

ANTIOXIDANTS AND STABILIZERS. XXIX.*

REACTION OF 2,2'-METHYLENEBIS(4-METHYL-6-TERT-BUTYL PHENOL) WITH TERT-BUTOXY AND TERT-BUTYLPEROXY RADICALS

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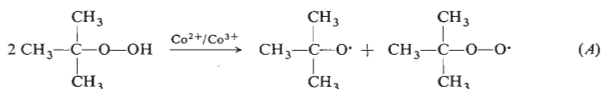
After a reaction of 2,2'-methylenebis(4-methyl-6-tert-butylphenol) (*I*) with tert-butoxy radicals generated from tert-butyl peroxide or di-tert-butyl peroxalate, dimer *II* and trimer *III* of bisphenol *I* were isolated. Both these compounds are also obtained in a reaction of bisphenol *I* with tert-butyl hydroperoxide in the presence of cobalt(II) naphthenate. The reaction course is affected by the molar ratio of the reagents. In a mixture where tert-butyl hydroperoxide does not exceed an equimolar ratio, dimer and trimer are formed as main products along with intensely brown coloured compounds whose amount increases at a higher content of hydroperoxide. The reaction of bisphenol *I* with a high excess of tert-butyl hydroperoxide yields a cyclohexadienone derivative *IV*.

2,2'-Methylenebis(4-methyl-6-tert-butyl phenol) (*I*) is an important weak-staining antioxidant produced on a technical scale. It is used to stabilize organic substrates, especially polymeric. To explain the mechanism of participation of bisphenol *I* in the process of inhibited oxidation, it is necessary to know products into which it is transformed. Nothing is known as yet about their chemical nature. This is why, in order to investigate the stabilization properties of compounds formed from 2,2'-methylenebis(4-methyl-6-tert-butyl phenol)¹ under the action of tert-alkylhydroperoxides or the ROO• or RO• radicals (*i.e.* active species formed from an oxidized hydrocarbon substrate), a model reaction was carried out, simulating the interaction of antioxidant *I* with the ROO• and RO• radicals. This reaction is regarded as a process by which the phenolic antioxidant interrupts the chain autoxidation reaction. We chose the alkoxy and peroxy radicals derived from the simplest tertiary alkyl group, *i.e.* tert-butyl group.

The reaction of bisphenol *I* with tert-butoxy radicals generated by thermal decomposition of tert-butyl peroxide^{2,3} or di-tert-butyl peroxalate⁴ yields as its main products a dimer *II*, a small amount of trimer *III* and a number of other compounds in insignificant concentrations, detectable by means of TLC; they also include some

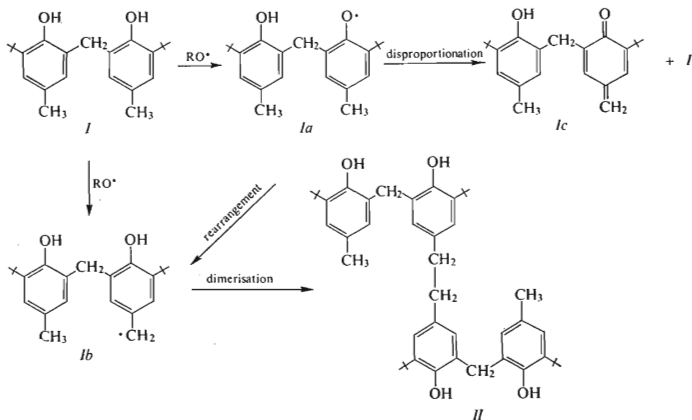
* Part XXVIII: Angew. Makromol. Chem. 15, 137 (1971).

deep-brown compounds (at least seven according to TLC). They give an intense colour to the reaction mixture; in spite of being present in an insignificant amount, they are the cause of discolouring of the organic substrates stabilized with bisphenol *I*. These compounds do not possess polymeric character; some of them are reduced with hydrosulphite. Attempts at their isolation have so far been unsuccessful. A similar composition has been observed with the reaction mixture obtained from bisphenol *I* and tert-butyl hydroperoxide at room temperature and in the presence of cobalt (*II*) naphthenate at the molar ratio bisphenol *I*: hydroperoxide 1:1 to 2:1. During the reaction the radicals tert-C₄H₉O[•] and tert-C₄H₉OO[•] are generated from tert-butyl hydroperoxide according to⁵

