Flash Photolysis Studies of Phenyl-substituted Phenols, Quinones, and the Corresponding Free Radicals. Part 1. Quantitative Study of the Dimerization of Phenyl-substituted Phenoxyl Radicals

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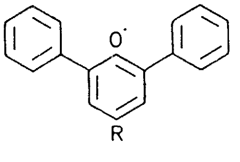
Kinetic and thermodynamic parameters of equilibrium systems of phenyl-substituted phenoxyl radicals and their dimers are described. The experimental procedure involves measurement of absorption maxima and extinction coefficients and recording of the kinetics of intermediates by a flash-photolysis apparatus. The phenoxyl radicals were generated in three different ways: (a) the classical way, *i.e.* oxidation of the corresponding phenol with a one-electron transfer agent, (b) by photolysis of the corresponding dimers, and (c) by photolysis of the parent phenols. The transition states for radical dimerization and decay of the less sterically hindered phenyl-substituted phenoxyl radicals are less ' strict ' compared with those for similar reactions involving t-butyl-substituted phenoxyl radicals. $\Delta S^{\ddagger}_{1}$ and $\Delta S^{\ddagger}_{-1}$ for phenyl-substituted phenoxyl radicals ($\Delta S^{\ddagger}_{1}$ 0—6, $\Delta S^{\ddagger}_{-1}$ 4 cal mol^{-1} K^{-1}) are much higher than those for t-butyl-substituted phenoxyl radicals [$\Delta S^{\ddagger}_{1}$ −(30—40), $\Delta S^{\ddagger}_{-1}$ −(10—20) cal mol^{-1} K^{-1}]. Heating the dimer of 2,6-diphenyl-4-methoxyphenoxyl in *o*-dichlorobenzene at 130 °C leads to a variety of reaction products, originating from intra- and inter-molecular radical coupling.

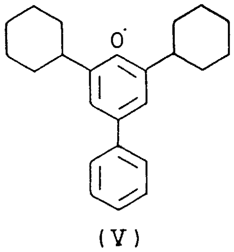
THE chemistry of phenoxyl radicals has developed during the last 10—15 years. Reactivities and physicochemical properties of short-lived, as well as of sterically hindered and long-lived phenoxyl radicals, have been studied in detail.[1-7] The phenyl-substituted phenoxyl radicals represent, in a sense, an intermediate class of radicals and as such are of great interest since certain phenyl-substituted phenols appear to be very effective chain-breaking antioxidants in polyolefins.[8]

An interesting feature of phenyl-substituted phenoxyl radicals is their ability to exist in solution in equilibrium with relatively stable dimers.[8-10] The structure of the dimers and the spin-density distribution in phenyl-substituted phenoxyl radicals have been studied.[8,11,12] 4-(2,6-Diphenyl-4-methoxyphenoxy)-4-methoxy-2,6-diphenylcyclohexa-2,5-dienone and 4-(2,4,6-triphenylphenoxy)-2,4,6-triphenylcyclohexa-2,5-dienone can even be isolated as crystalline materials.[8,9]

The present study deals with absorption spectra of phenoxyl radicals ArO$^{\cdot}$ of structure (I)—(V) and with the kinetic and thermodynamic parameters of the equilibrium system (1). Phenols corresponding to (I)—(V) are denoted (IH)—(VH).



(I) R = OCH_3
(II) R = OC_2H_5
(III) R = $O{-}n{-}C_{18}H_{37}$
(IV) R = Ph



(V)

$$D \underset{k_{rec}}{\overset{k_{diss}}{\rightleftharpoons}} 2ArO^{\cdot} \qquad (1)$$

RESULTS AND DISCUSSION

The phenoxyl radicals (I)—(V) were generated by oxidation of the corresponding phenols with an excess of PbO_2 in n-propanol solution. The solutions were intensely coloured (Table 1 and Figure 1) and exhibited e.s.r. signals. The dependence of the solution absorption in the longwave range on the initial phenol concentration indicated that the Lambert–Beer law was not followed for the phenoxyl radicals (I)—(V). Consequently, the radicals in solution were in equilibrium with the dimers [equilibrium (1)].

