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Antioxidants and Stabilizers

XXXV. On the Character of Discolouring Compounds Formed from 2,2′-Methylene-bis-(4-methyl-6-tert.-butylphenol) during Oxidative Degradation of Polymers

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SUMMARY:

A model reaction of 2,2′-methylene-bis-(4-methyl-6-tert.-butylphenol) (I) with tert.-butylhydroperoxide in the presence of cobalt-II-acetylacetonate yielded coloured products which cause the discolouration of substrates stabilized with antioxidant I. Dimer V, trimer VI and tetramer VIII were identified, and their relation to the colourless oligomeric products II and III was proved. The structure of dimer V was confirmed by an independent synthesis. The formation of analogous compounds was proved by an investigation of the oxidation of tetralin; it is discussed in connection with the oxidation of isotactic polypropylene. Both materials were stabilized with antioxidant I.

ZUSAMMENFASSUNG:

Braungefärbte Produkte, die die Ursache der Verfärbung der mittels 2,2′-Methylen-bis-(4-methyl-6-tert.butylphenol) (I) stabilisierten Substrate sind, wurden mittels einer Modellreaktion von Antioxidant I mit tert. Butylhydroperoxid in Anwesenheit von Kobalt(II)-Acetylacetonat erhalten. Dimer V, Trimer VI and Tetramer VIII wurden identifiziert; ihr Zusammenhang mit farblosen oligomeren Produkten II und III wurde bewiesen. Die Struktur des Dimeren V wurde durch unabhängige Synthese bestätigt. Die Bildung von analogen Verbindungen während der Oxidation des mit Antioxidant I stabilisierten Tetralins wurde bewiesen und ihr Vorkommen in oxidierten stabilisierten isotaktischen Polypropylenen wird diskutiert.

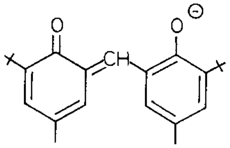
Introduction

During the inhibition of the thermooxidative degradation of polymers by phenolic antioxidants (InH), termination of the kinetic chain of autoxidation occurs due to the reaction with ROO˙ radicals formed in the propagation step.

According to a simplified conception, such inhibition is formulated by the following scheme:

$$\text{InH} + \text{ROO}^{\cdot} \longrightarrow \text{In}^{\cdot} + \text{ROOH}.$$

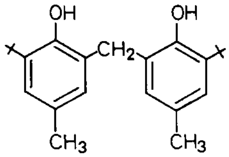
Aryloxy radical $\text{In}^{\cdot}$ and hydroperoxide are formed in the system. The content of the originally present antioxidant decreases. Conversely, however, the products formed in the complicated complex of the parallel and subsequent reactions accumulate in the stabilized polymer and may consequently, conformable to their nature, affect its stability and appearance. In connection with the complex study of the relationships between the chemical composition of antioxidants and their efficiency, it is necessary to know the part to be played by antioxidants under the conditions of an inhibited oxidation reaction. In this work we report the results of a detailed study devoted to the transformation of 2.2′-methylene-bis-(4-methyl-6-tert.butylphenol) (I) which is an important antioxidant widely used in industry. It is produced by a number of chemical works and applied in practice in the stabilization processes of polyolefins and rubbers. When comparing the antioxidative efficiency of extensive series of variously substituted bisphenols in tetralin[1] and isotactic polypropylene[2], bisphenol I belongs among the most efficient alkylidenebisphenols. In spite of being placed among the non-staining antioxidants, it causes discolouration of the protected substrate when applied in a process. Even though bisphenol I has been used in practice for a long time, nothing is known as yet either about the composition of the products of its transformation or about the effects of such products on the oxidative degradation of polymers. It was only O'SHEA[3] who suggested for the coloured products a purely speculative structure of the anion:



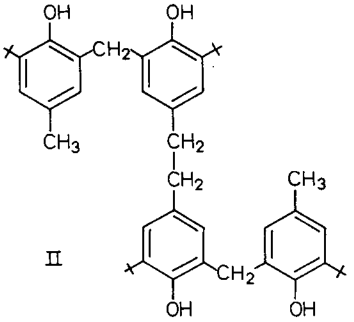
Owing to the importance of methylenebisphenol I we investigated the products of its transformation. Using a model reaction of bisphenol I with tert.-butylperoxyl (modelling the tertiary alkylperoxyl formed during autoxidation of polypropylene) we prepared colourless as well as coloured products. The first of them were isolated and characterized[4]. The coloured reaction products which impair the stabilized polymeric substrate have been dealt with in this paper.

