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ORGANIC SYNTHESIS
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2,6-Bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)cycloalkanone: Synthesis and Prospects for Use as Stabilizer for Ethylene–Propylene Rubber

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Abstract—A phenolic antioxidant was synthesized by the reaction of *N,N*-dimethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine with cyclohexanone. The influence of temperature, reactant ratio, pressure, and time on the yield of the product, 2,6-bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)cyclohexanone, was examined. The antioxidant obtained, taken both separately and in synergistic mixtures with alkylphenol and phosphites, showed high performance in inhibition of the thermal aging of ethylene–propylene rubber.

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Phenolic antioxidants (PAOs) are widely used as nonstaining stabilizers for polymers [1–6]. These agents terminate oxidation chains by the reaction of phenolic hydroxyl with peroxy radicals ($\mathrm{InH} + \mathrm{ROO}^{\cdot} \rightarrow \mathrm{In}^{\cdot} + \mathrm{ROOH}$). Despite the structural diversity of the phenolic compounds described, only a very limited number of them are used as PAOs because of the difficult availability of the raw materials and lack of commercially acceptable production technologies. Therefore, it is necessary to search for effective PAOs that can be prepared by easy-to-implement processes from readily available raw materials.

The majority of PAOs contain a 3,5-di-*tert*-butyl-4-hydroxyphenyl fragment in their structure [7]. Such fragment can be introduced, in particular, using *N,N*-dimethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine as reactive agent [8]. A series of effective PAOs have been developed on its basis. Syntheses involving this compound occur under relatively mild conditions with good yield.

This study is aimed to expand the range of PAOs prepared using *N,N*-dimethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine (Mannich Base, MB). Our approach was based on the concept of priority formation of bisphenolic PAOs, which are considerably less volatile than monophenolic AOs and exhibit high performance.

As a rule, dialkyl-substituted phenolic fragments are linked in bisphenolic AOs by bridges of various structures. As starting reagent for the formation of the bridge, we used commercially available cyclohexanone (CH). Its incorporation into the stabilizer structure can be expected to enhance the stabilizer performance owing to the additionally arising inhibition route, scavenging of alkyl radicals initially generated in the course of the polymer aging, because it is known that lactones and cyclic ketones react with alkyl radicals at high rates [9, 10].

EXPERIMENTAL

The reaction of MB with CH was performed in a round-bottomed flask equipped with a stirrer, a bubbler, a reflux condenser, and a thermometer. The flask was charged with the calculated amount of the reactants, and the temperature was elevated to 135–145°C. The reaction mixture was stirred at this temperature for 2–3 h in a nitrogen flow at atmospheric or reduced pressure. The reaction completion was judged from the disappearance of the spot of the starting MB on the thin-layer chromatogram (Silufol UV-254 plates; eluent: hexane–acetone, 5 : 1 by volume). After the reaction completion, an alkanol (C_1–C_4) was added, and the bottoms were cooled to room temperature. The precipitate that formed was filtered off, washed with cooled alkanol, and dried to constant weight. A white crystalline powder with mp 220–221°C was isolated.

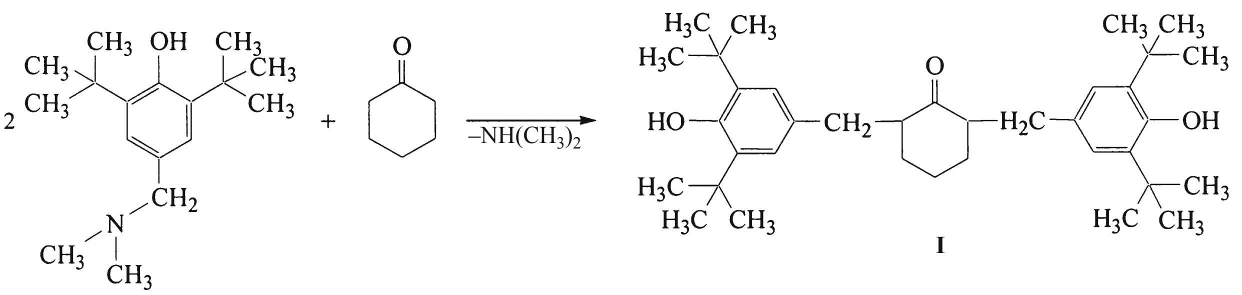
The IR spectra were recorded with a Specord-61 NIR spectrophotometer using attenuated total internal reflection (ATIR) technique, and the ^{1}H NMR spectra were taken with an AvanceIII-400 device (Bruker, 400 MHz) at 25°C from solutions in acetone-d_6. The chemical shift was determined relative to signals of the residual protons of the deuterated solvent.

The elemental analysis of the isolated product was performed with a CHNS-O Elementar Vario El cube universal elemental analyzer.

