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# Antioxidants and Stabilizers

# LXVI. Oxidation and Photooxidation of Methyl- and Octadecyl-3-(3,5-di-tertbutyl-4-hydroxyphenyl)propionates. Quenching of Singlet Oxygen<sup>a</sup>

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#### SUMMARY:

Photooxidation of the methyl ester (Ib) and octadecyl ester of 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid (Ic) sensitized with methylene blue gives rise to cyclohexadienone hydroperoxides IIIb or IIIc. The reaction proceeds via singlet oxygen. The photochemical stability of both hydroperoxides was examined in the presence and absence of sensitizer.The thermal decomposition of both hydroperoxides leads to the respective startingphenols Ib or Ic. Oxidation of Ib with lead dioxide yields IV, an effective quencher $of singlet oxygen, the effect of which approaches that of <math>\beta$ -carotene. In a neutral medium IV is stable against oxidation. The transformations are investigated with respect to the system of processes occurring in the aging of stabilized polyolefins.

#### ZUSAMMENFASSUNG:

Die Cyclohexadienonhydroperoxide IIIb und IIIc entstehen durch methylenblau-sensibilisierte Photooxidation von Methyl- (Ib) und Octadecylester (Ic) der 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionsäure. Die Reaktion verläuft über den Singulett-Sauerstoff. Es wurde die photochemische Stabilität der beiden Hydroperoxide in Anwesenheit und Abwesenheit des Sensibilisators verfolgt. Beide Hydroperoxide spalten sich thermisch unter Bildung der Ausgangsphenole Ib bzw. Ic. Die Verbindung IV, die einen wirksamen Quencher (Löscher) von Singulett-Sauerstoff darstellt, entsteht durch die Oxidation von Ib mittels Bleidioxid. Sie nähert sich in ihrer Wirkung dem  $\beta$ -Karotin. Die Verbindung IV ist gegen weitere Oxidation im neutralen Milieu beständig. Es wurden die Umwandlungen von Ib und Ic im Hinblick auf die Prozesse, die während der Alterung von stabilisierten Polyolefinen verlaufen, verfolgt.

<sup>&</sup>lt;sup>a</sup> Part LXV: L. Taimr and J. Pospíšil, this journal 52 (1976) 31.

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## Introduction

It was found in investigating the oxidation of stabilizers of polyolefins, 2,6-di-tert-butyl-4-methylphenol (Ia) and 2,2'-methylenebis(4-methyl-6-tert-butylphenol), with singlet  $oxygen^{1,2}$  that the reaction was rather fast.



The reaction is of great importance in practical uses of the antioxidants, because under the conditions of atmospheric aging polymeric materials come into contact with singlet oxygen. Besides the loss of the antioxidants, their transformation products also become operative, interfering with the whole process in a rather complicated way. The investigation was continued because of the importance of such reactions with methyl and octadecyl esters of 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid (Ib, Metilox<sup>®</sup>; Ic, Irganox 1076<sup>®</sup>, Ciba-Geigy, A. G.) chosen for further study. The latter ranks among important antioxidants used in industry, characterized by low volatility and good compatibility with polyolefins. The objective of the investigation was oxidation of the above phenols with singlet oxygen and comparison with 2,6-di-tert-butyl-4-methylphenol having a similar structure (Ia), and a study of the properties and possibilities of preparation of compounds similar to 3,5, 3',5'-tetra-tert-butylstilbenequinone (IIa), obtained by one-electron oxidation of phenol Ia<sup>3,4</sup>.



Compounds of this type are also formed in the polymer during aging<sup>5</sup>. Since they behave as effective quenchers of singlet oxygen<sup>6</sup>, the knowledge of their properties is closely connected with the subject under investigation.