Results and Discussion

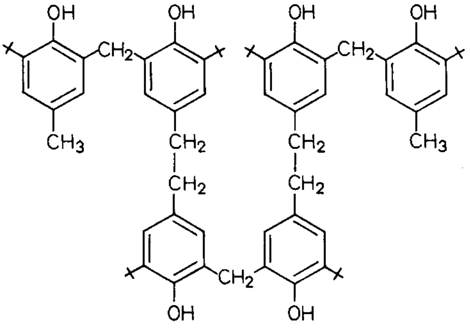
Oxidation of low-molecular weight and polymeric hydrocarbons inhibited with 2,2′-methylene-bis-(4-methyl-6-tert.-butylphenol) (I) gives rise to products whose formation and composition were tried to explain in terms of a reaction with tert.-butylperoxyl. For the generation of the agent we used the decomposition of tert.-butylhydroperoxide catalyzed by cobalt-II-acetylacetonate. The reaction can be controlled by choosing the ratio of the reaction components, thus modelling the interaction of the inhibitor during the initial stages of the induction period and in a fully developed oxidation in the presence of a large concentration of ROOH. The use of an oxidizing agent in excess induces the formation of the peroxidic derivative of cyclohexadienone[4] (IV); if the agent reacts with the antioxidant I in excess, a mixture is formed con-



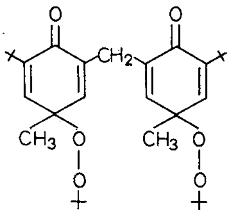
I



II



III

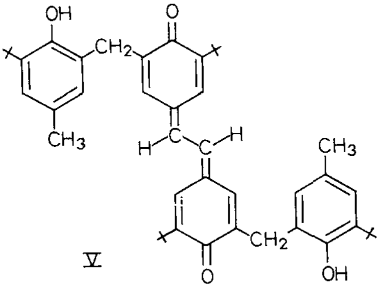


IV

taining colourless dimer II and trimer III and a number of brown-coloured compounds which may be of an oligomeric or a polymeric character, depending on the reaction conditions. Reaction mixtures of a similar composition are also formed in the reaction of antioxidant I with the tert.-BuO' radicals which are formed during autoxidation by a quadratic termination of the tert.-BuOO' radicals or by a decomposition of tert.-BuOOH (reaction was modelled by the tert.-BuO' radicals generated by the thermal decomposition of tert.-butylperoxalate).

The concentration of the individual coloured products in the reaction mixture is low; however, with respect to their total number and high absorption they cause an almost black-brown colouration of the reaction mixtures.

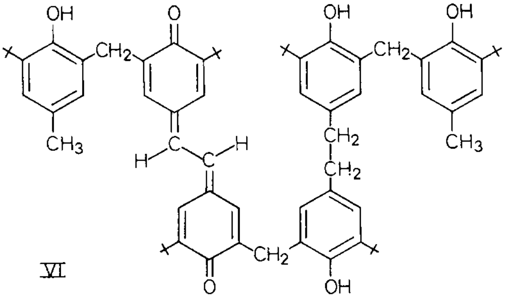
Experimental conditions were found leading to the formation of a comparatively large amount of coloured low molecular weight compounds, and three of the latter were isolated in a small amount by column chromatography, namely, compound V in a chromatographically pure form, compound VI, which seemed pure judging by its GPC and containing an insignificant amount of impurities by the TLC data, and compound VIII, not quite pure and having the formula $C_{92}H_{118}O_8$.



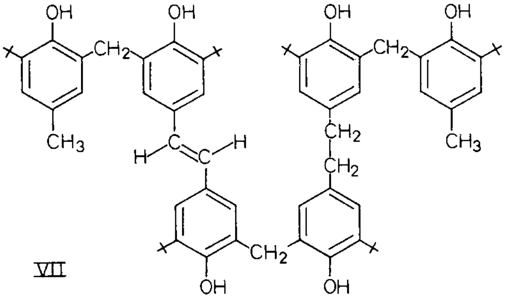
V

Another part of the paper is devoted to the detection of their structure.

Hydrogenation of compound V in the presence of platinum yields dimer II and another compound, later proved as having structure XIII, which undergoes an easy oxidation in the air on a silicagel plate while regenerating V. Similarly, hydrogenation of the brown compound VI gives rise to a colourless trimer III and compound VII. After hydrogenation of the brown product VIII the reaction mixture contained a compound whose chromatographic behaviour indicates that it is probably a tetramer. By reduction with sodium dithionite, compound V yields XIII and VI yields VII. These results, indicating a genetic connection between compounds V and VI, on the one hand, and the already identified dimer II or trimer III, on the other, are in accordance with the osmometric determination of molecular weights and with the behaviour during



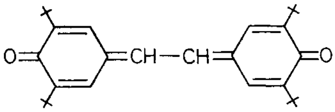
VI



VII

the GPC analysis (Table 5), where it was not possible to distinguish the pairs II and V or III and VI on the basis of the elution volumes. Compound VIII corresponds to a tetramer by its V_e value. Mass spectroscopy cannot be used in this case for the molecular weight determinations owing to the low volatility and instability of the isolated oligomers at an elevated temperature.

