

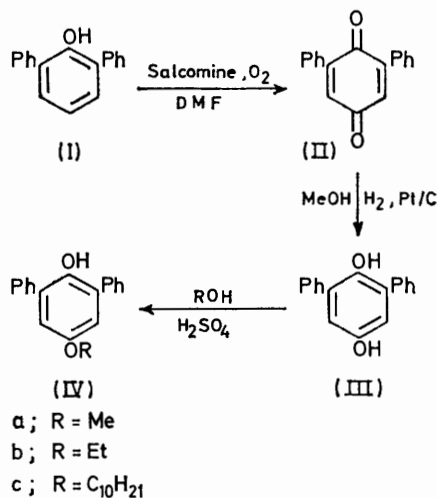
## Antioxidative Properties of Phenyl-substituted Phenols. Part I. The Mechanism of Synergism between 4-Alkoxy-2,6-diphenylphenols and $\beta\beta'$ -Disubstituted Diethyl Sulphides

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A pronounced synergism between 4-alkoxy-2,6-diphenylphenols and  $\beta\beta'$ -disubstituted diethyl sulphides has been observed in the inhibition of autoxidation of polypropene at 180 °C. The mechanism of this synergistic action (at temperatures  $\geq 150$  °C) has been investigated. N.m.r. model experiments have shown that the phenolic antioxidant (AH) is regenerated continuously from the phenoxyl radical (A $\cdot$ ) by hydrogen atom donation by the sulphenic acid, a product originating from the  $\beta\beta'$ -disubstituted diethyl sulphide. This observation is of possible contributory importance to the understanding of the mechanism of synergistic effects.

THE autoxidation of organic compounds can be inhibited by antioxidants of various types.<sup>1-3</sup> In antioxidant combinations, effects in excess of the additive value are frequently observed.<sup>4</sup> This phenomenon, called synergism, has found wide-spread use particularly in the stabilisation of polyolefins.<sup>5,6</sup> Several explanations have been suggested for the synergism between chain-breaking antioxidants such as hindered phenols and peroxide decomposers such as dialkyl sulphides,<sup>7</sup> but a detailed mechanism has yet to be given.

The present study deals with the mechanism of synergism between 4-alkoxy-2,6-diphenylphenols and some  $\beta\beta'$ -disubstituted diethyl sulphides.<sup>8</sup>



**Syntheses.**—(a) *Phenols.* 4-Alkoxy-2,6-diphenylphenols were synthesised according to Scheme 1. Oxidation of 2,6-diphenylphenol (I) to the quinone (II) was performed in 92% yield with oxygen in dimethylformamide at room temperature with bis(salicylidene)ethylenediaminecobalt(II) (salcomine) as a homogeneous catalyst.<sup>9</sup> The oxidation of 2,6-diphenylphenol to 2,6-diphenylbenzoquinone could equally well be carried out by lead

<sup>1</sup> K. U. Ingold, *Chem. Rev.*, 1961, **61**, 563.

<sup>2</sup> G. Scott, *Chem. and Ind.*, 1963, 271.

<sup>3</sup> G. Scott, *Eur. Polymer J. (Suppl.)*, 1969, 189.

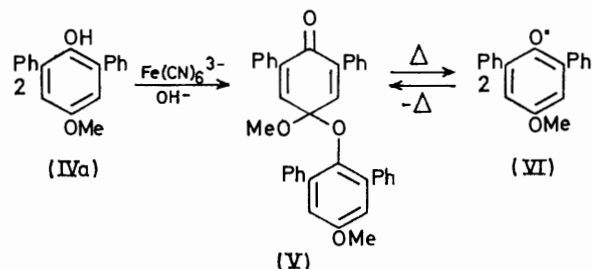
<sup>4</sup> W. L. Hawkins, H. Sautter, and F. H. Winslow, *Amer. Chem. Soc. Div. Polymer Chem.*, 1963, preprints 4(1), 4331.

<sup>5</sup> W. L. Hawkins and H. Sautter, *J. Polymer Sci. A*, 1963, **1**, 3499.

<sup>6</sup> F. Geleji, Z. Holly, G. Ocskay, and T. Wein, *J. Polymer Sci. C*, 1968, **16**, 3695.

