

ANTIOXIDATIVE EFFECTS OF SPIROBIINDANOLS AND 2-ALKOXYPHENOLS IN TETRALIN*

M. PRUSÍKOVÁ and J. POSPÍŠIL

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

Received August 6th, 1974

Antioxidative properties of spirobiindanols *I–IV* and 2-alkoxyphenols *V* and *VI* in the stabilization of tetralin oxidized at 60°C in presence of 2,2'-azobis(isobutyronitrile) were investigated. Tetrols of type *IV* were found to be the most active compounds. Partial etherification of the pyrocatechol ring generally causes the loss of the antioxidative effect.

A systematic study of the antioxidative properties of various groups of phenols provided knowledge about the basic effects of structure on activity^{1–3}. The antioxidative activities were estimated on the basis of the effects upon the extent and course of oxygen absorption in an oxidized organic substrate. Data on mono- and polynuclear phenols were obtained, allowing a rational choice of stabilizers. This work is dealing with a study of the properties of phenols having a spirobiindane skeleton in the stabilization of tetralin. Most of the compounds under investigation are readily available synthetically; the advantageous properties of some of them have been described in the stabilization of isotactic polypropylene⁴. In order to complete the knowledge about the partial etherification of antioxidants of the pyrocatechol type we also investigated the stabilizing effect of 2-alkoxyphenols.

EXPERIMENTAL

Chemicals. Spirobiindanols *I–IV* and 2-alkoxyphenols *V* and *VI* used as antioxidants were chromatographically pure; their properties are given in ref.^{4–6} 2,2'-Azobis(isobutyronitrile) (initiator), m.p. 103°C (acetone). Tetralin (substrate) was purified similarly to the preceding work⁷, b.p. 203°C.

Method for the determination of the antioxidative activity and evaluation of results. The antioxidative activity was determined by measuring oxygen consumption in tetralin at atmospheric pressure using a thermostated volumetric absorption apparatus⁷ at 60°C. The initiator concentration was $5 \cdot 10^{-3}$ M, the antioxidants concentration was $2 \cdot 10^{-4}$ M. The activities of the individual compounds were calculated from the τ values giving time in min needed for the absorption of 100 ml oxygen/mol tetralin. 2,2'-Methylenebis(4-methyl-6-tert-butylphenol) was used as standard for calculating the relative activity A_r after ref.⁷. The stoichiometric coefficient n for

* Part LV in the series Antioxidants and Stabilizers; Part LIV: This Journal 40, 987 (1975).

compounds exhibiting an induction period on the absorption curve was calculated using ref.⁸ S_r is the ratio of slopes of the absorption curves in the inhibited (S_x) and uninhibited (S_0) oxidation. It was calculated from the relationship $S_r = S_x/S_0$ for an intercept on the curve corresponding to the absorption of 100–200 ml oxygen/mol tetralin. A_r , S_r , and n are given in Tables I and II.

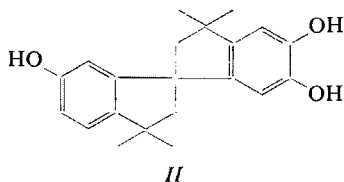
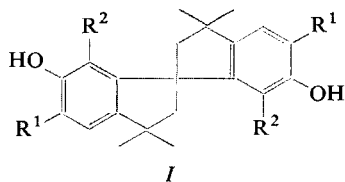
RESULTS AND DISCUSSION

Phenolic antioxidants of the *I–IV* type with a spirobiindane skeleton are greatly nonvolatile and therefore suited for the stabilization of polymeric substrates⁴. This paper reports the results of an investigation of their antioxidative activity determined at 60°C by measuring oxygen absorption in tetralin. The oxidation was initiated with 2,2'-azobis(isobutyronitrile). 11 compounds of the same structural type were investigated; 2,2'-methylenebis(4-methyl-6-tert-butylphenol) was used as standard, being an important technical antioxidant which allows a comparison with respect to the effects of structure in the group of compounds under investigation, and also with respect to its technical application.