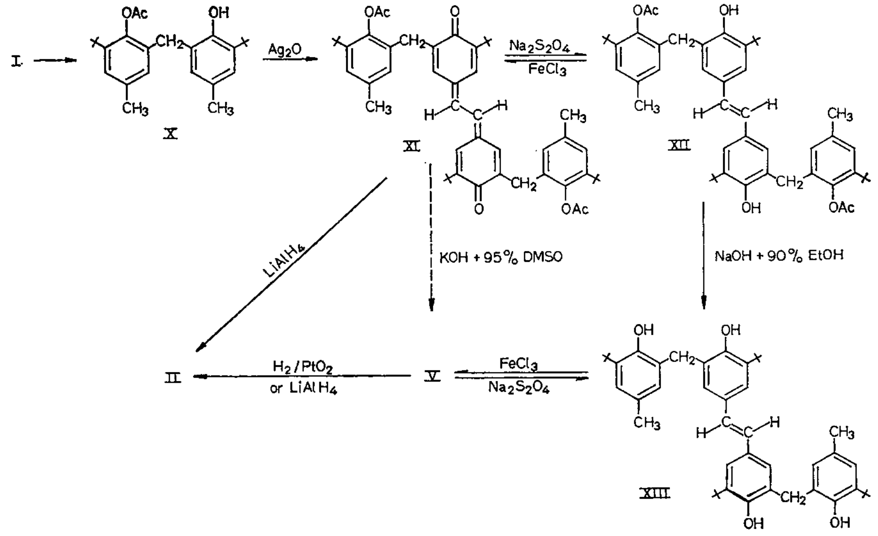
The structures were detected by using spectroscopy in the IR, UV and visible regions, as well as NMR spectroscopy (Tables 1–3). All the three oligomeric products absorb in the visible region at 463 nm with inflexions at 436 and 408 nm. The absorption intensity allows a conclusion that compounds VI and VIII do not contain structures which cause absorption (i.e. the stilbenequinone structure) in a number higher than compound V. To verify the structure, 3.5.3′.5′-tetra-tert.-butylstilbenequinone (IX) was prepared as the model compound:



IX

and a similar spectrum was found. Absorptions are only shifted to shorter wavelengths (447, 420 nm, inflexion at 396 nm); the absorption corresponding to the inflexion 436 nm exhibits a clear maximum. In the IR spectrum of a diluted solution in the region 3100–3650 cm^{-1}, only the frequency of the OH group bonded intramolecularly by a hydrogen bridge to oxygen (3260 and 3450 cm^{-1}) was found for compound V, while for compounds VI and VIII we found a free sterically hindered OH ($\tilde{\nu}_{OH} = 3625$ cm^{-1}) and OH bonded intramolecularly by a hydrogen bridge to the π electrons (3500 cm^{-1}, cf.[5, 6]), apart from the OH group mentioned above.

The NMR spectra of compounds V, VI and VIII are in accordance with the suggested structure (Table 1); however, with respect to the complex part of the spectrum corresponding to the aromatic and olefinic hydrogen atoms they cannot be used for an unambiguous detection of the structure. For this reason, we attempted a verification of the structure of compound V by its syntheses, which at the same time could be used as a method of preparation of this compound in a larger amount. First, one half of the molecule of antioxidant I was deactivated by a partial acetylation. An attempt of an oxidative coupling of monoacetate X to yield stilbenequinone XI by means of the system tert.-BuOOH + Co^{++} revealed that only colourless products were formed. Silver oxide was therefore used as the oxidation agent. The stability of stilbenequinone XI is rather low, and it could not be purified completely for this reason. The absorption of stilbenequinone XI in the visible region (454, 427 nm and an inflexion at 402 nm) lies between the absorption of the brown compounds V, VI and VIII and that of the model tetra-tert.-butylstilbenequinone. Attempts to hydrolyze the latter compound to obtain V on a preparative scale were unsuccessful owing to the instability of XI in an acid medium and to the