The induction period of oxidation of ethylene–propylene rubber (EPDM) was determined on a manometric oxidation setup in an oxygen atmosphere [$p(O_2)$ = 250 mmHg] at 170–175°C [1] as the time of the onset of attaining the stationary rate of the polymer oxidation.

RESULTS AND DISCUSSION

The reaction of MB with CH was performed at varied values of the MB : CH ratio (from 2 : 1 to 2 : 1.2), reaction time, and temperature. The reaction of *N,N*-dimethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine with cyclohexanone can be described by the following scheme:



The IR spectrum of the isolated product contains stretching vibration bands of the HO group at 3665 cm^{-1}, bending vibration bands of the aromatic ring in the region of 735 cm^{-1}, and stretching vibration bands of the C=O group in the region of 1705 cm^{-1}.

^{1}H NMR spectrum (acetone-d_6, 400 MHz, ppm, *J*, Hz): 1.41 s (36H, CH_3), 2.26 dd (2H, CH, ^3J = 8.7, ^2J = 14), 2.78 d (4H, CH_2, ^2J = 6.6), 2.64 m (2H, $C\underline{H}C{=}O$, ^3J = 8.7, CH, ^3J = 8.7, $^2J_{AM}$ = 14), 3.09 dd (2H, CH, ^3J = 8.7, ^2J = 14), 5.81 s (2H, OH), 6.98 s (4H, H_{arom}). Found, %: C 80.39, H 10.07. $C_{36}H_{54}O_3$. Calculated, %: C 80.90, H 10.11.

The data obtained are consistent with the structure of 2,6-bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)cyclohexanone (**I**).

The target product yield increases with an increase in the reactant ratio, MB : CH, from 2 : 1 to 2 : 1.1 (Fig. 1) and in the reaction temperature from 135 to 145°C.

Because the reaction involves the release of dimethylamine, it seemed appropriate to remove it from the reaction mixture to accelerate the process. To this end, 1 h after the start of the reaction, the pressure in the system was reduced. However, this did not affect

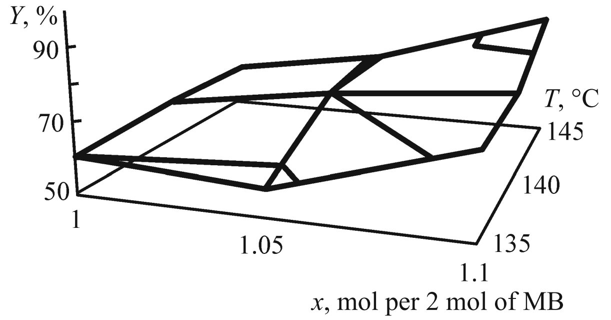


Fig. 1. Influence of temperature *T* and reactant ratio on the yield *Y* of target product **I**. Reaction time 3 h, *P* = 760 mmHg. (*x*) CH amount.

Table 1. Influence of the conditions on the target product yield in the reaction of 3,5-di-*tert*-butyl-4-hydroxy-*N,N*-dimethylbenzylamine with cyclohexanone. Reaction time 3 h

MB : CH molar ratio	*T*, °C	*P*, mmHg	Solvent for product precipitation	Yield of **I**, %
2 : 1.1	145	760	n-C_4H_9OH	86
2 : 1.1	135	760	n-C_4H_9OH	76
2 : 1.1	135	660	n-C_4H_9OH	75
2 : 1.1	135	660	n-C_4H_9OH	63[a]
2 : 1.2	135	700	n-C_4H_9OH	85
2 : 1.1	140	660	CH_3OH	84
2 : 1.1	140	660	C_2H_5OH	80
2 : 1.1	140	660	i-C_3H_7OH	76
2 : 1.1	140	660	n-C_4H_9OH	80
2 : 1.0	140	660	n-C_4H_9OH	63

[a] Reaction time 2 h.

significantly the reaction rate and the target product yield (Table 1).

The synthesized product **I** was tested as EPDM stabilizer. The stabilizer performance was evaluated by the length of the induction period of the polymer oxidation in the course of thermal oxidative aging.

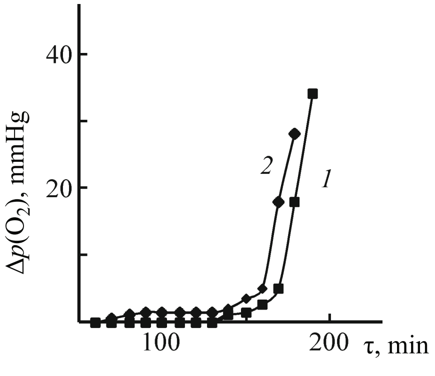


Fig. 2. Kinetic curves of oxidation of EPDM rubber containing various phenolic antioxidants. $p(O_2)$ = 250 mm Hg, c_{AO} = 0.2 wt %, T = 170–175°C; the same for Figs. 3 and 4. [$\Delta p(O_2)$] pressure change and (τ) time; the same for Fig. 6. Antioxidant: (*1*) **I** and (*2*) **II**.