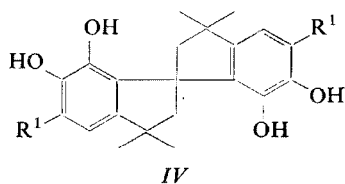
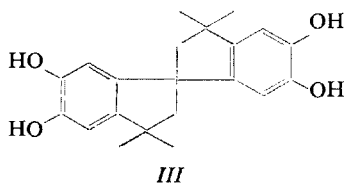
The basic compound of the series, *i.e.* 3,3,3',3'-tetramethyl-1,1'-spirobiindane-6,6'-diol (*Ia*) is a very weak antioxidant. It follows from Table I that in spirobiindanes derived from monohydric phenols (*Ia–Ie*) the antioxidative activity is increased by the introduction of one alkyl group into each aromatic ring of the molecule. In particular, an important increase in A_r is caused by the alkylation of positions 5,5' by a bulky tertiary alkyl group (*cf.* *Ib*, *Ic*). An activity comparable with the standard was exhibited by the tert-butyl derivative *Ic*.

Spirobiindanediol *Ie* containing two methyl groups on each aromatic ring is more active than the corresponding monomethylated derivative *Ib*. However, the increase in activity due to the presence of a second methyl group in the ring and estimated with respect to A_r is not so pronounced as in the case of the comparison of the antioxidative properties of 2-methylphenol and 2,6-dimethylphenol⁹. This difference is caused by different structural effects in the molecules of mononuclear phenols and phenols of type *I* in which more complicated steric effects and bonds on the indane ring become operative. The difference in effects upon the stabilizing activity due to the methylation of the ring can be seen if the courses of oxygen absorption are compared: spirobiindanediol *Ia* and its methyl derivative *Ib* do not give rise – similarly to the other 5,5'-dialkyl derivatives *Ic* and *Id* – to an induction period (Fig. 1), while in presence of 3,3,5,7,3',3',5',7'-octamethyl-1,1'-spirobiindane-6,6'-diol (*Ie*) the induction period is clearly visible on the absorption curve of oxygen. The calculated value of the stoichiometric coefficient n of these compounds is very close to 4.

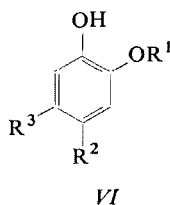
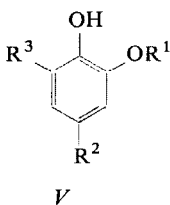
The antioxidative activity of mononuclear phenols is increased by the presence of a further hydroxyl group in the position *ortho*³. This finding also holds for a polynuclear skeleton: the spirobiindane derivative *III* derived from pyrocatechol was the most active antioxidant in the series of spirobiindanols studied in isotactic polypro-



- Ia*, $R^1 = R^2 = H$
Ib, $R^1 = CH_3$, $R^2 = H$
Ic, $R^1 = C(CH_3)_3$, $R^2 = H$
Id, $R^1 = C(CH_3)_2CH_2C(CH_3)_3$
Ie, $R^1 = R^2 = CH_3$
If, $R^1 = OCH_3$, $R^2 = H$
Ig, $R^1 = OCH_2CH_3$, $R^2 = CH_3$