sensitivity to alcohols in an alkaline medium (cf.[7]). Only in the case of hydrolysis with potassium hydroxide in dimethylsulphoxide it was possible to detect in the reaction mixture by TLC a small amount of V along with a number of other compounds. Stilbenequinone XI was therefore first reduced with sodium dithionite to XII which is sufficiently stable in a non-oxidizing medium, while the olefinic bond provides for an easy oxidizability back to the stilbenequinone structure. On purifying on a chromatographic column, the structure of XII was proved by the NMR spectrum, elemental analysis, mass spectroscopy (used only to determine the molecular weight), comparison of the UV spectrum with the model 4,4'-vinylene-(2,6-di-tert.-butylphenol), comparison of the OH bond frequency of a diluted solution (3490 cm^{-1}) with that of compound X (3510 cm^{-1}) and reoxidation with ferric chloride to XI. Hydrolysis of XII to XIII was carried out with sodium hydroxide in a 90% ethanol under argon; the structure of XIII was confirmed by elemental analysis, and by the NMR, UV and IR spectra (the OH bond frequency in a diluted solution is the same as for dimer II). Oxidation of XIII with aqueous ferric chloride yielded a brown dimer V; the comparison of the total IR spectra in the KBr pellets proved the identity with the product of a direct reaction of antioxidant I with tert.-butylhydroperoxide. Reduction with dithionite transforms V back into XIII. The process of the syntheses can be seen from the scheme.

The structure of VI was verified by its reduction to VII with sodium dithionite.

A precise mechanism of the formation of oligomers cannot be deduced from the experimental results obtained so far. It is sure, however, that the cyclohexadienone derivative IV is formed by termination reaction between alkylperoxyl and a mesomeric form of the radical In·. By analogy with the reactions of mononuclear phenols, there is the highest probability of an intermediary formation of quinomethide, despite the fact that, according to experimental observations, colourless oligomers are formed in the first phase of the reaction in a greater amount than brown oligomers. The quinomethide mechanism necessitates the formation of both types of products in equal quantities. It seems likely, however, that in the phase which follows the formation of oligomers the "brown" compounds oxidize more rapidly. In the model study we have proved that the brown oligomers V, VI and VIII rapidly oxidize in

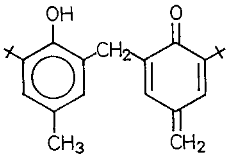


Table 1. Chemical shifts of the oxidation products of Bisphenol I in the NMR spectra.

Compound (solvent)	τ values (Intensity)						
	$C(CH_3)_3$	CH_3	CH_3CO	CH_2–CH_2	CH_2	OH	H[a]
V ($CDCl_3$)	8.70 8.67 (36) 8.60	7.75 (6)	—	—	6.34 6.29 (3–4)	[b]	multiplet 2.27–3.1 (10)
VI[c] (CCl_4)	8.51 (54)	7.75 (6)	—	7.21 (3–4)	6.37 6.23 (6)	4.53	multiplet 2.26–3.17 (14)
VIII[d] (CCl_4)	8.71 (72)	7.79 (6)	—	7.45 (6)	6.39 6.25 (8)	4.47	multiplet 2.29–3.17 (18)
XII ($CDCl_3$)	8.67 (36) 8.61	7.84 (6)	7.65 (6)	—	6.32 (4)	4.88	multiplet 2.64–3.36 (10)
XIII ($CDCl_3$)	8.61 (36) 8.59	7.74 (6)	—	—	6.08 (4)	4.90	multiplet 2.72–3.12 (10)

[a] On the aromatic ring or the stilbenequinone skeleton.

[b] No absorption was found.

[c] Compound still exhibits absorption at 1.31 and 1.40 τ (total intensity 4), can be due to impurities.

[d] Compound still exhibits absorption at 1.29 (2) τ.

the presence of Co^{++} ions and of an excess of tert.-BuOOH to form a mixture of colourless products; no formation of the cyclohexadienone derivative IV has been proved in this process. Under the same conditions 2.6-ditert.-butyl-1.4-benzoquinone was formed from 3.5.3′.5′-tetra-tert.-butylstilbene-4.4′-quinone in a great amount.

Some of both the colourless and coloured oligomeric products of the bisphenol I transformation obtained in model reactions were found even in the reaction mixtures arising from the oxidation of hydrocarbon substrates oxidized in the presence of this antioxidant. The investigation carried out in the isotactic polypropylene (oxidation temperature 180 °C) was less successful owing to the thermal instability of some of the compounds. Of all the colourless compounds, only unreacted antioxidant I was reliably detected in the polypropylene samples extracted after completion of one half of the induction period; however, we established at the same time[8] that during the inhibition of the oxidation of polypropylene with a mixture of bisphenol I and its dimer II the latter compound is consumed faster. This fact can be responsible for the absence of major amounts of oligomers II or III in the mixture of the products of transformation. Under these conditions, neither an analogue of the peroxy derivative of cyclohexadienone IV nor its isomer can be present among the products, because we found that compound IV undergoes thermal decomposition at 150 °C (similarly, the simpler peroxycyclohexadienone derived from 2.6-di-tert.-butyl-4-methylphenol is thermally unstable).

