SYNTHESIS OF THE MONOMERIC ANTIOXIDANT
3,5-di-tert-butyl-4-hydroxy-styrene by the thermal decomposition
of trans-3,5-di-tert-butyl-4-hydroxycinnamic acid

D. Munteanu*, C. Csunderlik** and I. Tincul***

*CHEMICAL RESEARCH INSTITUTE, CENTRE FOR PLASTICS, STR. GARII 25, R-1900
TIMISOARA
**DEPARTMENT OF ORGANIC CHEMISTRY, CHEMICAL ENGINEERING FACULTY,
POLYTECHNICAL INSTITUTE, TIMISOARA, ROMANIA

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The thermal decomposition of trans-3,5-di-tert-butyl-4-hydroxy-cinnamic acid (BHC) in the solid state, in aqueous solution and in solutions in organic solvents was studied in order to develop a preparative method for the synthesis of the monomeric antioxidant 3,5-di-tert-butyl-4-hydroxystyrene (BHS). Thermal methods of analysis showed that, during the solid-state decomposition of BHC, its decarboxylation was accompanied by desalkylation and polymerization of the styrenic decomposition products. BHC decarboxylation is aqueous solution was also accompanied by polymerization. A kinetic study of BHC decomposition in organic solvents by ¹H-NMR spectrometry revealed that only the decomposition of BHC in aprotic dipolar solvents such as dimethylsulphoxide and dimethylformamide, at temperatures lower than 150°C, could be used as a preparative method for the synthesis of BHS. The decarboxylation of BHC took place by zero-order kinetics through a mechanism involving the ionization of BHC in the aprotic dipolar solvent. The reaction rate increased drastically with increasing solvent polarity and in the presence of trace amounts of BHC sodium salt. Both monomeric antioxidants, i.e. BHS and BHC, may be used to obtain polymer-bound antioxidants, e.g. by melt-grafting onto polyethylene.

Improved polymer stabilization continues to be an area of much intense effort in both industrial and academic laboratories. Two factors are responsible for the effectiveness of stabilizers: the intrinsic stabilizer behaviour and the permanence of the stabilizer in the polymer. The effectiveness of antioxidants may be increased by improvement of the antioxidant permanence...
in the polymer, and by minimizing physical losses due to incompatibility, volatility and extractability of the antioxidants during processing and use. Basically, there are two approaches to attain an increase of the persistence of an antioxidant. One is to produce antioxidants of high molecular weight and therefore of low volatility or extractability. The other is to bind the antioxidant to the polymer chemically, thereby guaranteeing its permanence in the polymer matrix. Many attempts have been made to do this and routes to obtain such permanent antioxidants have been reviewed [1-8].

Some routes to obtain high molecular weight or polymer-bound antioxidants make use of monomeric antioxidants, i.e. dual functional compounds bearing an antioxidant function and a polymerizable group. The monomeric antioxidants are capable of homopolymerization, random copolymerization with different monomers, and graft copolymerization onto polymer chains. General methods for the synthesis of monomeric antioxidants have been reported [1, 4]. However, many of the are sophisticated and expensive methods which require unusual reactants.

It was the objective of our work to prepare the monomeric antioxidant 3,5-di-tert-butyl-4-hydroxystyrene (BHS) by a simple method, i.e. the thermal decomposition of trans-3,5-di-tert-butyl-4-hydroxy-cinnamic acid (BHC), and to study the mechanism of the decarboxylation reaction

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R- \text{CH} = \text{CH}- \text{COOH} \rightarrow R- \text{CH} = \text{CH}_2 + \text{CO}_2
\]

Experimental

Synthesis of 3,5-di-tert-butyl-4-hydroxycinnamic acid (BHC)

The first step in the synthesis of BHC was the synthesis of 3,5-di-tert-butylbenzaldehyde (BHA) by a new approach, i.e. the Duff synthesis. A solution of glycoboric acid, i.e. the catalyst, in ethylene glycol, i.e. the solvent, was first obtained by heating a mixture of ethylene glycol and boric acid at 150°. Then, 2,6-di-tert-butyl-phenol and hexamethylenetetramine