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Note

Determination of 2,6-di-(tert.-butyl)-4-methylphenol in rubber-base materials and identification of an oxidation product from 2,6-di-(tert.-butyl)-4-methylphenol

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It is well-known that 2,6-di-(*tert.*-butyl)-4-methylphenol (BHT) is widely used in the rubber and plastics industry as an antioxidant. In many rubber-base systems, BHT is added to prevent oxidative deterioration during processing and to prevent aging which eventually could cause deterioration of the rubber and its attendant properties[1].

An experimental rubber-base mass which was purposely fortified with BHT was found to discolor slightly to a faint yellow color. Through a series of intricate experiments, the yellow-colored material was separated from the rubber-base mass by solvent extraction, then separated from the additional residual rubber-base components by column chromatography, further purified, isolated, concentrated by thin-layer chromatography (TLC) and identified by a variety of analytical techniques.

This paper deals with the isolation and identification of this yellow colored material which was identified as 3,5,3′,5′-tetrabis(*tert.*-butyl)stilbenequinone.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade.

Column and thin-layer chromatography

Silica gel (60–200 mesh) from J. T. Baker (Phillipsburg, N.J., U.S.A.) was used for column chromatography. Chromatographic columns (15 × 1.7 cm, I.D.) were equipped with a PTFE stopcock and sintered glass disc.

Silica gel GF plates (20 × 20 cm, 250 nm layer thickness) from Analtech. (Newark, Del., U.S.A.), were used for purification, separation and concentration of the colored material.

Gas chromatography (GC)

A Perkin-Elmer Model 3920B gas chromatograph equipped with a flame ionization detector (FID) was employed for the quantitative determination of BHT. An automatic sampler, Model 7670A (Hewlett-Packard) and computing integrator, Sigma 10 (Perkin-Elmer) were connected to the gas chromatograph and used for

automatically injecting the samples and computing results. A coiled stainless-steel column (183 × 0.32 cm I.D.) containing 3% SP2100 coated on 100–120 mesh Supelcoport (Supelco, Bellefonte, Pa., U.S.A.) was used. The gas chromatograph was operated isothermally under the following conditions: injector temperature, 200°; column temperature, 140°; carrier gas (helium) at a flow-rate of 40 ml/min and a detector temperature of 200°.

Analysis of BHT

A GC procedure was developed which allowed for the quantitative determination of BHT in a rubber base or in an adhesive which is coated on a tape.

A 10-ml volume of a solvent mixture of light petroleum–absolute ethanol (60:40) was employed to extract the BHT from 0.1 g mass in a 20-ml serum vial with the aid of a shaker (Spex Mixer Mill, Spex Industries, Metuchen, N.J., U.S.A.). A 1 microliter injection of the supernatant solution was injected into the GC column. A standard BHT solution was prepared to contain 0.5 mg/100 ml of solvent mixture and a 1-μl injection of this solution was made to provide quantitative data. The retention time for the BHT peak was 5.5 min.

The technique was automated so that injections were made with an automatic sample injector and the data calculated with a computing integrator. This not only provided increased accuracy and precision of the data generated but allowed one to more effectively utilize the gas chromatograph by having it perform its operation unattended overnight.

Separation and purification of yellow material from rubber mass

Both outer edges from a roll of experimental rubber-base tape were cut (approximately 32 × 0.004 m each) so that enough material could be collected for eventual identification. It should be mentioned that the outer edges contained the most apparent yellow color in the mass.

The two samples were separately extracted with 50 ml of light petroleum–absolute ethanol (60:40) and the resulting solutions were separately evaporated. Hexane was added and the solutions placed on two separate 8-cm silica gel columns that were previously washed and equilibrated with hexane. The initial chromatographic separation was performed by eluting with 50 ml of hexane since this left the yellow-colored material remaining in the column while eluting the matrix components. The eluent was then changed to toluene which eluted the yellow-colored material.