The yields of phenyl-substituted phenoxyl radicals upon oxidation of the corresponding phenols were close to 100%,[8,9] in other words $[ArOH]_0 = [\overline{ArO^{\cdot}}] + 2[\overline{D}]$, where $[ArOH]_0$ is the initial concentration of phenol, and $[\overline{ArO^{\cdot}}]$ and $[\overline{D}]$ are the equilibrium concentrations of radical and dimer, respectively.

Apart from simple alkyl-substituted phenoxyl radicals,

TABLE 1

Long-wavelength absorption maxima and extinction coefficients of phenols, phenoxyl radicals, and dimers (I)—(V) in propanol at 20 °C

Compound	$\lambda_{max.}$/nm	$10^{-3}\varepsilon_{max.}$/ l mol^{-1} cm^{-1}
(IH)	315 ± 5	9 ± 1
(IIH)	315 ± 5	7 ± 1
(IIIH)	315 ± 5	7 ± 1
(IVH)	310 ± 5 [a]	4.5 ± 0.5
(VH)	270 ± 5	18 ± 2
(I)	405 ± 5,	50 ± 10
	650 ± 10	4 ± 1
(II)	405 ± 5,	30 ± 5
	650 ± 10	2.6 ± 0.5
(III)	405 ± 5,	25 ± 5
	650 ± 10	2.4 ± 0.5
(IV)	550 ± 10,	6 ± 2
	750 ± 10	2.2 ± 0.5
(V)	355 ± 5,	50 ± 15
	510 ± 10	6 ± 2
Dimer of (I)—(III)	300 ± 5	10 ± 1

[a] Shoulder.

phenyl-substituted phenoxyl radicals have absorption spectra not only at 400 nm, but also at $\lambda > 500$ nm (Table 1, Figure 1).[2,3,9] Absorption bands of phenyl-substituted phenoxyl radicals are more intense compared with those of alkyl-substituted phenoxyl radicals (Table 1).[2] This phenomenon is due to the participation of the phenyl groups in the conjugated system of the radical.[9,10,12]

Flash photolysis of the dimers of phenoxyl radicals (I)—(V) generated radicals by reaction (2). A light

$$\mathrm{D} \xrightarrow{h\nu} 2\mathrm{ArO}^{\cdot} \qquad (2)$$

flash increased the concentration $[\overline{\mathrm{ArO}}^{\cdot}]$ with subsequent relaxation of the system to equilibrium. The curves obtained obeyed first-order kinetics, and the first-order rate constant increased with the steady-state concentration of radicals in solution ($[\overline{\mathrm{ArO}}^{\cdot}]$ *ca.* 10^{-5}M). Under the experimental conditions the $\Delta[\overline{\mathrm{ArO}}^{\cdot}] \ll [\overline{\mathrm{ArO}}^{\cdot}]$ relaxation to equilibrium was in fact completely reversible. This permitted an estimate of k_{rec} from spectral oscillograms, making use of equation (3) where ΔD_0 denotes the

$$\ln(\Delta D_0/\Delta D) = k_{\mathrm{rec}}(4[\overline{\mathrm{ArO}}^{\cdot}] + K)t \qquad (3)$$

immediate flash-induced change in optical density of the solution, K is the equilibrium constant of reaction (1); $K = k_{\mathrm{diss}}/k_{\mathrm{rec}} = 2[\mathrm{ArO}^{\cdot}]^2/([\overline{\mathrm{ArOH}}]_0 - [\overline{\mathrm{ArO}}^{\cdot}])$. The values of K over the range 0—40 °C were obtained by spectrophotometry (Figure 1) and thus ΔH_0 values were obtained (Table 2, Figure 2). Our results were in good agreement with those obtained by Dimroth *et al.*[9] [*e.g.* our K value for radical (IV) was $4 \pm 2 \times 10^{-5}$ compared with $2.4 \pm 1 \times 10^{-5}$ for triphenylphenoxyl].