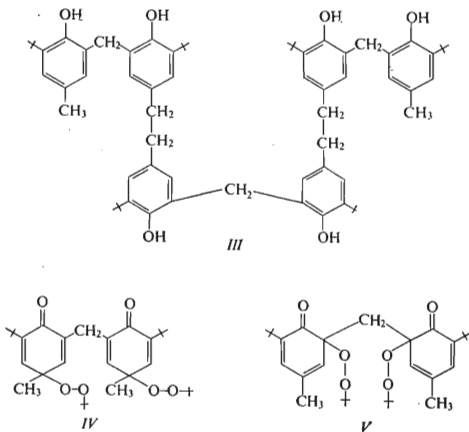


It follows from the identity of the products that the tert-butyl peroxy radicals react with an excess of bisphenol *I* in the same way as the tert-butoxy radicals.

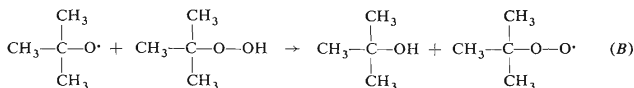
An increase in the amount of tert-butyl hydroperoxide in the reaction mixture leads to an increase in the amount of brown products; at the same time, however, their molecular weight is also increased. At the molar ratio bisphenol *I*: tert-butyl hydroxyperoxide 1:2 the reaction mixture already contains — according to the GPC analysis ($V_e = 82.9$ lim) — a prevailing majority of brownblack coloured high-molecular-weight compounds.



The experimental data do not allow us to suggest an exact mechanism of formation of dimer II. By analogy with the behaviour of mononuclear phenols⁶, three possibilities can be considered (Scheme 1): a) formation of the aryloxy radical *Ia*, its rearrangement to yield a benzyl radical followed by dimerization; b) direct formation of benzyl radical *Ib* and its dimerization; c) disproportionation of aryloxy radical *Ia* to yield a derivative of quinonemethide *Ic* and starting bisphenol *I* and dimerization of quinonemethide to yield dimer *II* and a derivative of stilbenequinone (not given in the scheme). The same sequence of reactions can explain the formation of trimer *III*.



A different course was found for the reaction if a large molar excess of tert-butyl hydroperoxide was used. The reaction is a modification of the preparation of a cyclohexadienone derivative from 2,6-di-tert-butyl-4-methyl phenol⁷. In the presence of a sufficient amount of the catalyst a rather fast exothermic reaction takes place in the benzene or tert-butyl alcohol solution. After turning brown for a short time, the reaction mixture clears up again and does not contain any phenolic compounds. The cyclohexadienone derivative *IV* has been isolated from the reaction mixture. The mother liquor still contains a mixture of diastereoisomers of *IV* and probably an isomeric cyclohexadienone derivative *V*. The formation of this compound is probably a consequence of the fact that in the presence of a large excess of tert-butyl hydroperoxide the concentration of the reactive radicals $\text{tert-C}_4\text{H}_9\text{O}\cdot$ is reduced by the reaction



All derivatives of cyclohexadienone are formed by termination of the corresponding mesomeric form of the aryloxy radicals *Ia* with tert-butyl peroxy radicals. For their formation, a certain minimum concentration of the radicals $(\text{CH}_3)_3\text{COO}\cdot$ seems to be indispensable, so that the arising aryloxy radicals would terminate with them before forming dimer *II*.

For all the compounds under investigation, an interpretation of the NMR spectra has been made and the presence of functional groups established (Table I).