The experimental data (Fig. 2) showed that the suggested stabilizer **I** taken in a concentration of 0.2 wt % well competes in the performance with Agidol 2 commercial stabilizer [bis(2-hydroxy-5-methyl-3-*tert*-butylphenyl)methane, **II**].

An important way to enhance the performance of stabilizing additives is the use of mixed formulations that exhibit the synergistic effect [1, 7]. Synergistic effects are observed most frequently in mixtures of substituted phenols with phosphites [8, 9].

To examine the possibility of using the stabilizer under consideration more efficiently, we formulated such mixtures with tris(2,4-di-*tert*-butylphenyl) phosphite (**III**) as the phosphite component. Compound **III** is one of the most effective AOs of this class. The data obtained (Fig. 3) show that there is a strong synergistic effect at **I** to **III** weight ratios from 1 : 3 to 3 : 1.

The synergistic effect also takes place in phenol–phenol mixtures in the case when the rate constants of the reactions of the inhibitors with peroxy radicals differ by no less than an order of magnitude. Gurvich et al. [10] presented a series of rate constants of the reactions of peroxy radicals with phenolic inhibitors. It is seen from

Table 2. Influence of the antioxidant ratio on the time τ before the onset of EPDM oxidation. $T = 165–170°C$, $p(O_2) = 250$ mmHg, $c_{AO} = 0.2$ wt %

Content, wt %			τ, min	Practical synergism,[a] $S_{pr} = \tau_{sm}/\tau_1^0$
I	**II**	**III**		
0	0	0.2	90	–
0	0.2	0	160	–
0	0.133	0.067	260	1.625
0	0.067	0.133	210	1.313
0.2	0	0	170	–
0.133	0	0.067	220	1.294
0.067	0	0.133	180	1.060
0.067	0.067	0.067	440	2.588
0.067	0.133	0	360	2.250
0.133	0.067	0	420	2.471

[a] (τ_1^0) Induction period of polymer oxidation in the presence of the more effective mixture component at its molar concentration equal to that of the sum of the inhibitors.

these data that, for 2,6-di-*tert*-butylphenol stabilizers, the logarithms of the rate constants of these reactions, log *k*, are 4.17–4.37, whereas for Agidol 2 (II) log *k* is 5.6. Thus, with mixtures of AOs **I** and **II**, we can expect the synergistic effect. As seen from Fig. 4, the synergistic effect is indeed observed at the **I** to **II** weight ratios from 1 : 3 to 3 : 1.

Because the synergistic effects were observed in both phenol **I**–phosphite **III** and phenol **I**–phenol **II** mixtures, we suggested that, with the ternary mixture **I** + **II** + **III**, the two synergistic effects could be combined.

To confirm this assumption and find the optimum composition of the ternary stabilizing mixture, we used a three-factor planning matrix (Table 2). The experimental results showed that the induction period of the polymer oxidation considerably increased in the ternary mixture, reaching a maximum at the AO weight ratio of 1 : 1 : 1 (Fig. 5).

To determine how the structure of the phosphite affects the oxidation resistance of the polymer, we formulated mixtures containing, along with phenolic AOs **I** and **II**, also tris(nonylphenyl) phosphite (Polygard, IV) as phosphite component. The stabilizers were taken in 1 : 1 : 1 weight ratio corresponding to the strongest synergistic effect in mixtures of **III** with phenolic AOs.

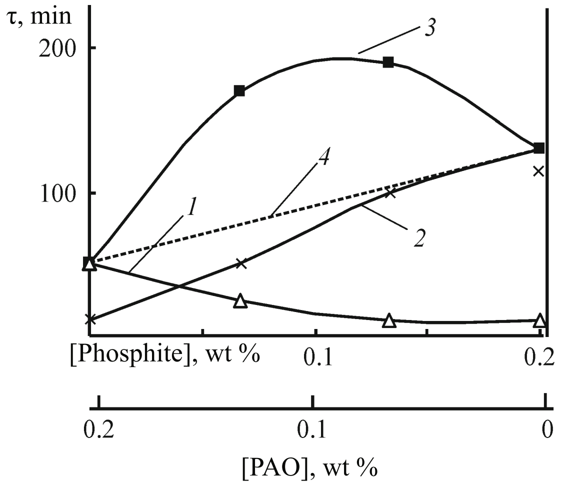


Fig. 3. Induction period τ of EPDM oxidation as a function of the stabilizer type and concentration. Antioxidant: (*1*) **III**, (*2*) **I**, and (*3*) mixture of **I** and **III**; (*4*) straight line corresponding to the additive stabilizing effect.