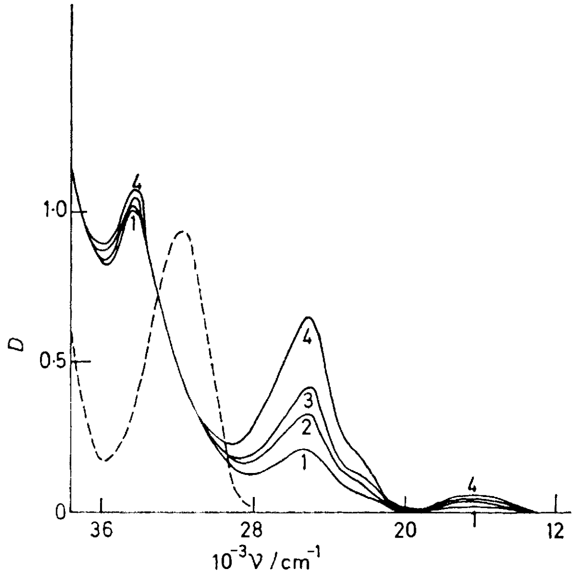


FIGURE 1 Absorption spectra of solutions of dimer (initial concentration 10^{-4}M) of 2,6-diphenyl-4-methoxyphenoxyl radical in propanol at different temperatures (1, 5 °C; 2, 20 °C; 3, 30 °C; 4, 40 °C) and that of 2,6-diphenyl-4-methoxyphenol (10^{-4}M) in propanol at 20 °C (dashed line)

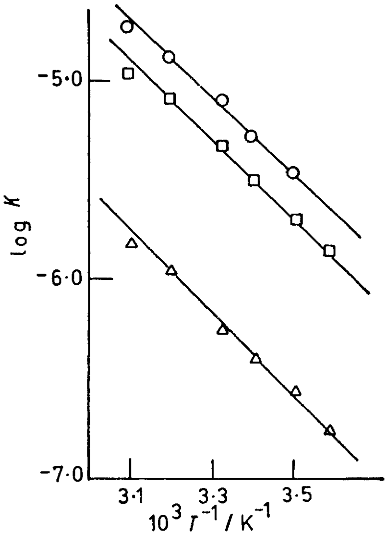


FIGURE 2 Plot of log K against T^{-1}: △, compound (I); □, compound (II); ○, compound (III)

It was possible to obtain k_{rec} with the aid of equation (3) for various temperatures from the temperature dependence of $[\overline{\mathrm{ArO}}^{\cdot}]$ and K and to estimate the activation energy (Figure 3), enthalpy, and entropy of the recombination reaction (1). The relevant parameters for the dissociation reaction have also been calculated (Table 2).

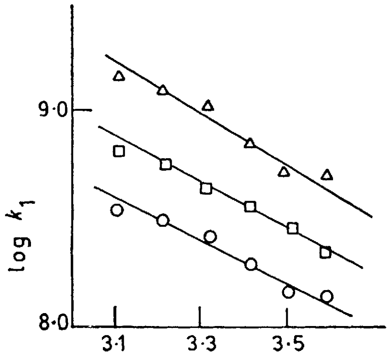


FIGURE 3 Plot of log k_1 against T^{-1}: △, compound (I); □, compound (II); ○, compound (III)

TABLE 2

Rate, equilibrium, and thermodynamic [a] data for reaction (1) of phenoxyl radicals (I)—(V) in propanol at 20 °C

Radical	$10^{-8}k_{\mathrm{rec}}$/ l mol^{-1} s^{-1}	$10^{-2}k_{\mathrm{diss}}$/ s^{-1}	10^7K/M	ΔH^0	$\Delta H^{\ddagger}_{\mathrm{rec}}$	$\Delta H^{\ddagger}_{\mathrm{diss}}$	ΔS^0	$\Delta S^{\ddagger}_{\mathrm{rec}}$	$\Delta S^{\ddagger}_{\mathrm{diss}}$	ΔG^0	$\Delta G^{\ddagger}_{\mathrm{rec}}$	$\Delta G^{\ddagger}_{\mathrm{diss}}$
(I)	7 ± 1	3 ± 1	4 ± 1	9.8 ± 0.5	5 ± 1	15 ± 2	4 ± 2	0 ± 3	4 ± 5	8.6 ± 0.2	5.0 ± 0.1	13.6 ± 0.2
(II)	3.5 ± 0.5	10 ± 5	30 ± 10	9.6 ± 0.5	4 ± 1	14 ± 2	7 ± 2	−5 ± 3	2 ± 5	7.4 ± 0.2	5.4 ± 0.1	12.8 ± 0.2
(III)	1.9 ± 0.5	10 ± 5	50 ± 10	9.5 ± 0.5	4 ± 1	14 ± 2	8 ± 2	−6 ± 3	2 ± 5	7.1 ± 0.2	5.7 ± 0.1	12.8 ± 0.2
(IV)	0.8 ± 0.1	30 ± 5	400 ± 200							5.9 ± 0.2	6.1 ± 0.1	12.0 ± 0.2
(V)	0.27 ± 0.1	10 ± 5	400 ± 200							5.9 ± 0.2	6.9 ± 0.1	12.8 ± 0.2