## **Results and Discussion**

The reaction of Metilox<sup>®</sup> (Ib) and Irganox 1076<sup>®</sup> (Ic) with singlet oxygen was studied predominantly by using photooxidation sensitized with methylene

blue. This sensitizer is commonly used for generating singlet oxygen, and its spectrum in the visible region remains virtually unoverlapped by the spectra of effective quenchers, such as  $\beta$ -carotene, nickel dibutyldithiocarbamate or tetra-tert-butylstilbenequinone IIa, so that by using a suitable light filter one can rule out the screening effect of the quenchers and employ them in studying the oxidation mechanism. A mixture of methanol and dichloromethane, in which all the components used are readily soluble, was employed as solvent.

Only one main product is formed in the sensitized photooxidation of the two antioxidants (Tab. 1, Fig. 1); it was isolated in a yield of 57% (from Ib), or 38% (from Ic) and identified as the hydroperoxy derivative of cyclohexadienone (IIIb, c).



The lower yield in the oxidation of Irganox  $1076^{\text{(s)}}$  can be explained by a lower oxidation rate and thus a larger participation of side reactions, on the one hand, and by larger losses in the crystallization, on the other. (The product is readily soluble in organic solvents. This is connected with the high compatibility of both the starting phenol Ic and the hydroperoxidic

Tab. 1. Photooxidation of phenolic antioxidants Ia, b, c (conc. 0.05 mol/l) at  $30.5 \,^{\circ}\text{C}$ . v is the oxidation rate in ml O<sub>2</sub>/min, measured at the beginning of oxidation after establishment of thermal equilibrium.

Antioxidant	V <sup>a</sup>	$\mathbf{v}^{\mathbf{b}}$
2,6-Di-tert-butyl-		- <u></u>
4-methylphenol (Ia)	$0.084 \pm 0.017$	$0.133 \pm 0.026$
Metilox <sup>®</sup> (Ib)	$0.059 \pm 0.012$	$0.063 \pm 0.012$
Irganox 1076 <sup>®</sup> (Ic)	$0.033 \pm 0.007$	$0.055 \pm 0.011$

<sup>a</sup> Sensitized with methylene blue (conc. 0.01 mol/l) in a solution of 9.7 ml dichloromethane and 0.3 ml methanol, light filter  $10\% \text{ K}_2\text{Cr}_2\text{O}_7$ , 1 cm.

<sup>b</sup> Sensitized with Rose Bengal (conc. 0.001 mol/l) in a solution of 5 ml dichloromethane and 5 ml methanol, light filter  $0.5\% K_2Cr_2O_7$ , 1 cm.

transformation product IIIc with polyolefins). The rates of oxidation decrease in the order 2,6-di-tert-butyl-4-methylphenol > Metilox<sup>®</sup> > Irganox<sup>®</sup>. The same dependence was observed also with Rose Bengal as sensitizer (Tab. 1); here, however, the difference in the oxidation rate of Metilox<sup>®</sup> and Irganox  $1076^{®}$  is smaller and lies already within the limits of experimental error. The oxidation rate of Irganox  $1076^{®}$  becomes markedly lower only in the later oxidation stage.

After consumption of one mole oxygen per one mole antioxidant the reaction rate becomes much slower, but another slow oxidation takes place in the presence of methylene blue. Both reaction stages are well discernible with



Fig. 1. Absorption curves of oxygen in the photooxidation sensitized with methylene blue (conc. 10<sup>-3</sup> mol/l) in the mixture dichloromethane-methanol (97:3); conc. of substrate 0.05 mol/l each time; 1: Ia, 2: Ib, 3: Ic, 4: IIIa.

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2,6-di-tert-butyl-4-methylphenol and Metilox<sup>®</sup>. In the case of Irganox  $1076^{\text{®}}$ , which is oxidized more slowly, both stages cannot be distinguished with such ease, and the rate continuously decreases (Fig. 1).

The second reaction stage is due to the sensitized photooxidation (or photolysis and oxidation of the products) of the cyclohexadienone-hydroperoxide type III formed in the reaction, as proved by the sensitized photooxidation of pure hydroperoxide IIIa. Fig. 1 shows that hydroperoxide IIIa is oxidized in the presence of methylene blue. This was not observed with Rose Bengal as sensitizer, but it was found that this sensitizer changed under the experimental conditions used. The Rose Bengal undergoes transformation in the presence of hydroperoxide also in an inert atmosphere (argon). In the absence of hydroperoxide IIIa Rose Bengal is stable also in oxygen.

