and the residue was treated with a solution of iodine in benzene to oxidize residual thiol to disulphide. The reduction product was then distilled in a high vacuum.

FIG. 1. *Ultra-violet absorption spectra of* tert.-*butylperoxy*-2 : 4 : 6-*trialkyl*cyclo*hexadienones*.



R	R′	R″	Curve	Concns. (g./l.) (4000 ⟶ 2100 Å); cell thickness (cm.) in parentheses			
Compounds (I)							
Me	Me	Me	···············	4·18 (5)	0·0209 (1)		
Me	Bu^t	Me	– – · – – – – – – – – ·	1·40 (5)	1·40 (1)	0·140 (1)	0·280 (1)
Me	Me	Bu^t	— · — · — · — · —	5·28 (5)	0·0264 (1)		
Bu^t	Me	Bu^t	— ··· — ··· — ···	5·74 (5)	0·0287 (1)		
Bu^t	Bu^t	Me	———————	4·80 (5)	0·0480 (1)		
Bu^t	Bu^t	Bu^t	– – – – – · – – – – – ·	3·30 (1)	1·65 (1)	0·0330 (1)	
Compounds (II)							
Me	Me	Bu^t	·· — ·· — ·· — ··	2·40 (5)	2·40 (1)	0·0240 (1)	
Bu^t	Me	Bu^t	— — — — — — —	0·750 (2·5)	0·150 (1)		

The crude product from (I; R = R′ = Me, R″ = Bu^t) had a boiling range of 70—130°/0·2 mm. and solidified partly. Filtration and washing with light petroleum gave a 52% yield of 4-*tert*.-butyl-2 : 6-dimethylphenol.

The crude material from (I; R = R′ = Bu^t, R″ = Me) boiled at 80—90°/0·3 mm. Seeding with 2 : 6-di-*tert*.-butyl-4-methylphenol yielded crystals (60%), m. p. 70°.

SPECTROSCOPY OF *tert*.-BUTYLPEROXY-2 : 4 : 6-TRIALKYL*cyclo*HEXADIENONES.

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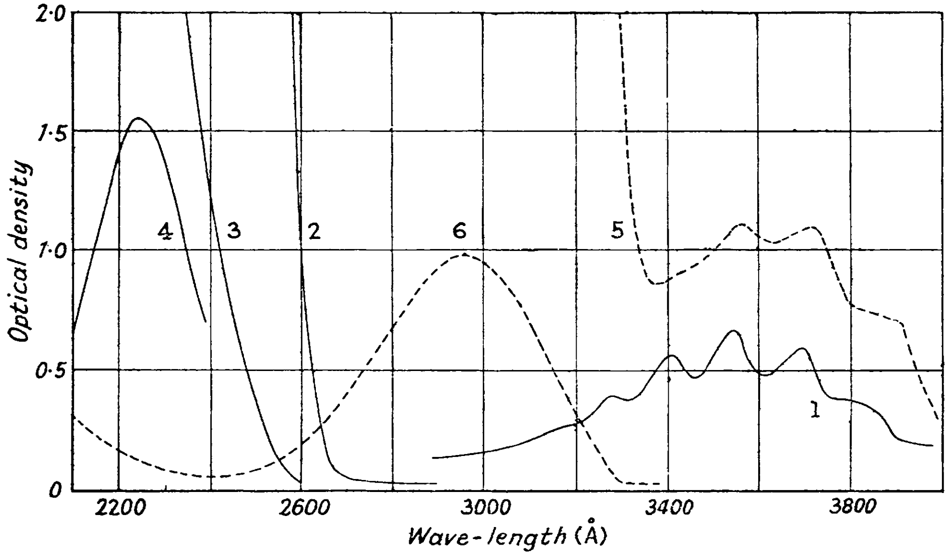
The ultra-violet absorption spectra of the peroxidic products in *iso*octane were recorded from 2100 to 4000 Å on a Cary-UV-recording spectrometer. They are shown in Fig. 1. The ultra-violet spectra of the reference compounds (III) and (IV) are in Fig. 2. Infra-red absorption spectra from 5·7 to 6·2 μ were investigated with a Beckman-IR-2 spectrometer with a lithium fluoride prism and carbon tetrachloride as solvent. Concentrations of 10% and a cell length of 0·096 mm. were used throughout.

Although additional work was carried out on the presence of hydroxyl groups and peroxy-linkages the spectroscopic data will not be presented, since they scarcely contributed to elucidation of structures.

Comparison of the ultra-violet spectra of the peroxides with those of (III) and (IV) shows the presence of the two types (I) and (II). Infra-red analysis shows the absence of hydroxyl groups in all compounds—enolization could occur only with a *meta*-substituted *tert.*-butylperoxide. Moreover, enolization would lead to an alkyl-phenol with a strong band around 2800 Å characteristic of the benzene nucleus. The ultra-violet spectra clearly show that such bands are absent.

FIG. 2. *Ultra-violet absorption spectra of* 4-*dichloromethyl*-4-*methyl*cyclo*hexa*-2 : 5-*dienone* (III) *and* 2-*dichloromethyl*-2-*methyl*cyclo*hexa*-3 : 5-*dienone* (IV).



	Concn. (g./l.)	Cell thickness (cm.)		Concn. (g./l.)	Cell thickness (cm.)
(III), 1	1·934	5	(IV), 5	1·922	1
2	1·934	1	6	0·0384	1
3	0·0386	1			
4	0·0193	1			

The introduction of one or more *tert.*-butyl groups *ortho* to the carbonyl group removes the fine structure exhibited in the weak band around 3700 Å, in accordance with previous experience. If the fine structure is neglected, the main absorption regions are only slightly affected by the nature of the substituents.

The spectra prove the structures allotted in the preceding sections.

Although less promising than the ultra-violet region the so-called infra-red double-bond region was included, since all the samples have complicated double-bond systems. However, it did not provide a general means of discriminating between (I) and (II); they depended on the conjugated systems as well as on the nature of the substituents. The only compound known from the ultra-violet spectrum to be of type (II) did *not* exhibit the intense band at 6·07 ± 0·004 μ present in all the compounds of type (I). This result, though of no great importance, is in agreement with the conclusions drawn from the ultra-violet data.

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