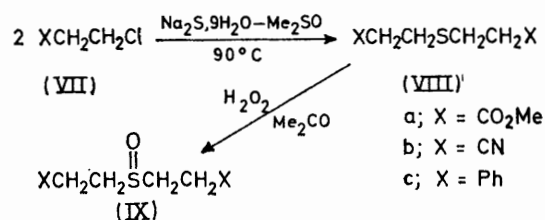
dioxide in formic acid.<sup>10</sup> Catalytic reduction of (II) gave quantitatively the corresponding 2,6-diphenylhydroquinone (III). The 4-alkoxy-2,6-diphenylphenols (IV) were obtained by refluxing (III) in the appropriate alcohols.<sup>11</sup>

4-Methoxy-2,6-diphenylphenoxyl (VI) was prepared in methanol by oxidation of (IVa) with alkaline potassium



ferricyanide. The stable phenoxyl radical was obtained in quantitative yield as its dimeric quinone acetal (V). This dimer (V) dissociates into phenoxyl radicals on heating in solution producing a dark green colour, which disappears on cooling. N.m.r. and i.r. spectroscopy established the structure of quinone acetal (V).

(b) *Sulphur compounds.* The  $\beta$ -activated diethyl sulphides were prepared<sup>12</sup> according to Scheme 2. The



corresponding sulphoxides were prepared according to the method of ref. 13.

**Synergistic Effects** (See *Experimental Section*).—(a)

<sup>7</sup> N. P. Neureiter and D. E. Bown, *Ind. Eng. Chem. Prod. Res. Develop.*, 1962, **1**, 236.

<sup>8</sup> C. R. H. I. de Jonge, H. J. Hageman, and W. J. Mijs, Netherlands P. 71-02009.

<sup>9</sup> H. M. van Dort and H. J. Geursen, *Rec. Trav. chim.*, 1967, **86**, 520.

<sup>10</sup> C. R. H. I. de Jonge, H. M. van Dort, and L. Vollbracht, *Tetrahedron Letters*, 1970, 1881.

<sup>11</sup> H. J. Hageman, *Tetrahedron*, 1969, **25**, 6015.

<sup>12</sup> H. J. M. Sinnige, personal communication.

<sup>13</sup> D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 1949, 2442.

**Phenols and sulphides.** The synergistic effect between 4-methoxy-2,6-diphenylphenol (IVa) and the  $\beta\beta'$ -disubstituted diethyl sulphides (VIIIa—c) was tested in

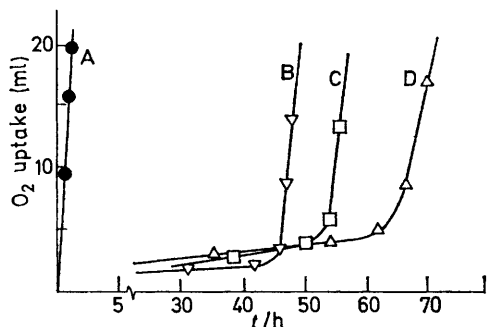


FIGURE 1 Synergistic effect between 4-methoxy-2,6-diphenylphenol (IVa) and A, no additive; B, sulphide (VIIIa); C, sulphide (VIIIb); D, sulphide (VIIIc); in polypropene at 180 °C

isotactic polypropene at 180 °C in accordance with the method of Pospisil.<sup>14</sup> The dependance of oxygen uptake on time is depicted in Figure 1. A marked synergism is evident, activation of the  $\beta$ -hydrogen atoms in the sulphides playing an important role.<sup>15</sup>

(b) *Phenols and sulphoxides.* The same synergistic effect could also be obtained with 4-methoxy-2,6-diphenylphenol (IVa) and the sulphoxides (IXa—c). The results in Figure 2 show that there is a negligible difference in synergistic action with 4-methoxy-2,6-diphenylphenol between the sulphides and the sulphoxides.

(c) *Phenoxy radicals.* We also studied the synergistic action of 4-methoxy-2,6-diphenylphenoxy (VI) with the sulphides and sulphoxides. Negligible differences were observed with the results obtained with 4-methoxy-2,6-diphenylphenol (IVa) (see Figure 3).

In the presence of the sulphides and sulphoxides only, no inhibition occurred in polypropene at 180 °C.