It was not possible to determine thermodynamic parameters of reaction (1) for radicals (IV) and (V) due to extreme instability of radicals in propanol on heating. Flash-excitation of phenol solutions in propanol (10^{-3}M) generated phenoxyl radicals (I)—(V) [reaction (4)].

$$\mathrm{ArOH} + h\nu \begin{array}{l} \nearrow \mathrm{ArO^{\cdot}} + \mathrm{H^{+}} + e_{\mathrm{solv}} \\ \\ \searrow \mathrm{ArO^{\cdot}} + \mathrm{H} \end{array} \qquad (4)$$

The absorption spectra of phenoxyl radicals obtained by flash photolysis of phenols and dimers, and the absorption spectra of oxidized phenol solutions coincided within experimental error.

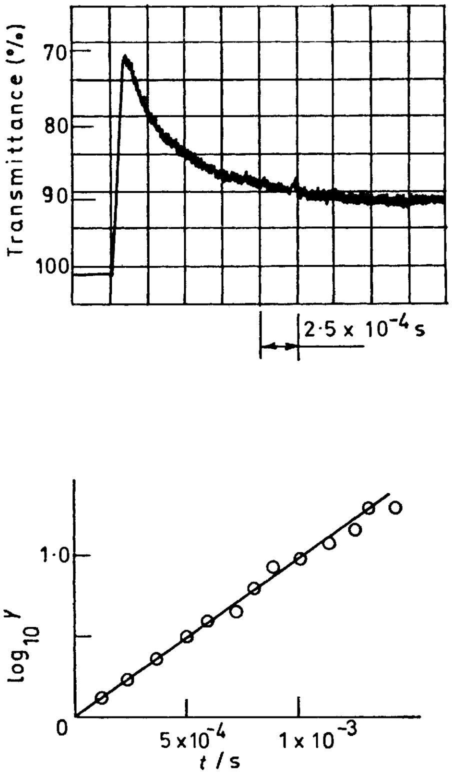


FIGURE 4 Oscilloscope trace at 650 nm due to formation and decay of 2,6-diphenyl-4-methoxyphenoxyl and the corresponding linear plot, produced in the flash-photolysis of solutions of 2,6-diphenyl-4-methoxyphenol (10^{-3}M) in propanol (20 °C)

Phenoxyl radicals obtained by reaction (4) recombined to form dimers (Figure 4). The K value is expressed as in equation (5). The $[\overline{\mathrm{ArO}}^{\cdot}]_0$ value can be calculated

$$K = 2[\overline{\mathrm{ArO}}^{\cdot}]^2/[\overline{\mathrm{ArO}}^{\cdot}]_0 - [\overline{\mathrm{ArO}}^{\cdot}] \qquad (5)$$

from radical absorption immediately after the flash (Figure 4), $[\overline{\mathrm{ArO}}^{\cdot}]$ from residual absorption after the flash at t *ca.* 10^{-2} s. The k_{rec} value can be calculated from spectral oscillograms and the resulting linear plots (Figure 4). The values of K and k_{rec} so obtained were in agreement with those obtained independently by photolysis of the dimers.

The presence of oxygen has no effect on the decay kinetics of the phenoxyl radicals.

$$2.3 \log_{10}\left(\frac{[\mathrm{ArO}^{\cdot}]_0 - [\overline{\mathrm{ArO}}^{\cdot}]}{[\mathrm{ArO}^{\cdot}] - [\overline{\mathrm{ArO}}^{\cdot}]} \cdot \frac{[\mathrm{ArO}^{\cdot}] + [\overline{\mathrm{ArO}}^{\cdot}] + K/2}{[\mathrm{ArO}^{\cdot}]_0 + [\overline{\mathrm{ArO}}^{\cdot}] + K/2}\right) = 2k_{\mathrm{rec}}([\overline{\mathrm{ArO}}^{\cdot}] + K/4)t \qquad (6)$$