In the absence of sensitizer hydroperoxides IIIa, b, c are quite stable at the wavelength used, but photooxidation takes place at shorter wavelengths. Light absorption exhibited by these hydroperoxides at 378 nm (maximum; under the experimental conditions absorption reaches up to 430 nm) is quite sufficient for the reaction.

It may be assumed that the mechanism of photooxidation of Metilox® and of Irganox 1076<sup>®</sup> is the same as for 2,6-di-tert-butyl-4-methylphenol<sup>1</sup>, i.e. that it is singlet oxygen in the first place that attacks the phenol molecule, while the excited sensitizer is operative to a much less extent, if at all. This was verified with Irganox 1076<sup>®</sup> whose behaviour differs more from 2,6-di-tert-butyl-4-methylphenol than that of Metilox<sup>®</sup>. The oxidation was performed with chemically generated singlet oxygen. The decomposition of an adduct of triphenylphosphite with ozone<sup>7</sup>, occurring at a low temperature and in a neutral medium, was chosen for this purpose. Irganox 1076<sup>®</sup> oxidizes very slowly; the reaction mixture contained a large amount of the starting antioxidant. By comparing with a control test carried out without antioxidant Ic it was proved that the reaction mixture contained only one product, namely, hydroperoxide IIIc. This compound was found to be identical with hydroperoxide formed in the photooxidation by means of chromatography using various detectors. An attempt at isolating this compound by column chromatography on silicagel ended in decomposition. For this reason, the photooxidation mechanism was also proved by examining the effect of quenchers of singlet oxygen on the reaction rate. The results are summarized in Fig. 2. All the quenchers used, i.e.  $\beta$ -carotene<sup>8</sup>, nickel dibutyldithiocarbamate<sup>9</sup> and tetra-tertbutylstilbenequinone (IIa)<sup>6</sup> reduce the oxidation rate. Acceleration in the later oxidation stage with  $\beta$ -carotene and nickel dibutyldithiocarbamate is due



Fig. 2. Absorption curves of oxygen in the photooxidation of antioxidant Ic (conc. 0.05 mol/l) sensitized with methylene blue (conc.  $10^{-3}$  mol/l) in the mixture dichloromethane-methanol (97:3) in the presence of quenchers; 1: without quencher, 2: nickel dibutyldithiocarbamate, 3:  $\beta$ -carotene, 4: IIa, 5: IV.

to the gradual disappearance of the quencher from the reaction mixture, as demonstrated also by TLC. On the other hand, the quencher IIa is stable under the experimental conditions.

In the second part of the work we investigated the synthesis and photochemical properties of a compound formed from Metilox<sup>®</sup> by oxidation analogous to the formation of stilbenequinone IIa from 2,6-di-tert-butyl-4-methylphenol. Lead dioxide was chosen as the oxidizing agent<sup>4</sup>. The reaction is accelerated by the presence of a small amount of methanol, but it also occurs in its absence. A larger amount of methanol leads to the formation of some further products, which have not been investigated in greater detail. The analysis of the main product has revealed that the compound involved is IV and not IIb. The structure of IV was also verified by demonstrating connections with V and VI described in the literature<sup>10,11</sup> (Scheme 1). By reduction with sodium dithionite, IV is readily transformed into VI. The reduction may also be carried out by hydrogen on platinum after Adams, because further hydrogenization to yield bisphenol with fully reduced aliphatic bonds proceeds very slowly. By oxidation with potassium ferricyanide in an alkaline medium VI is almost quantitatively retransformed into IV; oxidation can