- IVa*, $R^1 = H$
IVb, $R^1 = C(CH_3)_3$



- Va*, $R^1 = R^2 = CH_3$, $R^3 = H$
Vb, $R^1 = CH_3$, $R^2 = CH_2CH_2CH_3$, $R^3 = H$
Vc, $R^1 = CH_2CH_3$, $R^2 = CH_3$, $R^3 = H$
Vd, $R^1 = CH_2CH_3$, $R^2 = H$, $R^3 = CH_3$
Ve, $R^1 = CH_2CH_3$, $R^2 = CH_3$, $R^3 = C(CH_3)_3$
Vf, $R^1 = CH_2CH_3$, $R^2 = C(CH_3)_3$, $R^3 = CH_3$
Vg, $R^1 = CH_2CH_3$, $R^2 = R^3 = C(CH_3)_3$
Vh, $R^1 = CH_2CH_3$, $R^2 = CH_3$, $R^3 = C(CH_3)_2CH_2C(CH_3)_3$
Vi, $R^1 = CH_2CH_3$, $R^2 = C(CH_3)_2CH_2C(CH_3)_3$, $R^3 = CH_3$
Vj, $R^1 = C(CH_3)_3$, $R^2 = C(CH_3)_2CH_2C(CH_3)_3$, $R^3 = H$
Vk, $R^1 = R^3 = C(CH_3)_3$, $R^2 = C(CH_3)_2CH_2C(CH_3)_3$
Vla, $R^1 = R^2 = CH_3$, $R^3 = C(CH_3)_3$
Vlb, $R^1 = R^2 = CH_3$, $R^3 = C(CH_3)_2CH_2C(CH_3)_3$
Vlc, $R^1 = CH_2CH_3$, $R^2 = H$, $R^3 = CH_3$
Vld, $R^1 = CH_2CH_3$, $R^2 = CH_3$, $R^3 = C(CH_3)_3$
Vle, $R^1 = R^2 = R^3 = H$

pylene⁴. A further increase in the number of hydroxyl groups (in compounds with the pyrogallol or hydroxyhydroquinine structure) did not exhibit any favourable effect. The reason could be sought in the increased oxidative deactivation of these compounds with oxygen and in the impaired compatibility of the polar antioxidant molecule with the nonpolar polyolefin. The increase in the number of hydroxyl groups in the nonalkylated spirobiindanol led to such a decrease in solubility also in tetralin that the derivatives containing six hydroxyl groups in the molecule did not any more

TABLE I

Antioxidative Properties of Spirobiindanols I–IV in Tetralin Oxidation, 60°C

Meaning of A_r , S_r and n and data on concentration *cf.* Experimental.

Antioxidant	A_r	n	S_r	Antioxidant	A_r	n	S_r
<i>Ia</i>	0.19	—	0.66	<i>II</i>	0.95	2.97	0.37
<i>Ib</i>	0.61	—	0.57	<i>III</i>	0.95	3.15	0.43
<i>Ic</i>	1.00	—	0.43	<i>IVa</i>	1.51	5.56	0.30
<i>Id</i>	0.92	3.97	0.35	<i>IVb</i>	1.33	5.24	0.39
<i>Ie</i>	0.76	4.07	0.65				
<i>If</i>	0.53	—	0.67				
<i>Ig</i>	0.57	3.02	0.84				

TABLE II

Antioxidative Properties of Pyrocatechol (*VIe*) and 2-Alkoxyphenols of Type *V* and *VI* in Tetralin Oxidation, 60°C

Symbols and conditions similar to Table I.

Derivative	A_r	n	S_r	Derivative	A_r	n	S_r
Compounds <i>V</i>				<i>i</i>	0.27	—	1.07
<i>a</i>	0.32	—	—	<i>j</i>	0.08	—	0.78
<i>b</i>	0.28	—	—	<i>k</i>	0.25	1.32	0.95
<i>c</i>	0.39	—	—	Compounds <i>VI</i>			
<i>d</i>	0.24	—	—	<i>a</i>	0.36	1.86	0.76
<i>e</i>	0.34	—	—	<i>b</i>	0.24	—	0.89
<i>f</i>	0.23	1.33	0.93	<i>c</i>	0.21	—	0.71
<i>g</i>	0.20	—	—	<i>d</i>	0.37	1.94	0.81
<i>h</i>	0.35	—	0.79	<i>e</i>	0.76	3.15	0.82

dissolve in a concentration needed for the comparison with the whole series of compounds under investigation. Therefore only spirobiindanetriols were used in the investigation. Their solubility in a nonpolar substrate is increased by the alkylation of the aromatic rings of the molecule. However, such modification of the molecule need not always have a favourable effect on the improvement of the antioxidative properties⁴.