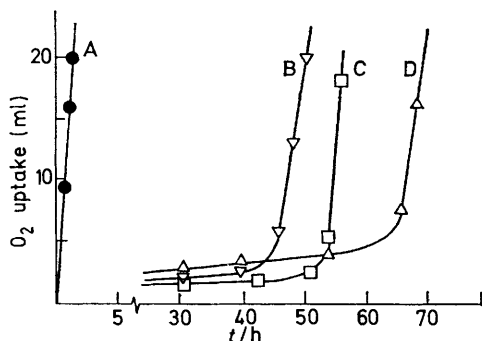


FIGURE 2 Synergistic effect between 4-methoxy-2,6-diphenylphenoxy (VI) and A, no additive; B, sulphoxide (IXa); C, sulphoxide (IXb); D, sulphoxide (IXc) in polypropene at 180 °C

**Mechanism of Synergistic Action.**—The behaviour of 4-methoxy-2,6-diphenylphenoxy (VI) towards sulphoxides (IX) was investigated with n.m.r. spectroscopy. Recent studies of Armstrong and Scott<sup>16</sup> unequivocally

<sup>14</sup> J. Pospisil, L. Taimr, and L. Kotulak, in 'Stabilization of Polymers and Stabilizer Processes,' ed. R. F. Gould, Amer. Chem. Soc. Publications, Washington, 1968, p. 169.

established the disproportionation pattern of sulphoxides in the presence of stable radicals.

The reaction of 4-methoxy-2,6-diphenylphenoxy (VI) and sulphoxide (IXc) was carried out at 150 °C in *o*-dichlorobenzene. The results obtained are consistent with the reaction Scheme 3. Starting from equimolecular amounts of (VI) and (IXc), we found that within 5 min, sulphoxide (IXc) had completely disproportionated and that 4-methoxy-2,6-diphenylphenol (IVa) was obtained quantitatively. The n.m.r. spectrum clearly showed the presence of a 1:1 mixture of styrene and 4-methoxy-2,6-diphenylphenol.

There are several ways of arresting an undesired radical

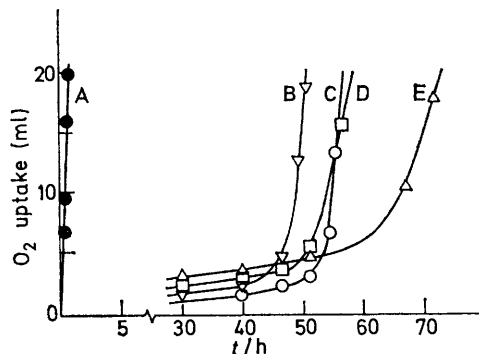
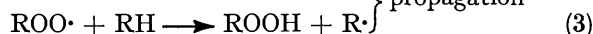


FIGURE 3 Synergistic effect between 4-methoxy-2,6-diphenylphenoxy (VI) and A, no additive; B, sulphide (VIIIa); C, sulphide (VIIIc); D, sulphoxide (IXc); E, sulphoxide (IXb)

chain process. The steps common to virtually all autoxidations include (1)—(3) where RH denotes the



organic substrate. Propagation is stopped by the action of an antioxidant (AH) by reactions (4) and (5). The



chain reaction can be propagated by a variety of radicals [equations (2), (3) and (6)], several of which originate from homolytic cleavage of hydroperoxides [equation (6)].



From our experimental data we conclude that at high temperatures disproportionation products of the sulphoxides play an important role in the regeneration of 4-methoxy-2,6-diphenylphenol (IVa) from the corresponding phenoxy radical (VI). This observation is consistent with Scheme 4, being one of a variety of reactions, which are involved in the thermal decomposition of sulphoxides in the presence of stable phenoxy radicals.<sup>16</sup> The phenoxy radical (VI) is stable towards oxygen. Thus the formation of peroxides by insertion

<sup>15</sup> C. A. Kingsbury and D. J. Cram, *J. Amer. Chem. Soc.*, 1960, **82**, 1810.

<sup>16</sup> C. Armstrong and G. Scott, *J. Chem. Soc. (B)*, 1971, 1747.



was washed with water and cold ethanol. Recrystallisation from hexane provided 2,6-diphenylhydroquinone (III) (33 g, 82%), m.p. 180.4—181 °C.