- <sup>a</sup> Lead dioxide
- <sup>b</sup> Potassium ferricyanide in alkaline medium
- <sup>c</sup> Silver oxide, ref.<sup>12</sup>
- <sup>d</sup> Taken from literature<sup>10</sup>
- e Rearrangement on aluminium oxide, ref.<sup>10</sup>
- $^{\rm f}$  Hydrogenization on platinum or reduction with  $\rm Na_2S_2O_4$

also be performed with lead dioxide. In the oxidation of phenol Ib with lead dioxide, V was also isolated as a side product; it is an intermediate, and consists of two compounds, according to TLC. Here we have a mixture of the two described<sup>10</sup> diastereomers, as proved by comparing NMR spectra with the literature data and by carrying out the described rearrangement to the more stable bisphenol VI. Further oxidation with lead dioxide transforms V into IV. V may also be obtained by oxidizing phenol Ib with potassium ferricyanide in an alkaline medium. The oxidation can also be performed by using silver oxide as described in the literature<sup>12</sup>, where, however, the structure of V was wrongly determined as quinonemethide VII:



According to reactions in Scheme 1, it seems very likely that IV is formed from Metilox<sup>®</sup> via intermediates V and VI. Lead dioxide is operative here as an oxidizing agent and as catalyst in the rearrangement of V to VI, similarly to aluminium oxide.

Sensitized photooxidation of 1,3-cyclohexadiene, which proceeds via singlet oxygen<sup>13</sup>, was used in the investigation of IV as quencher of singlet oxygen. The results are summarized in Tab. 2. IV is approximately as effective a quencher of singlet oxygen as tetra-tert-butyl-stilbenequinone (IIa). Similar results were obtained also in the sensitized photooxidation of Irganox 1076<sup>®</sup> (Fig. 2) and 2,3-dimethyl-2-butene. IV, similarly to stilbenequinone IIa, is very stable towards oxidation, if the reaction is carried out in a neutral medium. Compared with IIa, it is more readily soluble in organic solvents, and one may infer that it will exhibit higher compatibility with polymers.

Phenol Ic is oxidized with lead dioxide similarly to Ib, but the orangecoloured product formed in the reaction could not be isolated in a completely pure form. The compound dissolves readily in nonpolar solvents and also behaves as an effective quencher of singlet oxygen.

The final part of the work is dealing with the thermal properties of hydroperoxides IIIb and IIIc by means of DTA and by the chromatographic analysis Tab. 2. Relative initial rates of the photooxidation, w, of 1,3-cyclohexadiene (conc. 0.05 mol/l) sensitized with methylene blue (conc. 0.001 mol/l) in the mixture 9.7 ml dichloromethane + 0.3 ml methanol in the presence of various quenchers (conc.  $0.9 \times 10^{-3} \text{ mol/l}$ ) at 30.5 °C.

Quencher	w <sup>a</sup>
	1.00
IIa	0.18
IV	0.17
Nickel dibutyldithiocarbamate	0.09
β-carotene	0.05
IIa IV Nickel dibutyldithiocarbamate β-carotene	0.1 0.1 0.0 0.0

<sup>a</sup> Related to rate without quencher.

of the decomposed mixture. At a rate of heating of  $10^{\circ}$ C/min both compounds decompose exothermally at ca.  $130^{\circ}$ C, with a maximum near  $170^{\circ}$ C. In both cases the main decomposition product is always antioxidant Ib or Ic. The compounds behave in the same way as hydroperoxides derived from 2,6-di-tert-butyl-4-methylphenol (Ia)<sup>1</sup> and from 2,2'-methylene-bis(4-methyl-6-tert-butylphenol)<sup>2</sup>.

#### *Experimental*

## Materials

Methyl and octadecyl esters of 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid (Ib, Metilox<sup>®</sup>; Ic, Irganox 1076<sup>®</sup>), Ciba-Geigy A. G., Switzerland; 2,6-di-tert-butyl-4-methylphenol (Ia), J. Dimitrov Works, ČSSR; methylene blue, Lachema, ČSSR; Rose Bengal (3',4',5',6'-tetrachloro-2,4,5,7-tetraiodofluoresceine disodium salt), Fluka, Switzerland, recrystallized from the ethanol-ether mixture (according to TLC on silicagel in the system 9 parts isopropyl alcohol + 1 part aqueous ammonia conc., containing a small amount of coloured impurity); 1,3-cyclohexadiene, Fluka, Switzerland; 2,3-dimethyl-2-butene, Fluka, Switzerland;  $\beta$ -carotene, Koch-Light Laboratories, England, recrystallized from the mixture chloroform-methanol; nickel dibutyldithiocarbamate, Dimitrov Works, ČSSR, recrystallized from ethanol; 3,5',5'-tetra-tert-butylstilbenequinone (IIa), prepared after Cook<sup>3</sup>; 2,6-di-tert-butyl-4-methyl-4-hydroperoxy-2,5-cyclohexadiene-1-one (IIIa), prepared after Kharasch<sup>14</sup>.