Coloured products of the transformation of bisphenol I are formed from the onset of the oxidation of polypropylene. Owing to the proved decrease in stability of the coloured oligomers V, VI and VIII their structures are altered at the oxidation temperature of polypropylene, and the identification of the individual compounds in the complex mixture is not precise. This is why a

Table 2. Bond frequencies of the OH group in bisphenol I and in the isolated colourless and coloured products of its transformation. 0.04% solutions of the compounds in CCl_4 were used; cell 10 mm; $\tilde{\nu}$ given in cm^{-1}.

Compound	$\tilde{\nu}$ (free OH)	$\tilde{\nu}$ (bonded OH)			
I	3630 (w)	3510 (m)	3450 (w)[a]	—	—
II	3630 (w)	3510 (m)	3450 (w)[a]	—	—
V	—	—	—	3260 (s)	3190 (m)[a]
VI	3620 (w)	3500 (m)	3450 (w)[a]	3250 (s)	3180 (m)[a]
VII	3625 (w)	3505 (m)	3450 (w)[a]	—	—
VIII	3625 (w)	3500 (m)	3450 (w)[a]	3250 (m)	3180 (w)[a]
X	—	3510 (m)	—	—	—
XII	—	3490 (m)	—	—	—
XIII	3625 (w)	3510 (m)	3450 (w)[a]	—	—

[a] Inflexion.

discussion of the formation of coloured compounds during the oxidation of hydrocarbons inhibited with bisphenol I is based on the results of the initiated oxidation of stabilized tetralin carried out under milder conditions. The coloured products were formed intensively during the oxidation of a mixture containing a bimolar excess of the initiator compared to the antioxidant. At 64 °C, a mixture of brown-coloured oligomers is formed in tetralin, besides the colourless products; trimer VI is the main coloured product. Under the conditions employed, about 6% of the antioxidant present was transformed into the brown compounds (the yield was calculated in relation to trimer VI).

The transformation products of antioxidant I containing phenolic rings exhibit antioxidative activity during the stabilization of polypropylene[8].

Table 3. Absorption of transformation products of bisphenol I and of model compounds 3.5.3'.5'-tetra-tert.-butylstilbene-4.4'-quinone (IX) and 4.4'-vinylenebis-(2.6-di-tert.-butylphenol) (XIV) in the UV and visible region. Compounds were measured in a 10 mm cell in cyclohexane in a concentration from $6 \cdot 10^{-6}$ to $8 \cdot 10^{-5}$ mole/l.

Compound	λ (nm)	$\varepsilon \cdot 10^{-3}$	Compound	λ (nm)	$\varepsilon \cdot 10^{-3}$
V	462	71.8	XI[e]	454	21.8
	436[a]	—		427	14.4
	408[b]	—		402[a]	—
	283	7.3	XII	347[a]	—
VI	463	59		332	35.2
	435[a]	—		312	32.5
	405[b]	—		292[a]	—
	283	12.4		237[a]	—
VII	347[a]	—	XIII	348[a]	—
	330	32		330	35.4
	312	32		312	35.7
	302[a]	—		301[a]	—
	289	28.6		290[a]	—
VIII	463	36.3		243[a]	—
	437[a]	—	XIV[f]	343[a]	—
	408[b]	—		327	24.2
	283	13.5		308	24
IX[c]	447	112		296[a]	—
	420	75		235	13.8
	396[a]	—		211	25
	241[d]	8.5			

[a] Inflexion.

[b] Not very distinct inflexion.

[c] INGOLD[10] gives 448, 420, 395 nm.

[d] Rich splitting.

[e] Raw product.

[f] INGOLD[10] gives 307, 325, 295 nm.

However, the coloured products formed as a result of the possible transformations of the primary radical In· during the induction period are a disagreeable accompanying phenomenon of the application of 2.2′-methylene-bis-(4-methyl-6-tert.-butylphenol); the determination of their structure allows to estimate their possible participation in the total process of the degradation of polypropylene.