Most recombination (dimerization) reactions of radicals are limited by diffusion. The activation energy for diffusion-limited chemical reactions $E_a = B + RT$ (B is the activation energy of viscous flow) is described by the empirical relation (7) where η_0 and B are constant for the given fluid.

$$\eta = \eta_0 \exp B/RT \qquad (7)$$

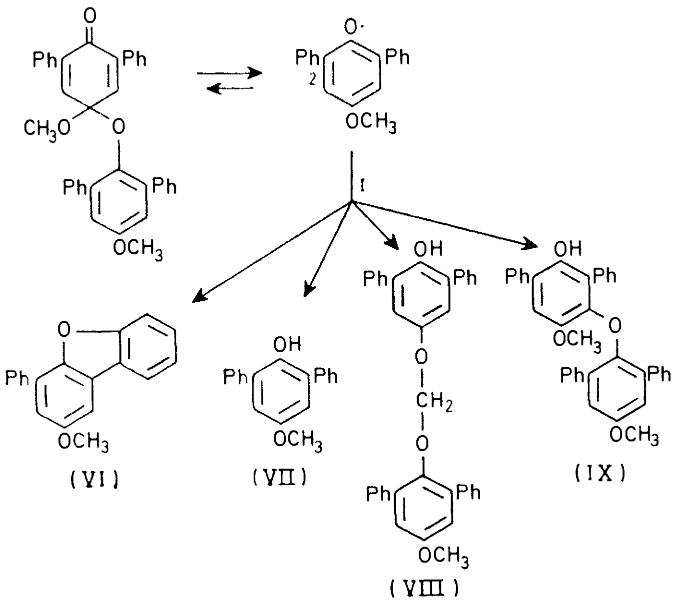
Since $E_a = \Delta H^{\ddagger} + RT$, for diffusion-limited reactions $\Delta H^{\ddagger} = B$. The dimerization of radicals (I)—(III) seems to be a process limited by diffusion. This is supported by the facts that $\Delta H^{\ddagger}_{\mathrm{rec}}$ for these radicals reasonably correlate with the solvent activation energy ($B = 4.27 \pm 0.28$ kcal mol^{-1} for propanol), and the values of k_{rec} are only 5—10 times lower than the diffusion rate constant calculated by the Debye expression. Usually the Debye expression yields over-estimated values of k_{diff} for recombination of radicals limited by diffusion.

It can be seen from Table 2 that k_{rec} decreases with an increasing number of carbon atoms in the oxyalkyl substituent [for radicals (I)—(III)]. This is due to expansion of the radical diffusion radius and to a decrease in the diffusion coefficient with increasing volume (molecular weight) of the radical. However, the reaction cross-section seems to remain constant, and as a result the rate constant becomes lower. A further decrease of the rate constant is observed if the oxyalkyl substituent is replaced by phenyl (radical (IV)]. This is probably due either to steric hindrance on radical dimerization, or by electronic effects. Radical (V) differs from (IV) in that instead of phenyl substituents *ortho* and *para* to the active centre, the oxygen atom, it bears *o*-cyclohexyl substituents. The k_{rec} value becomes lower in passing from radical (IV) to (V), probably on account of steric hindrance.

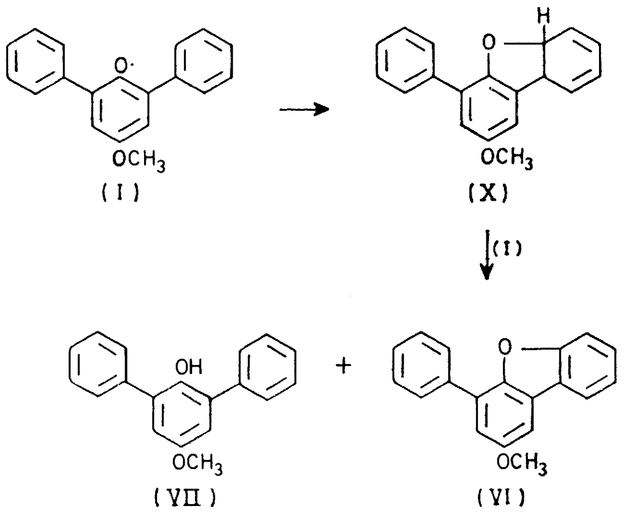
The values of k_{rec} for radicals (I)—(IV) (Table 2) are closer to k_{diff} than those of sterically non-hindered phenoxyl radicals, the decay of which is also limited by diffusion. It will be noted that the decay of sterically non-hindered phenoxyl radicals also yields an intermediate dimer with subsequent enolization.