4-Alkoxy-2,6-diphenylphenols (IV). General procedure. To a solution of 2,6-diphenylhydroquinone (III) (26.2 g, 100 mmol) in the appropriate alcohol (200 ml) was added, while stirring, concentrated sulphuric acid (25 ml) in the course of 3 h. After additional stirring for 21 h at 65°, the mixture was diluted with chloroform (200 ml) and washed with water. After evaporation of the chloroform a light yellow syrup was obtained, which gave the 4-alkoxy-2,6-diphenylphenol after crystallisation from hexane-benzene (95 : 5). 4-Methoxy-2,6-diphenylphenol (IVa) (24 g, 87%) had m.p. 67.6—68.1 °C (Found: C, 82.7; H, 5.8.  $C_{19}H_{16}O_2$  requires C, 82.6; H, 5.8%); 4-ethoxy-2,6-diphenylphenol (IVb) (21 g, 72%) had m.p. 89.1—89.9 °C (Found: C, 82.7; H, 6.2.  $C_{20}H_{18}O_2$  requires C, 82.8; H, 6.2%); and 4-n-decanoxy-2,6-diphenylphenol (IVc) (22 g, 55%) had m.p. 34.2—35.3 °C (Found: C, 83.3; H, 8.6.  $C_{28}H_{34}O_2$  requires C, 83.6; H, 8.5%).

4-Methoxy-2,6-diphenylphenoxyl (VI). To a solution of 4-methoxy-2,6-diphenylphenol (IVa) (1.0 g) in methanol (30 ml) and KOH (10 g) in water (250 ml) was added under nitrogen and with stirring a solution of potassium ferricyanide (10 g) in water (100 ml) over 0.5 h. A grey-white precipitate was formed, which was filtered off and washed with water. Crystallisation from hexane gave the phenoxyl radical, which was obtained as its dimeric quinone acetal (V) (0.94 g, 96%), m.p. 158.5—159.2° (Found: C, 82.8; H, 5.6.  $C_{38}H_{30}O_4$  requires C, 82.9; H, 5.3%),  $\nu_{max}$  2830w, 1680s, 1650s, and 700s  $cm^{-1}$ ,  $\tau$  (CDCl<sub>3</sub>) 2.20—2.90 (20H, m, aromatic), 3.03 (2H, s, aliphatic), 3.55 (2H, s, aromatic *m*-H), 6.05 (3H, s, aromatic OMe), and 7.05 (3H, s, aliphatic OMe).

$\beta\beta'$ -Disubstituted diethyl sulphides (VIII). General procedure. To a solution of the appropriate chloride (VII) (1 mol) in dimethyl sulphoxide was added Na<sub>2</sub>S<sub>9</sub>H<sub>2</sub>O (0.55 mol) and the mixture was stirred at 90 °C for 2 h. The mixture was diluted with chloroform, washed with water, and dried. After evaporation *in vacuo* at 30 °C the residue was distilled *in vacuo*. Bis- $\beta$ -methoxycarbonyl-ethyl sulphide (VIIIa) (128 g, 62%) had b.p. 105—106 °C at 0.4 mmHg (Found: C, 46.8; H, 7.1; S, 15.6.  $C_8H_{14}O_4S$  requires C, 46.6; H, 6.8; S, 15.5%); bis- $\beta$ -cyanoethyl sulphide (VIIIb) (99 g, 71%) had b.p. 152—154 °C at 0.6 mmHg (Found: C, 51.5; H, 5.7; S, 23.0.  $C_6H_8N_2S$  requires C, 51.4; H, 5.7; S, 22.8%); and bisphenethyl sulphide (VIIIc) (194 g, 80%) had b.p. 151 °C at 0.2 mmHg (Found: C, 79.2; H, 7.6.  $C_{16}H_{18}S$  requires C, 79.3; H, 7.4%).

$\beta\beta'$ -Disubstituted diethyl sulphoxides (IX). General procedure. To a solution of the  $\beta\beta'$ -disubstituted diethyl sulphide (VIII) (0.1 ml) in acetone (100 ml) was added 30% hydrogen peroxide (20 ml). After refluxing for 2 h the mixture was concentrated *in vacuo* at 30 °C. Crystallisation gave the sulphoxides (IX). Bis- $\beta$ -methoxycarbonyl-ethyl sulphoxide (IXa)<sup>16</sup> (17.5 g, 78%) had m.p. 59.3—59.7 °C [from acetone-pentane (1 : 1)]; bis- $\beta$ -cyanoethyl sulphoxide (IXb) (10.4 g, 74%) had m.p. 107.1—109.2 °C (from acetone) (Found: C, 46.0; H, 5.3; N, 17.8; S, 20.8.  $C_6H_8N_2OS$  requires C, 46.2; H, 5.1; N, 18.0; S, 20.5%); and bisphenethyl sulphoxide (IXc) (20.7 g, 80%) had m.p. 70.2—70.4 °C [from hexane-acetone (95 : 5)] (Found:

C, 74.2; H, 7.2; S, 12.5.  $C_{16}H_{18}OS$  requires C, 74.4; H, 7.0; S, 12.4%),  $\nu_{max}$  1045m (SO) and 700s  $cm^{-1}$ ,  $\tau$  (CDCl<sub>3</sub>) 2.82 (10H, s, aromatic) and 7.22 (8H, s, aliphatic).