TABLE I
Chemical Shifts in the NMR Spectra of Compounds *I-IV*

Groups	Bisphenol <i>I</i>		Dimer <i>II</i>		Trimer <i>III</i>		Acetate of <i>II</i>		Acetate of <i>III</i>		<i>IV</i>	
	τ	<i>J</i>	τ	<i>J</i>	τ	<i>J</i>	τ	<i>J</i>	τ	<i>J</i>	τ	<i>J</i>
	$\text{C}(\text{CH}_3)_3$	8.66	18	8.65	36	8.68	54	8.72	36	8.70	54	8.82
$\text{OC}(\text{CH}_3)_3$	—	—	—	—	—	—	—	—	—	—	8.86	42
CH_3^a	7.79	6	7.78	6	7.81	9	7.79	6	7.78	—	8.79	—
CH_3CO	—	—	—	—	—	—	7.86	12	7.82	24	—	—
CH_2-CH_2	—	—	7.25	4	7.21	8	7.27	4	7.21	8	—	—
CH_2	6.19	2	6.16	4	6.18	6	6.45	4	6.40	6	6.73	2
OH	4.38	2	4.42	4	4.35	6	—	—	—	—	—	—
H^a	3.09	4	3.05	8	3.10	12	3.28	4	3.24	6	3.53	2
							2.97	4	2.95	6	3.38	2

^aOn the aromatic ring or in cyclohexadienone.

EXPERIMENTAL

The NMR spectra were recorded in deuteriated chloroform using a JNM-3-60 spectrometer with hexamethyldisiloxane as an internal standard (τ 9.95). The IR spectra were recorded with a Perkin-Elmer apparatus, type 457, using the KBr pellets. The UV spectra were measured with an Optica Milano CF 4 R spectrometer. The mass spectrum was obtained on an AEI MS 902 spectrometer. For thin layer chromatography, precoated silicagel sheets Silufol (Kavalier, Czechoslovakia) were used. Gel chromatography was carried out using poly(styrene-co-divinylbenzene)¹. For column chromatography, silicagel according to Pitra was used, 60–120 μ .

Compounds Used

2,2'-Methylenebis(4-methyl-6-tert-butyl phenol) (*I*) (J. Dimitrov Chemical Works, Bratislava), repurified by crystallization from hexane, m.p. 131°C. tert-Butyl hydroperoxide (Chemical Works, Velvety), concentrated by vacuum distillation to a 95% product, b.p. 28–9°C/5 Torr. tert-Butyl

peroxide (Fluka AG), chromatographically pure. Di-tert-butyl peroxalate prepared according to⁴. Cobalt(II) naphthenate, cobalt content 10.80%.

Dimer II

a) *By reaction of bisphenol I with tert-butyl hydroperoxide*: To a solution of 34 g of bisphenol I (0.1 mol) and 1 g of cobalt(II) naphthenate in 100 ml of benzene, a solution of 0.05 mol of 95% tert-butyl hydroperoxide in 20 ml benzene was added while stirring at room temperature for 4 h. The mixture was left to stand overnight. According to GPC, it also contains, besides unreacted bisphenol I, dimer II, trimer III and small amounts of other compounds ($V_e = 111.3$ and 87.7). Using the two-dimensional TLC method (Silufol sheets, chloroform-hexane 1 : 1 and ether-hexane 1 : 3 as mobile phases), another three colourless phenolic compounds and seven brown-coloured compounds were detected in small amounts in the presence of the phenolic compounds I-III. The reaction mixture was fractionated on a chromatographic column (silica gel-benzene). The fraction enriched with dimer II was chromatographed again. The fraction containing almost pure dimer (which, however, was also present in other fractions) was first crystallized from hexane and then from the mixture benzene-hexane; it yielded 2.4 g of white product, m.p. 197.5 to 198.5°C. For $C_{46}H_{62}O_4$ (679.0) calculated: 81.37% C, 9.20% H; found: 81.38% C, 9.16% H. The IR spectrum proved the presence of the phenolic groups and absence of the carbonyl group; the NMR spectrum (Table I) and the mass spectrum are in accordance with structure II. The acetyl derivative of dimer II, m.p. 102-3°C. For $C_{54}H_{70}O_8$ (847.15) calculated: 76.56% C, 8.33% H; found: 76.61% C, 8.47% H.