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### Analytical methods

NMR spectra were recorded with a JEOL PS-100 spectrometer; UV spectra were recorded with a Varian Cary 14 spectrometer, and Perkin-Elmer type 457 apparatus was used for obtaining IR spectra. DTA was carried out on a Du Pont 900 Differential Thermal Analyzer; mol. wt. was determined with a Vapour-Pressure-Osmometer, Hitachi Perkin-Elmer, model 115 (benzene). In TLC, precoated silicagel sheets (Silufol UV 254 with a luminescence indicator, Kavalier, ČSSR) were used, with detection under a UV lamp (254 nm) and with spraying (8g potassium permanganate in 500 ml water + 1.5 ml conc. sulphuric acid: reagent in excess was carefully washed out with water after spraying). Hydroperoxides of type III were moreover detected by spraying with a freshly prepared 10% solution of sodium iodide in water (starch is the binding agent for silicage).

#### Photolyses and Photooxidations

The light stability of cyclohexadienone hydroperoxides IIIb, IIIc in the absence of sensitizer was examined in a quartz cell (1.5 cm thick) in a heptane solution (5 ml, conc.  $5 \times 10^{-3}$  mol/l) at 30 °C in an inert atmosphere (argon) or in oxygen (oxygen consumption was followed volumetrically) with a mercury lamp (1000 W, DRŠ-1000, SSSR) and glass or interference filters.

All photochemical reactions occurring in the presence of sensitizer (conc.  $10^{-3}$  mol/l) were performed in an apparatus described elsewhere<sup>1</sup> using a 600 W halogen bulb (Tesla) and liquid light filters (1 cm, 10% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> for methylene blue, 0.5% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> for Rose Bengal). Concentration of the substrate was 0.05 mol/l each time. The stability of hydroperoxide IIIa was measured in an oxygen or argon atmosphere in the presence of Rose Bengal (solution in the mixture dichloromethan:methanol, 1:1) or methylene blue (mixture dichloromethane:methanol, 97:3). Sensitized photooxidations of antioxidants Ia, Ib, Ic and 1,3-cyclohexadiene were carried out under conditions given in Tab. 1, 2 and Fig. 1.

*Methyl-3-(1-hydroperoxy-4-oxo-3,5-di-tert-butyl-2,5-cyclohexadiene-1-yl)propionate (IIIb)* 

Prepared by the photooxidation of Metilox<sup>®</sup> (Ib) sensitized with methylene blue under conditions given in Tab. 1, but with pure methanol used as solvent. The reaction mixtures of three oxidations were joined, the solvent was removed by distillation, the residue was extracted with ether in presence of a small amount of anhydrous magnesium sulphate. After refiltering and removal of ether from the filtrate by distillation the remaining oil was recrystallized from hexane. The yield was 0.28 g (57% theor.) of crystalline compound, m. p. 95.5–96.5°C.

C<sub>18</sub>H<sub>28</sub>O<sub>5</sub> (324,4) Calcd. C 66.64 H 8.70 Found C 66.61 H 8.84

NMR spectrum (CDCl<sub>3</sub>) fits the structure. Arrangement: group,  $\tau$  (intensity): OOH, broad peak 1.16 (1); H on the ring, 3.41 (2); methoxyl, 6.32 (3); methylene, multiplet 7.60–8.06 (4); tert-butyl, 8.76 (18).

