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Antioxidants and stabilizers

CXIV. A new transformation product of processing antioxidant 2,6-ditert-butyl-4-methylphenol in the presence of metal ions

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Summary

2,6-Ditert-butyl-4-methyl-4-(3,5-ditert-butyl-4-hydroxybenzyl)-2,5-cyclohexadiene-1-one (III) is formed from BHT (I) as a minority transformation product during the ageing of BHT doped polyethylene. To determine the structure of III and to obtain an authentic model compound, synthesis was performed using an independent procedure. The transformation product III is reported for the first time and can be considered as a source of secondary phenoxy radicals detected in aged polyolefins.

Introduction

In spite of its volatility, 2,6-ditert-butyl-4-methylphenol (BHT, I) has been used as an important processing stabilizer for polyolefins. The basic activity mechanism involves the ability to break oxidation chains by reactions with alkylperoxyls. As a consequence, 2,6-ditert-butylphenoxyl (IIa) is formed. The latter reacts in its mesomeric forms, IIa, IIb, and various products of transformation of BHT are formed. Compounds were isolated and identified which are able - depending on their structure - to affect actively the ageing of polymers under conditions of thermal oxidation or photo-oxidation (1-3). Polyolefins contain trace amounts of metallic impurities. The contents of the latter differs qualitatively and quantitatively depending on the manufacturing technology of polyolefins. Other metallic impurities are inserted additionally during processing, by means of fillers and/or during application. Some of the impurities may catalyze the dealkylation of phenolic antioxidants (4). During elucidation of BHT transformations in polyethylene doped with various ions of transition metals and during independent model reactions in liquid systems we observed (5) the formation of a new product, not reported up to now among transformation products of BHT (1-3). We optimized conditions for the synthesis of this new product using model arrangement and used the product for identification purposes.

Experimental

10 g BHT (I, chromatographically pure, m.p. 67°C) was dissolved in 10 ml chlorobenzene and 2g of recrystallized copper (II) acetate were added. The mixture was kept at 100°C under intensive mixing and air inlet. The composition of the mixture was checked continuously by means of chromatographic analyses

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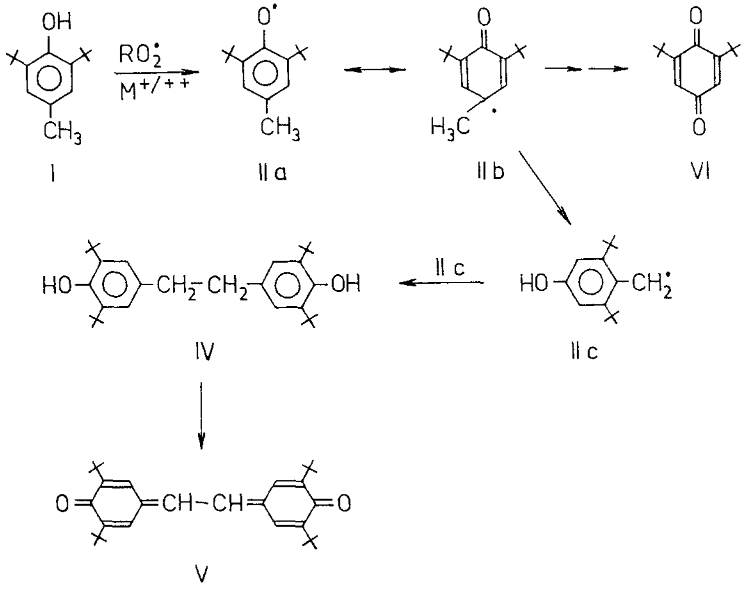
(5): TLC (silicagel, heptane + toluene 1:1) and HPLC (silicagel SGX C 18, methanol + water 9:1). The reaction was stopped after 7.5 h. The maximum of the new product III was formed under these conditions. The reaction mixture was filtered off and products were separated by column chromatography (column 80 × 3.5 cm, packed with silicagel Silpearl, gradient elution heptane ⟶ heptane + toluene 1:1). The following compounds (for structures see Scheme 1) were successively eluted: I, IV, III, V, and VI and traces of other compounds. Fractions containing the new product III were concentrated in vacuum at ambient temperature and kept under nitrogen. Decomposition of III took place at elevated temperature (45°C). 2,6-Ditert-butyl-4-methyl-4-(3,5-ditert-butyl-4-hydroxybenzyl)-2,5-cyclohexadiene-1-one (III), light yellow crystals, m.p. 102-104°C (heptane), yield 2.5%. Elemental analysis (for $C_{30}H_{46}O_2$, m.w. 438.7) calculated 82.14% C, 10.57% H, found 82.17% C, 10.80% H. Mass spectrum (VG FAB-2B): molecular peak 438, fragments 423, 382, 367, 326, 284, 256, 246, 231, 219, 205, 57. IR spectrum (Perkin-Elmer Model 577): characteristic bands at 3620 cm^{-1} (free -OH groups), 1620-1655 cm^{-1} (carbonyl groups). NMR spectrum (Varian Unity 200): ^1H NMR (200 MHz, $CDCl_3$) contains in agreement with structure III singlets of isolated protons (shifts in τ) 8.933 (t-Bu), 8.845 (CH_3), 8.715 (t-Bu), 7.369 (CH_2), 5.115-5.079 (broadened OH), 3.607 (CH=C), 3.312 (H_{Ar}) in corresponding integral intensities. ^{13}NMR (200 MHz, normal and ATP arrangements) contains the respective signals (for numbering of carbon atoms see structure III, Scheme 2; shifts in ppm related to HMDS). 24.367 (6), 27.541 (11), 28.391 (13), 32.213 (10), 36.083 (12), 46.182 (5), 123.580 (7), 124.503 (3), 125.637 (2), 130.557 (9), 133.256 (4), 144.588 (8), 150.502 (1), 184.207 (14). In addition to the reported signals, both ^1H NMR and ^{13}C NMR spectra contain also signals of compound IV in a changeable intensity and minority signals of impurities, (dependent on the age of the sample; for instability of II, see Results and Discussion).