Bis- $\beta$ -methoxycarbonyl- $\beta\beta'$ -dimethylethyl sulphoxide (X). To a solution of methanol (48 g, 1.5 mol) and pyridine (40 g, 0.5 mol) in chloroform (100 ml) was added the diacid chloride of 2,2,6,6-tetramethyl-4-thiaheptanedioic acid (3 g, 0.125 mol) with stirring and cooling to 10 °C over 20 min. After additional stirring for 20 min the mixture was poured into water (500 ml). The chloroform layer was washed with water (3 × 100 ml). After evaporation, the product was distilled *in vacuo* to give the diester (29 g, 88%). To a solution of the diester (26.2 g, 0.1 mol) in acetone (100 ml) was added 30% hydrogen peroxide (20 ml). After refluxing for 2 h the mixture was concentrated. Addition of hexane gave the sulphoxide (X) (15 g, 54%), m.p. 45—48° (Found: C, 51.7; H, 7.9; S, 11.8.  $C_{12}H_{22}O_5S$  requires C, 51.8; H, 7.9; S, 11.5%).

4-*t*-Butylperoxy-4-methoxy-2,6-diphenylcyclohexa-2,5-dienone (XI). According to the procedure of Campbell and Coppinger,<sup>21</sup> *t*-butyl hydroperoxide (25 ml) was added to a solution of 2,6-diphenylphenol (5 g, 20 mmol) in *t*-butanol (50 ml), followed by two drops of a solution of cobalt naphthenate in ethyl acetate. After heating for 1 h at 70 °C the product was isolated by evaporation of *t*-butyl alcohol. The residue was crystallised from hexane to give the peroxycyclohexadienone (XI) (4.7 g, 71%), m.p. 68° (Found: C, 83.0; H, 7.4.  $C_{23}H_{24}O_2$  requires C, 83.1; H, 7.2%),  $\nu_{max}$  2830w, 1680s, 1650s, and 700s  $cm^{-1}$ ,  $\tau$  (CCl<sub>4</sub>) 2.5—2.9 (10H, m, aromatic), 3.12 (2H, s, aliphatic), 6.53 (3H, s, OMe), and 8.77 (9H, s, Bu<sup>t</sup>).

Oxygen Uptake Measurements.—Synergistic effects of 4-methoxy-2,6-diphenylphenol (IVa) and the  $\beta\beta'$ -disubstituted diethyl sulphides (VIIIa—c) and the corresponding sulphoxides (IXa—c) as well as the synergistic effects of 4-methoxy-2,6-diphenylphenoxyl (VI) and the  $\beta\beta'$ -disubstituted diethyl sulphides and sulphoxides were tested in unstabilised isotactic polypropene according to the method of ref. 14. Powdered polypropene (1.000 g) was mixed with the phenol (2 mg) and the sulphide or sulphoxide (5 mg). This mixture was homogenised with acetone (5 ml). The solvent was carefully evaporated *in vacuo* at 40 °C and the sample was placed in a tube connected with a gas burette filled with oxygen. Oxygen uptake was measured at regular intervals at 180 °C.

*N.m.r.* Measurements.—The spectrometer was equipped with a variable temperature unit for direct reading to within ( $\pm 0.5$  °C). Measurements were performed with a solution of 4-methoxy-2,6-diphenylphenoxyl (VI) and sulphoxide (IXc) at 150 °C in *o*-dichlorobenzene. After 5 min, formation of styrene and regeneration of 4-methoxy-2,6-diphenylphenol (IVa) were observed,  $\tau$  (*o*-dichlorobenzene) 4.45 (1H, d, vinylic), 4.95 (1H, d, vinylic), and 6.38 (3H, s, OMe).

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<sup>21</sup> T. W. Campbell and G. M. Coppinger, *J. Amer. Chem. Soc.*, 1952, **74**, 1469.