Table 4. R_F values of the oxidation products of bisphenol I and of model compounds 3.5.3′.5′-tetra-tert.-butylstilbene-4.4′-quinone (IX), 4.4′-vinylenebis-(2.6-di-tert.-butylphenol) (XIV), 4.4′-ethylene-bis-(2.6-di-tert.-butylphenol) (XV), 2.6-di-tert.-butyl-4-methylphenol (XVI), 1-acetoxy-2.6-di-tert.-butyl-4-methylbenzene (XVII), and 2.2′-diacetoxy-3.3′-di-tert.-butyl-5.5′-di-methyldiphenylmethane (XVIII) on a silicagel layer. Developed in the system 1 part by vol. of ether + 2 parts by vol. of heptane.

Compound	R_F	Detection	Compound	R_F	Detection
I	0.47	a	XI	0.29	b
II	0.34	a	XII	0.31	a
III	0.18	a	XIII	0.23	a
V	0.50	b	XIV	0.61	a
VI	0.39	b	XV	0.66	a
VII	0.13	a	XVI	0.67	a
VIII	0.22	b	XVII	0.57	c
IX	0.73	b	XVIII	0.35	c
X	0.52	a			

[a] Freshly prepared mixture of 15% ferric chloride and 1% potassium ferricyanide.
[b] Compound is visible without detection.
[c] Conc. sulphuric acid with 0.5% 4-methoxy-benzaldehyde.

Experimental

Analytical Methods

The NMR spectra were studied in deuterated chloroform or tetrachloromethane on a JEOL PS-100 spectrometer with hexamethyldisiloxane as an internal standard ($\tau = 9.25$). The IR spectra were measured with a Perkin-Elmer type 457 apparatus in tetrachloromethane in cells 10 mm thick and in the KBr pellets. The spectra in the UV and visible regions were measured with a Varian Cary 14 spectrometer in a cell 10 mm thick in cyclohexane. The mass spectra were recorded with an AEI MS 902 spectrometer. Silicagel plates SILUFOL (Kavalier, Czechoslovakia) were used for TLC. Silicagel 60–120 μ was used for column chromatography. Gel chromatography was performed on columns filled with the styrene – divinylbenzene copolymer with the exclusion limit of molecular weights 1500; a Waters type R 403 differential flow refractometer was used for detection. DTA was made on a Du Pont model 900 apparatus. Molecular weights were determined with a Vapour-Pressure-Osmometer, Hitachi Perkin-Elmer, model 115.

Table 5. The GPC elution volumes V_e of bisphenol I, of its transformation products and of the reference compounds (benzene [XIX] and polystyrene [XX]).

Compound	I	II	III	V	VI	VII	VIII	XI	XIII	XIX	XX
V_e (volume counts)	105.5	93	86.5	93	86	85.5	81.5[a]	92[b]	92[c]	136	70.5

[a] A minor amount of impurities at $V_e = 77$ and 85.

[b] Impurities at $V_e = 84$ and 86.

[c] A weak inflexion at $V_e = 90$, probably a geometric isomer.

Compounds Used

2.2′-Methylene-bis-(4-methyl-6-tert.-butylphenol) (I) (J. Dimitrov Works, Bratislava) was repurified by crystallization from hexane, mp 131 °C. Technical 65% tert.-butylhydroperoxide (Chemical Works Velvěty) was concentrated by distillation in vacuo to a 95% product, bp 28–29 °C/5 Torr. Cobalt-II-acetylacetonate was obtained according to[9] and dried in vacuo over phosphorus pentoxide.

Reaction of Antioxidant I with tert.-Butylperoxide Radicals

A solution of 2.5 g (0.025 mole) 95% tert.-butylhydroperoxide in 30 ml benzene was added dropwise during 30 min to a refluxed solution of 17 g (0.05 mole) 2.2′-methylene-bis-(4-methyl-6-tert.-butylphenol) and 0.5 g cobalt-II-acetylacetonate in 150 ml of benzene. The reaction was carried out in an inert atmosphere (argon). The reaction mixture was heated to boil for another 15 min, benzene was removed by distillation in vacuo and the remaining dark-brown oil was fractionated on a silicagel column impregnated with dimethylformamide (137 ml/550 g silicagel). A mixture of hexane (3 parts by vol.) and ether (1 part by vol.) was used as the mobile phase. Only fractions designated further by (a), (b), and (c) containing coloured products in a major amount were treated.

Isolation of the Brown Dimer V

Fraction (a) (after concentration 9.9 g) contained compound V along with a considerable excess of the starting material I, according to the TLC data. The fraction was dissolved in a small amount of hexane, the bisphenol present in the mixture crystallized overnight in a refrigerator and was removed by filtration. The filtrate was fractionated on silicagel saturated with dimethylformamide (134 ml/200 g silicagel) and eluated with hexane. The fraction containing chromatographically pure product V was collected. Recrystallization from the toluene-hexane mixture yielded 0.017 g of black-brown crystals, mp 262–263 °C (exothermic decomposition takes place immediately after melting, according to DTA).