In the stabilization of tetralin one could clearly see the effect of the change in the total amount of the hydroxyl groups on the increase in the relative activity of non-alkylated compounds in the series diol *Ia* < triol *II*, tetrol *III* < tetrol *IVa*. According

FIG. 1
Oxygen Absorption in the Oxidation of Tetralin (60°C) Stabilized with Spirobiindanols ($V = \text{ml O}_2/\text{mol tetralin}$)

Stabilizers: ○ *Ia*, ⊙ *Ig*, ⊖ *Ib*, ⊕ *Ie*, ○ *Ic*, ● *IVb*, ⊙ *IVa*; - - - - - nonstabilized tetralin.

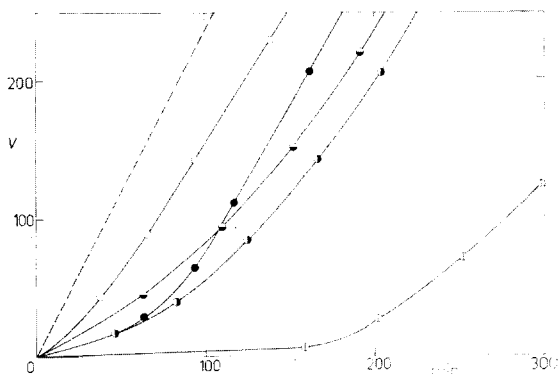
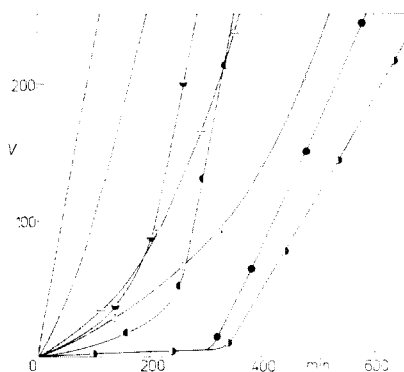


FIG. 2
Oxygen Absorption in the Oxidation of Tetralin (60°C) Stabilized with 2-Alkoxyphenols and Pyrocatechol ($V = \text{ml O}_2/\text{mol tetralin}$)

Stabilizers ● *Vd*, ⊙ *Va*, ○ *Vj*, ● *Vf*, ⊕ *Vle*; - - - - - nonstabilized tetralin.

to the results, in triol *II* the presence of the pyrocatechol part of the molecule plays a decisive role; another hydroxyl group in position 5 (comparison of *II* and *III*) did not improve the relative activity. The form of the oxygen absorption curves (Fig. 1) documents the strong antioxidative character of phenols *II–IV* which under the conditions used for the investigation can be compared with the standard or are more active. The very favourable properties of 3,3,3',3'-tetramethyl-1,1'-spirobiindane-6,7,6',7'-tetrol (*IVa*) are somewhat reduced by the alkylation of positions 5,5' (*IVb*). Both compounds of type *IV* are the most active compounds of the whole series of hydroxy derivatives of spirobiindane investigated and used for the stabilization of tetralin. If estimated on the molar basis, their activity is almost twofold compared with pyrocatechol. This fact is due to the substituents' effects of bonds belonging to the alicyclic part of the spirobiindanetetrol molecule. On the other hand, a difference compared to the stabilization of isotactic polypropylene has been observed⁴, for which tetrol *III* was the most active antioxidant. The activity of both isomeric derivatives of pyrocatechol is probably affected by the difference in the extent of the role played by the individual partial reactions of the inhibitive process (including deactivation of the antioxidant) at different temperatures of the oxidation of tetralin and polypropylene.

Another group under investigation consisted of spirobiindanediols *If* and *Ig* derived from 2-alkoxyphenols. Their antioxidative activity corresponds to spirobiindanediol *Ib*, in the estimation both of the A_r values and of the course of oxygen absorption. Consequently, their properties are typical of the derivatives of monohydric phenols. The comparison with A_r obtained for tetrol *III* confirms the results of measurements carried out in polypropylene⁴: partial etherification of the pyrocatechol ring in the derivatives of spirobiindanetetrol leads to a decrease in the antioxidative activity. Unlike data obtained by the oxidation of polypropylene the activity of the spirobiindanol derivative derived from 2-alkoxyphenol for the stabilization of tetralin is not increased even if other methyl groups in positions 7,7' are present.