b) *By reaction of bisphenol I with tert-butyl peroxide*: A mixture of 34 g of bisphenol I (0.1 mol) and 7.4 g tert-butyl peroxide (0.05 mol) was heated for 5 h in argon in an oil bath, 130-135°C; the temperature was then raised to 150-5°C and the heating continued for 25 h. Another 0.05 mol of tert-butyl peroxide was added and the mixture was heated for 90 h. According to TLC, the reaction mixture has a composition similar to the preceding case. Double chromatography on a silicagel column followed by crystallization yielded dimer II (1.9 g, identity proved by a mixed melting point).

c) *By reaction of bisphenol I with di-tert-butyl peroxalate*: A mixture of 2.34 g of di-tert-butyl peroxalate (0.01 mol) and 6.8 g of bisphenol I (0.02 mol) in 25 ml of benzene was left to stand for 1 h at room temperature and 1 h at 45-50°C. By means of TLC and GPC, it was proved that the mixture contained considerable amounts of dimer II and trimer III in the presence of unreacted bisphenol I.

Trimer III

The compound was isolated from an enriched fraction obtained on the chromatographic column in the process of separation of the reaction mixture formed from bisphenol I and tert-butyl hydroperoxide (molar ratio of the components 2 : 1, cf. preparation of dimer II), by evaporation of the solvent, in the form of a glassy brown-coloured substance which could not be purified thoroughly. The same product is formed from bisphenol I and tert-butyl peroxide. The GPC record shows but a single maximum (V_e 90.7); according to TLC, the white product also contains an insignificant amount of two brown compounds. According to the IR spectrum, the compound contains phenolic groups and does not contain any carbonyl group; the NMR spectrum is not at variance with structure III (with the exception of higher intensities of protons corresponding to the methyl groups on the aromatic ring; can be due to an impurity). The mass spectrum confirms structure III. Acetyl derivative of trimer III, m.p. 113-116°C. For $C_{81}H_{104}O_{12}$ (1269.7) calculated: 76.62% C, 8.25% H; found: 76.58% C, 8.36% H. The NMR spectrum (Table I) is not at variance with the structure suggested for trimer III.

2,2'-Methylenebis(4-methyl-4-tert-butyl peroxy-6-tert-butyl-cyclohexa-2,5-dienone) (IV)

a) To the solution of 1 g of bisphenol I (approx. 0.003 mol) in 10 ml of tert-butyl alcohol or benzene, 5 ml of 95% tert-butyl hydroperoxide (approx. 0.04 mol) and 1 ml of 2% benzene solution of cobalt naphthenate were added, and the mixture was refluxed for 1 h. According to GPC, the reaction mixture contains one main product (V_e 108.7) and a small amount of further compounds ($V_e = 113.7$ and 84.1). After the solvent and the excess of tert-butyl hydroperoxide were distilled off, the main product was chromatographically isolated on a silicagel column (benzene as the mobile phase) and recrystallized, first from hexane and then from methanol. Yield: 0.1 g (6.7% theor.), m.p. 139–142°C with partial decomposition (the compound undergoes slow decomposition in light). For $C_{31}H_{48}O_6$ (516.7) calculated: 72.06% C, 9.36% H; found: 72.15% C, 9.43% H. The NMR spectrum (Table I) is consistent with structure IV. According to the IR spectrum, the compound does not contain any phenolic groups: absorption at 1650 cm^{-1} (strong), 1677 (medium) and 1630 (medium) can be attributed to the cyclohexadienone structure⁸. In the UV spectrum, the absorption band at 232.5 nm suggests the cyclohexa-2,5-dienone⁸ structure; a weaker absorption at 280 nm in the case of a crude reaction mixture could be due to the presence of a small amount of isomeric cyclohexa-3,5-dienone analogue.

b) A mixture of 1 g of bisphenol I, 10 ml of benzene or tert-butyl alcohol, 5 ml of tert-butyl hydroperoxide and 0.1 g of cobalt(II) naphthenate was stirred at room temperature until it was dissolved, then left to stand in dark for three days. According to chromatographic data, the composition of the mixture is similar to that of the preceding case.

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