$C_{46}H_{58}O_4$ (675.0) Calcd. C 81.86 H 8.66
Found C 81.46 H 8.68.

Isolation of the Brown Trimer VI

Fraction (b) obtained from the oxidation of bisphenol I was used in the experiments. It contained 0.35 g of almost pure compound VI (which is also present in other fractions, together with dimer II).

Fraction (b) was dissolved in 3 ml of methanol and compound VI was precipitated in the form of an oil by adding a few drops of water. The oil crystallized after separation owing to friction. The yield was 0.30 g of deep-brown powder, mp not sharp, pure according to GPC, a few impurities pressent according to TLC.

Molecular weight for $C_{69}H_{88}O_6$: Calcd. 1013.5
Found 1120.

Isolation of Brown Tetramer VIII

Fraction (c) containing almost pure compound VIII (which is present also in other fractions) was used. On evaporation, 0.5 g of raw product was obtained. Further treatment was the same as for fraction (b). The yield was 0.30 g of deep-brown powder which according to GPC contained also a small amount of impurities at $V_e = 77$ and 85 volume counts, besides the main compound ($V_e = 81.5$ volume counts).

Molecular weight for $C_{92}H_{118}O_8$: Calcd. 1351.9
Found 1389.

An Independent Synthesis of the Brown Dimer V

2-tert.-Butyl-4-methyl-6-(2-acetoxy-3-tert.-butyl-5-methylbenzyl)-phenol (X)

17 g of 2.2′-methylene-bis-(4-methyl-6-tert.-butylphenol) (0.05 mole) was dissolved in 150 ml of glacial acetic acid and 7 ml of acetic anhydride (0.075 mole). 1.5 ml of conc. H_2SO_4 was added dropwise at room temperature and the mixture was allowed to stand one hour. Composition of the reaction mixture was checked chromatographically. The reaction was conducted in such a manner (by adding small amounts of acetic anhydride), that the mixture contained monoacetate X, diacetate, and only an insignificant amount of the initial material. For a better chromatographic resolution of compound I and X it is possible to use a silicagel plate impregnated with dimethylformamide (heptane as the mobile phase) or Whatman paper No. 1 impregnated with a 10% solution of paraffin oil in hexane, 80% methanol being the mobile phase (R_F of compound I and X is 0.53 and 0.24, respectively). The reaction mixture was then poured into an excess of water and ice. The raw product after crystallization was filtered off, dried and purified on a silicagel column (hexane and benzene 1 : 1 as the mobile phase). The oil thus obtained crystallized after the addition of a small amount of hexane; the yield was 5.7 g (29.8% theor.), mp 111–112 °C.

$C_{25}H_{34}O_3$ (382.5) Calcd. C 78.49 H 8.96
Found C 78.49 H 8.95.

Acetylated Dimers XI and XII

10 g of anhydrous magnesium sulphate and a suspension of silver oxide (washed with water, acetone and ether), freshly prepared from 34 g of silver nitrate, were added to a solution of 3.8 g monoacetate V (0.01 mole) in 50 ml of dry ether. The mixture was stirred at room temperature for one hour, filtered, washed with ether, and the filtrate was evaporated in vacuo. 4 g of raw compound XI was obtained in the form of an orange glassy material. (GPC cf. Table 5.) The product was dissolved in 80 ml of ether and shaken 5 min with 80 ml of 20% aqueous solution of sodium dithionite and 80 ml of methanol. The raw product XII (4.1 g) was obtained from the organic phase after dilution with ether and water. The product was purified on a silicagel column (to which 2% $Na_2S_2O_4$ was added; benzene as the mobile phase). Recrystallization from benzene and hexane yielded 1 g of chromatographically pure

acetate XII in the form of a white powder which crystallizes in two modifications, mp (under argon) 165–167 °C and 241–242 °C. The yield was 26.3%, related to the initial monoacetate X. The residues of the solvents are rather strongly bound in the compound.

$C_{50}H_{64}O_6$ (761.1) Calcd. C 78.91 H 8.48
Found C 78.58 H 8.50.

Molecular weight was checked by mass spectroscopy.