The behaviour of 2-alkoxyphenols compared to pyrocatechol was checked by using a series of compounds of types *V* and *VI*. Mono- and dialkylated 2-alkoxyphenols containing in the alkoxy group the methyl, ethyl or tertiary butyl group were studied (Table II). In the oxidation of tetralin carried out in presence of 2-alkoxyphenol oxygen is absorbed from the very beginning of the reaction. In most cases no induction period can be seen (Fig. 2). The ratio of slopes of the absorption curves in the inhibited and uninhibited oxidation (S_r) indicates that the course of oxygen absorption after completion of the induction period or in the region after absorption of 100 ml of oxygen by 1 mol of tetralin (for compounds not exhibiting an induction period) is not affected by the transformation products of 2-alkoxyphenols. The S_r values were not calculated for compounds in the presence of which the course of oxygen absorption in the range of 100–200 ml O_2 /mol tetralin was not linear.

The relative activity of 2-alkoxyphenols is not affected in any marked manner by the alkylation of the ring and lies within the range 0.49–0.96. The methoxy and ethoxy derivatives do not almost differ by their activity. The presence of the bulky tertiary butoxy group has an unfavourable effect. The stoichiometric coefficients n could be calculated only for Vf , Vk (1.32–1.33), Vla and Vld (1.86–1.94) which are the most active in the whole group of 2-alkoxyphenols under study. In no case do they exceed a value of 2.

A pronounced decrease in the antioxidative activity of 2-alkoxyphenols compared to pyrocatechol observed in the oxidation of tetralin is in agreement with the results of investigation of similar compounds at a high oxidation temperature of polypropylene¹⁰. A similar trend of the effect of structure was also detected in the stabilization of tetralin by methylenebis(2-alkoxyphenols) and methylenebispyrocatechols. Along with the results in the spirobiindane series it confirms the general character of this modification of the pyrocatechol arrangement of the antioxidant molecule.

It holds for the whole series of the hydroxy derivatives of spirobiindane that their S_r values are lower than unity regardless of the fact whether $I-IV$ contains the arrangement of monohydric phenols, 2-alkoxyphenols, or pyrocatechol. Thus, they indicate a certain retardative activity of the products obtained from the original antioxidants during inhibited oxidation, predominantly in its later stages.

We wish to thank Dr L. Taimr, Dr E. Hellinger and Mrs M. Kremlíčková for syntheses of compounds used throughout this work.

REFERENCES

1. Scott G.: *Atmospheric Oxidation and Antioxidants*. Elsevier, Amsterdam 1965.
2. Pospíšil J.: *Antioxidants*. Academia, Prague 1968.
3. Pospíšil J.: *IUPAC International Symposium on Macromolecular Chemistry*, Plenary and Main Lectures Volume, p. 789. Akadémiai Kiadó, Budapest 1971.
4. Pospíšil J., Kotulák L., Taimr L.: *Europ. Polym. J.* 7, 255 (1971).
5. Taimr L., Pospíšil J.: *Tetrahedron Lett.* 1961, 456.
6. Pospíšil J., Taimr L.: *This Journal* 30, 1092 (1965).
7. Prusíková M., Pospíšil J.: *Erdöl Kohle* 25, 80 (1972).
8. Zikmund L., Taimr L., Čoupek J., Pospíšil J.: *Europ. Polym. J.* 8, 83 (1972).
9. Prusíková M., Kotulák L., Pospíšil J.: *XXXIXth Congress of Industrial Chemistry*, Bucuresti 1970, Proceedings Vol. IV, p. 147.
10. Pospíšil J., Taimr L., Kotulák L.: *Advan. Chem. Ser.* 85, 169 (1968).

Translated L. Kopecká.