UV spectrum (heptane, conc.  $9.6 \times 10^{-5}$  mol/l, 1 cm); 232 nm ( $\varepsilon = 9.1 \times 10^{3}$ ), inflexion 270 nm. For a more concentrated solution ( $5 \times 10^{-3}$  mol/l) there was also absorption at 378 nm ( $\varepsilon = 29$ ) reaching up to approx. 430 nm. For hydroperoxide IIIa described in the literature<sup>14</sup> a similar spectrum was observed under the same conditions: 232 nm ( $\varepsilon = 9.4 \times 10^{3}$ ), inflexion 270 nm, 376 nm ( $\varepsilon = 23.3$ ).

Octadecyl-3-(1-hydroperoxy-4-oxo-3,5-di-tert-butyl-2,5-cyclohexadiene-1-yl)propionate (IIIc)

## a) By Sensitized Photooxidation of Ic

The reaction was carried out similarly to the preparation of IIIb in the presence of methylene blue in a dichloromethane: methanol solution (1:1). Crystallization from hexane yielded an almost white product, m. p. 64-65 °C, yield 38%.

$C_{35}H_{62}O_5$ (562,8)	Calcd.	C 74.69	H 11.15
	Found	C 74.80	H 11.17

NMR spectrum (CCl<sub>4</sub>) fits the structure. Arrangement: group,  $\tau$  (intensity); OOH, 1.11 (1); H on the ring 3.50 (2); methylene, triplet 5.99 (2), multiplet 7.7–8.1 (4); (CH<sub>2</sub>)<sub>16</sub>, 8.75 (approx. 32); tert-butyl, 8.78 (approx. 18).

UV spectrum is similar to those of the preceding hydroperoxides IIIa, b: 234 nm ( $\varepsilon = 9.8 \times 10^3$ ), inflexion 270 nm, 377 nm ( $\varepsilon = 27.6$ ).

#### b) By Oxidizing Ic with Chemically Generated Singlet Oxygen

To a solution of triphenyl phosphite (9.3 g) in dichloromethane (150 ml), ozone was introduced at  $-80^{\circ}\text{C}$  until blue colour due to the ozone present in excess appeared; the ozone was then removed by introducing argon. A solution of Ic (5.31 g=0.01 mol) in dichloromethane (50 ml) cooled to  $-15^{\circ}\text{C}$  was added to the mixture and the whole reaction mixture was then maintained at  $-15^{\circ}\text{C}$  two h, at  $-10^{\circ}\text{C}$  for one h, and then heated to room temp. Control test without Ic was carried out simultaneously and under the same conditions. Chromatographic analysis of both mixtures together with the standards showed that the former reaction mixture contained a large amount of unreacted phenol Ic, a smaller amount of hydroperoxide IIIc and no other product derived from Ic. Hydroperoxide IIIc decomposed during an attempt to isolate it on a silicagel column.

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Dimethyl-1,4-bis(4-oxo-3,5-di-tert-butyl-2,5-cyclohexadiene-1-ylidene)-2-butene-2,3-dicarboxylate (IV)

## a) Oxidation of Ib with Lead Dioxide

Phenol Ib (2.92 g, 0.01 mol) was dissolved in 50 ml dichloromethane; 0.5 ml methanol and 7.18 g lead dioxide (0.03 mol) were added. Stirring at ca. 30 °C for 20 h. 10 g silicagel was added to the reaction mixture (for column chromatography); the mixture was stirred and refiltered, washed with ether, and the filtrate concentrated. On dissolving the remaining oil in 20 ml hexane the product crystallized. Recrystallization from hexane yielded 1.2 g (41.5%) crystals, orange (less stable crystalline modification) or black-violet, with green metallic lustre (m. p. 142–5°C).

NMR (CDCl<sub>3</sub>): group,  $\tau$  (intensity); H on the ring, 2.93 and 2.95 (2), 3.15 and 3.18 (2); H on the chain, 3.44 (2); methoxyl, 6.12 (6); tert-butyl, 8.75 and 8.83 (36).