Dimer XIII

A solution of 1 g of NaOH in 3 ml water was added to a mixture of 1 g of acetate XII, 0.2 g $Na_2S_2O_4$ and 35 ml of ethanol against a flow of argon. The mixture was refluxed 40 min, cooled and acidified with dilute sulphuric acid. The whole operation until acidifying was performed in an inert atmosphere. The reaction mixture was diluted with ether and water until the solid phase was dissolved. 0.88 g of crystalline substance was then obtained from the ether layer, which yielded 0.45 g (50.7% theory) of white crystals, mp under argon 233–235 °C, after recrystallization from the benzene-hexane mixture.

$C_{46}H_{60}O_4$ (677.0) Calcd. C 81.61 H 8.93
Found C 81.53 H 8.94.

Dimer V

A solution of 0.1 g of dimer XIII in 200 ml of ether was shaken 3 min with 200 ml of 15% aqueous solution of ferric chloride and 200 ml of methanol. 500 ml of water were added to the mixture, and product V was isolated by ether extraction. Recrystallization from the toluene-hexane mixture, 0.09 g of dimer V (90.3% theory) was obtained, mp 260–264 °C with decomposition. Identity with the product prepared by oxidation of bisphenol I was proved by comparing the IR spectra in the KBr pellets and by the mixed mp.

Dimer II Obtained by Reduction of Dimers XI and V with Lithium Aluminium Hydride

10 mg of compound XI was reduced with an excess of lithium aluminium hydride by boiling ten minutes in dry tetrahydrofuran. After decomposition of the mixture with wet ether, water and diluted sulphuric acid, dimer II was detected in the ether extract as the main product by using TLC.

The same procedure was used to reduce compound V; dimer II (main product) and compound XIII (by-product) were found in the reaction mixture by TLC. A mixture of a similar composition was also obtained by hydrogenation (35 °C, 3 hrs.) of compound V on platinum after ADAMS in the mixture ethanol-ether under atmospheric pressure.

Reduction of Compounds V and VI with Sodium Dithionite

A solution of 0.2 g of compound VI in 10 ml of ether was reduced and the raw product was purified chromatographically in the same manner as in the case of compound XI. 0.13 g (65% theory) of trimer VII, mp 149–150 °C, was obtained.

$C_{69}H_{90}O_6$ (1015.5) Calcd. C 81.61 H 8.93
Found C 81.49 H 8.92.

Reduction of compound V carried out in the same way leads to compound XIII.

Oxidation of Compounds Having the Stilbenequinone Structure with tert.-Butylperoxide Radicals

0.2 g of 3.5.3′.5′-tetra-tert.-butylstilbene-4.4′-quinone (IX) was dissolved in 10 ml benzene; 0.5 g of tert.-butylhydroperoxide and 0.25 ml of a 1% solution of cobalt-II-acetylacetonate in benzene were added to the solution. After one hr. of boiling under a reflux (reaction is rather vigorous at the beginning) benzene was removed by distillation. From the oil remaining, after dilution with heptane a crystalline product was obtained which yielded after recrystallization from methanol 0.04 g (19.7% theor.) of pure 2.6-di-tert.-butyl-1.4-benzoquinone, mp and mixed mp with the authentic sample being 64–66 °C. The analytical yield determined by gel chromatography of the raw reaction mixture was 67.5%.

Preliminary oxidations of oligomers V, VI, and VIII carried out in the same manner showed that also in this case the reaction mixtures were quickly decolourized. The products were not identified.

Inhibited Oxidation of Tetralin and Identification of Coloured Products of the Transformation of Bisphenol I

50 ml of tetralin were oxidized with oxygen at 64 °C for 16 hrs. in an oxidation cell with shaking. Oxidation was initiated with azobisisobutyronitrile (10^{-3} mole/l) and inhibited with antioxidant I (5×10^{-4} mole/l). After evaporation of the greatest part of tetralin on a vacuum rotating evaporator (60–70 °C; 0.05 Torr) the coloured products were further concentrated on a silicagel layer; trimer VI was then detected by TLC in the extract as the main coloured products along with other brown oligomers. TLC was performed in a twodimensional arrangement, using the same system in both directions; the standards were used only for the second direction. The yield of the total of brown products related to trimer VI was 6.2% (determined by spectroscopy of the original reaction mixture in the visible region; brown oligomers absorb in tetralin at 474 nm).

Inhibited Oxidation of Isotactic Polypropylene

Oxidation of 20 mg of samples of isotactic polypropylene containing antioxidant I in an amount 0.05 mole/kg of polymer was carried out in a volumetric apparatus at 180 °C in oxygen by the method given in[8]. Oxidation was interrupted after one half of the induction period and then again after its completion. Polypropylene was extracted with chloroform, the extract was concentrated and analyzed by TLC.

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