Model compounds IV-VI used in the identification of transformation products were chromatographically pure.

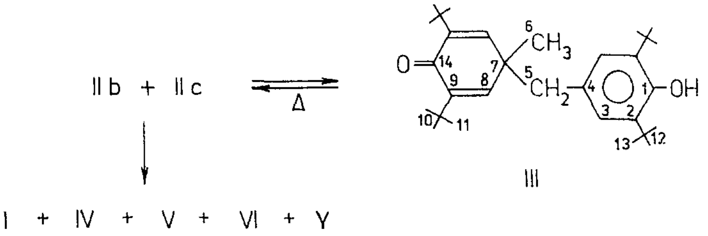
Results and Discussion

It is evident from the analytical data and from the behaviour that the new isolated transformation product of BHT has the structure of 2,6-ditert-butyl-4-methyl-4-(3,5-ditert-butyl-4-hydroxybenzyl)-2,5-cyclohexadiene-1-one (III). The generation of III during the oxidation of stabilized liquid hydrocarbons and hydrocarbon polymers containing catalytical metallic impurities is exemplified in Schemes 1 and 2. Formation of primary radicals IIa, IIb and of benzyl radical IIc generated via radical rearrangement is involved. Radical IIb takes part in the formation of peroxidic products (1-3). The latter are transformed consecutively to 2,6-ditert-butyl-1,4-benzoquinone (6).

The benzyl radical IIc is a precursor of coupling products 4,4'-ethylenebis(2,6-ditert-butylphenol) (IV) and tetratert-butylstilbenequinone (V). Both these compounds were formed in the reaction mixture and isolated. Compound III is formed by an interaction of IIb with IIc. The conditions for the synthesis of III are very favourable in the presence of metallic



SCHEME 1

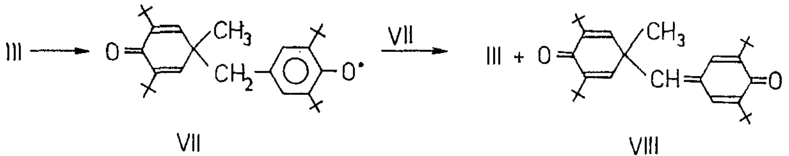


SCHEME 2

ions. Formation of III was not observed or reported in any of preceding mechanistic studies performed either by us or other research groups. Compound III may have been hidden during chromatographic analyses among other (mostly identified) minority products.

Transformation product III is very sensitive in solution to temperatures above 30°C and to polar solvents (hydrocarbons or trichlorobenzene were a suitable environment for synthesis, isolation and analysis). This implies the ability of III to survive for a long time in the matrix of hydrocarbon polymers and explains denaturation observed during the extraction of doped polymers with polar solvents and at elevated temperatures. Compound III is stable in contact with silicagel: chromatographic separation and analyses are therefore possible.

Thermolysis of III takes place at increased temperatures and thermally more stable IV is formed together with V (via oxidation of IV), I (via disproportionation of IIa), VI and a mixture of unidentified minority products Y (Scheme 2). Thermolability of III can be the reason why this product has not been isolated up to now and has not been described among



SCHEME 3

transformation products of BHT formed in weathered polyolefins. We consider (5) that phenoxyradicals VII generated from III due to the chain-breaking activity of the latter in autoxidized systems may be a more realistic explanation of the formation of EPR signals of secondary phenoxyradicals observed in aged polyolefins than formation of phenoxyradicals related to galvinoxyl (6). Formation of the latter requires an energetically relatively demanding loss of a methyl group. Radical VII is able to disproportionate (Scheme 3). Quinonemethide VIII contributes to discoloring properties of BHT in the polyolefin stabilization together with compounds V and VI and cyclopentadienones formed via photolysis of peroxidic products of BHT transformation (3).

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