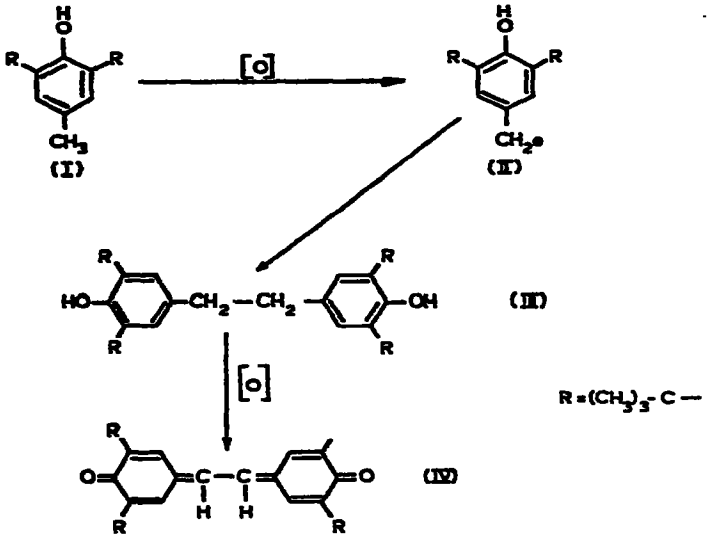
The toluene fractions were evaporated and the residues were again subjected to the same column chromatographic separation scheme for further purification. The resulting effluents were combined and evaporated to near dryness. The yellow-colored residue was dissolved in carbon tetrachloride and the entire sample solution streaked on a 20 × 20 cm silica gel plate. The TLC system employed was hexane–acetic acid (100:4) which was found to optimize the separation from other interfering components. Two passes were made on the same plate using this solvent system.

The yellow-colored zone was scraped from the TLC plate and extracted with acetone. The entire yellow solution was again streaked onto another 20 × 20 cm silica gel plate and chromatographed (two passes) with the hexane–acetic acid (100:4) solvent system. Once more the yellow material was scraped from the plate, extracted with acetone and developed as before. Based on the work of Spitz[2] and other

workers[3–5], the last two plates were purified by chromatographing them in the hexane–acetic acid system prior to adding the sample. This technique was employed because of potential impurities that might be present in the silica gel which could cause difficulty in the final identification of the yellow material[2]. After prepurification of the TLC plate, the sample was chromatographed as before and the resulting yellow material scraped from the plate, extracted with acetone and subjected to several different tests for identification.

Synthesis of oxidation product from BHT

The oxidation of 2,6-di-(*tert.*-butyl)-4-methylphenol (I) is known to yield 3,3,5′,5′-tetrabis(*tert.*-butyl)stilbenequinone (IV). It has stated in the literature[6,7] that structure III is easily oxidized to structure IV.



The method of Cook and co-workers[6,7] was employed for the synthesis of 3,3,5′,5′-tetrabis(*tert.*-butyl)stilbenequinone which is one of the many possible oxidation products[8] from BHT. An absorption spectrum in the visible region of this synthesized material was identical to that obtained by Leventhal *et al.*[9]. TLC of the material in both hexane–toluene (1:1) and hexane–acetic acid (100:4) showed the presence of only one major spot under ultraviolet light, white light and after spraying the plate with a 1% iodine–chloroform solution. The infrared spectrum of the synthesized compound was consistent with the profile shown by Bohn and Campbell[10]. Likewise, mass spectrometry conformed to the relative abundance data given by Leventhal *et al.*[9].

Reactivity of BHT in acid, base and under alkaline oxidative conditions was evaluated for additional background information and to establish the stability profile of BHT. BHT was dissolved in toluene and placed in 1 *N* sulfuric acid and 1 *N* sodium hydroxide. These systems were shaken for several hours and allowed to stand overnight. No yellow color was observed in either phase; however, addition of potassium

ferricyanide to these systems produced a yellow color in the toluene phase of the alkaline system. TLC of the yellow-colored toluene solution on a silica gel plate using hexane–toluene (70:30 and 50:50) and hexane–acetic acid (100:4) as separate solvents produced one major spot having the same R_F as the synthesized oxidation product of BHT.

RESULTS AND DISCUSSION

The yellow-colored material obtained after purification by column chromatography and TLC was found to have the same R_F value and the same basic visible absorption spectrum as compared to the synthesized 3,3′,5,5′-tetrabis(*tert.*-butyl)-stilbenequinone. Mass spectral data also indicated that the yellow color was due to the stilbenequinone compound as the relative abundance of the major ions compared well with the mass spectra of the synthesized compound and the data described in the paper by Daun *et al.*[11].

Based on the foregoing work, it was shown that eliminating BHT from the mass also eliminated the yellow color. The GC procedure aided in the evaluation of BHT remaining in the mass. From this GC procedure, one may be able to define the minimum level of BHT required to provide processing and aging protection for the mass and allow for correlation between the amount of BHT and degree of color formation. The major thrust of this paper is to make the reader aware of the chemical characteristics of BHT and how one may be able to cope with or eliminate color formation that has been identified as the yellow-colored oxidation product of BHT.

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