C<sub>36</sub>H<sub>48</sub>O<sub>6</sub> (576.8) Calcd. C 74.96 H 8.39 Found C 74.89 H 8.46

IR spectrum (KBr pellets): carbonyl  $1608 \text{ cm}^{-1}$ , ester group  $1730 \text{ cm}^{-1}$ ; OH bonds were not detected (4% solution in CCl<sub>4</sub>, 0.1 mm cell).

UV spectrum ( $5.53 \times 10^{-5}$  mol/l, cyclohexane, 1 cm cell): 437 nm ( $\varepsilon = 2.47 \times 10^{4}$ ), inflexions 427 and 471 nm.

In addition, a minor amount of yellow crystals of V was isolated from the filtrate after the first crystallization.

## b) By Oxidizing VI with Potassium Ferricyanide

A saturated solution of potassium ferricyanide in 10ml 2N KOH was vigorously stirred for 15min in an inert atmosphere with a solution of 0.2g bisphenol VI in 10ml benzene. The usual treatment gave 0.19 g IV (yield 95%), m. p. 142–145 °C. Oxidation can be carried out also with lead dioxide, e.g. in ether.

Dimethyl-1,4-bis(4-oxo-3,5-di-tert-butyl-2,5-cyclohexadiene-1-ylidene)-butane-2,3-dicarboxylate (V)

A saturated solution of potassium ferricyanide (ca. 30 g) in 100 ml 2N KOH was vigorously stirred with a solution of 2.9 g phenol Ib (0.01 mol) in 100 ml benzene for two h in an inert atmosphere (argon). The benzene layer was separated, shaken with water and dried with anhydrous magnesium sulphate; benzene was removed by distillation. Twofold crystallization from hexane yielded 1.1 g V (yield 38%), m. p. 157–160°C.

The product is identical with that obtained by oxidizing Ib with silver oxide (ref.<sup>12</sup>) and with the side product obtained in the oxidation with lead dioxide. Mol. wt. found 590, calcd. for  $C_{36}H_{50}O_6$  578.8.

According to TLC (silicagel, mixture of 4 vol. parts hexane + 1 part ether as the mobile phase), the product is a mixture of two compounds (compound present in the larger amount has a lower  $R_F$ ).

The NMR spectrum corresponds to the literature data<sup>10</sup> for both diastereomers of V (after correction of data on the intensity of H on the ring; in the literature cited here, double the true value is given by inadvertency, as revealed by comparison with the above structure of V). Three isomer prevails in the mixture.

The structure was verified also by the rearrangement on aluminium oxide described in ref.<sup>10</sup>; the product obtained in an almost quantitative yield is chromatographically uniform, and its m. p. (170–171 °C) and the NMR spectrum correspond to those given<sup>10</sup> for bisphenol VI.

Dimethyl-1,4-bis(4-hydroxy-3,5-di-tert-butylphenyl)-1,3-butadiene-2,3-dicarboxylate (VI)

## a) By Reducing IV with Sodium Hydrosulphite

A solution of 0.2 g IV in 100 ml ether was shaken with a solution of 5 g  $Na_2S_2O_4$ in 100 ml water and 100 ml methanol. The red solution quickly turned yellow. After ether and water were added, the ether phase was separated, dried with MgSO<sub>4</sub> and concentrated. On adding hexane and inoculating with VI (prepared by rearrangement of V), 0.13 g VI (yield 65%) was obtained, m. p. 170–171 °C. The compound is identical with the product obtained by rearrangement of V.

### b) By Catalytic Hydrogenation of IV

A solution of 0.2 g IV in 20ml ether was hydrogenated in the presence of  $PtO_2$  at room temp. and normal pressure. After 5–10 min the solution is light yellow. Treatment of the solution yielded 0.11 g VI (yield 55%), identical with the product obtained as sub a).

# Oxidation of Irganox $1076^{\text{@}}$ (Ic) with lead dioxide

Phenol Ic (5.3g=0.01 mol) was oxidized with lead dioxide similarly to Ib. A red dense oil was obtained. The spectrum of this raw product in the visible region is similar to that of IV: 444 nm, inflexions 427 and 475 (cyclohexane).

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