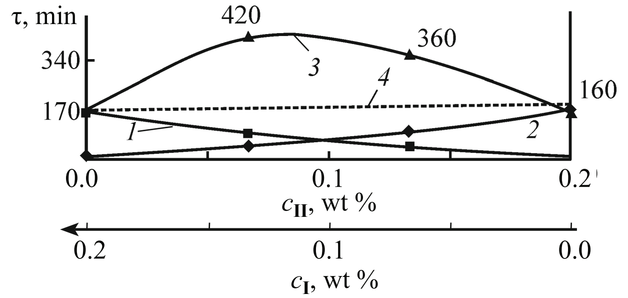


Fig. 4. Induction period τ of EPDM oxidation as a function of PAO weight ratio in the formulation. Antioxidant: (*1*) **I**, (*2*) **II**, and (*3*) mixture of **I** and **II**; (*4*) straight line corresponding to the additive stabilizing effect.

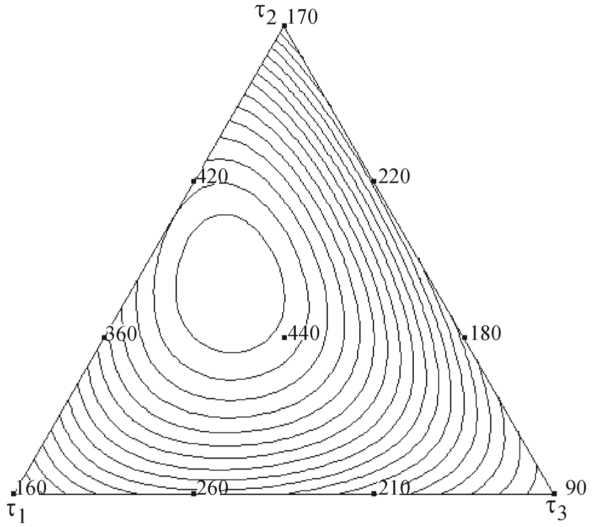


Fig. 5. Lines of equal time level (min) before the onset of oxidation in the presence of stabilizers **I** (τ_1 vertex), **II** (τ_2 vertex), and **III** (τ_3 vertex). c_{AO} = 0.2 wt %, $p(O_2)$ = 250 mmHg.

In this case, we also observed a supersynergistic AO effect (Fig. 6).

Among the formulations considered (Fig. 6), **I**–triaryl phosphite, **I**–alkyl-substituted phenol, and **I**–alkyl-substituted phenol–triaryl phosphite, the best results in EPDM stabilization were achieved with the **I**-alkyl-substituted phenol–phosphite ternary mixtures.

CONCLUSIONS

(1) Methods for preparing 2,6-bis(3,5-di-*tert*-butyl-4'-hydroxybenzyl)cyclohexanone by the reaction of 3,5-di-*tert*-butyl-4-hydroxy-*N,N*-dimethylbenzylamine and cyclohexanone in the bulk were optimized. The highest yield of the desired product, 86 wt %, was reached when the reaction was performed at 135–145°C for 3 h.

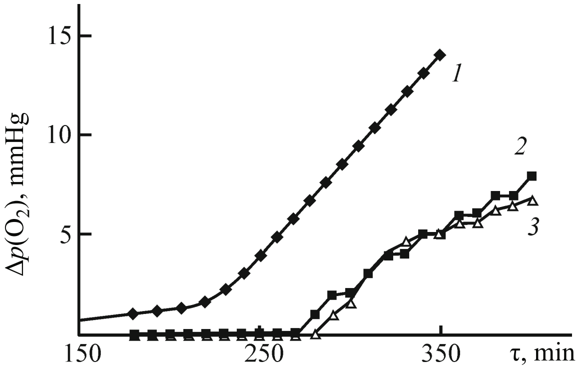


Fig. 6. Kinetic curves of oxidation of EPDM containing antioxidant mixtures. $p(O_2)$ = 250 mmHg, T = 170°C, c_{AO} = 0.2 wt %. AO mixture (weight ratio): (*1*) **I** + **IV** (2 : 1), (*2*) **I** + **II** + **IV** (1 : 1 : 1), and (*3*) **I** + **II** + **III** (1 : 1 : 1).

(2) The ways of using 2,6-bis(3,5-di-*tert*-butyl-4'-hydroxybenzyl)cyclohexanone for stabilization of ethylene–propylene rubber against thermal aging were examined. The product synthesized inhibits the oxidation on the same level as does Agidol 2 commercial stablizer.

(3) Binary mixtures of 2,6-bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)cyclohexanone with an alkylphenol and a phosphite and ternary mixtures 2,6-bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)cyclohexanone–Agidol 2–tris(2,4-di-*tert*-butylphenyl) phosphite [or tris(nonylphenyl) phosphite] exhibit a synergistic effect in inhibition of the thermal aging of ethylene–propylene rubber.

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