Unlike the case for 4-R-2,6-diphenylphenoxyl and sterically non-hindered phenoxyl radicals, reversible dimerization of the 4-R-2,6-di-t-butylphenoxyl radical series (R is a substituent capable of conjugation) occurs with lower rate constants, namely k_{rec} *ca.* 10^5—10^7 l mol^{-1} s^{-1} (normal solvents, room temperature). Thus, phenyl rings create less steric hindrance for the recombination of radicals (the effects caused by delocalization of an unpaired electron over the phenyl rings, and the effects due to the conjugative capacity of the *para*-substituent in the case of 4-R-2,6-di-t-butylphenoxyl radicals, *i.e.* the electron effects, are probably similar). The weaker steric hindrance of the radical oxygen atom by the phenyl rings, compared with that of t-butyl groups, can be understood by taking into account the fact that the phenyl group can readily rotate and at a near 90° angle to the benzene ring plane steric hindrance would not be large. It was found [12] that for radical (IV) the most probable angle between the *o*-phenyl substituent and the phenoxyl ring plane is 46°. The transition states for radical dimerization and decay are less ' strict ' compared with those for similar reactions involving 4-R-2,6-di-t-butylphenoxyl radicals. This is corroborated by the fact that the $\Delta S^{\ddagger}_{1}$ and $\Delta S^{\ddagger}_{-1}$ values for radicals (I)—(III) (Table 2) are much higher than those for phenoxyl radicals with t-butyl groups [$\Delta S^{\ddagger}$ −(30—40), $\Delta S^{\ddagger}_{-1}$ −(10—20) cal mol^{-1} K^{-1}].

Strictly speaking, the radicals are unstable in n-propanol solutions (at 20 °C their half-lives vary from several hours to several days for $[\text{ArO}^{\cdot}]_0$ *ca.* 10^{-4}—10^{-5}M). The presence of oxygen in the system also has no effect on the rate of the ArO˙ concentration decrease. When the solution is heated, the rate of radical decay becomes much higher. Heating the dimer of radical (I) in *o*-dichlorobenzene at 120 °C gave a variety of reaction products, originating from intra- and inter-molecular radical coupling (Scheme 1). Products (VIII) and (IX) were formed by intermolecular coupling in 18 and 14% yield, respectively. It was found that 4-methoxy-2,6-diphenylphenol (VII) was formed in 35% yield, whereas 2-methoxy-4-phenyldibenzofuran (VI) was obtained only in 8% yield. From the products found the only hydrogen source for the formation of (VII) is the intermediate intramolecularly coupled product (X), which ultimately leads to the furan (VI) (Scheme 2) (see Experimental section). From these observations it can be concluded that the highly coloured residual tar consists of dehydrogenated products. The precursors of the products are probably the hydrogen donors to the phenoxyl radical (I) to form 4-methoxy-2,6-diphenylphenol (VII).



SCHEME 1



SCHEME 2

EXPERIMENTAL

The absorption spectra and kinetic parameters for intermediates were recorded using a flash-photolysis apparatus described elsewhere.[13] The flash duration was $\tau_{1/2}$ 15 μs and the flash energy 500 J. Solutions were irradiated in quartz cuvettes (20 cm) by the light of a tubular xenon flashlamp (20 cm × 20 mm diam.). The dimer solutions were irradiated through a UFS-6 light filter (λ 320—390 nm), those of phenols through a UFS-5 light filter (λ 280—380 nm) (commercially available u.v. filters). A Specord spectrophotometer and a Varian-12A e.s.r. spectrometer were used to obtain absorption and e.s.r. spectra, respectively, for oxygen-free solutions. Temperatures were kept constant to ±0.51 °C. Solvents were distilled twice and dried over molecular sieves 3 Å before use. The starting phenols were prepared according to the method described previously.[8] M.p.s. were determined with a Leitz model 553215 microscope and are corrected. I.r. spectra (KBr disc or neat) were recorded on Hitachi EPI-G2 and Perkin-Elmer 457 spectrophotometers. N.m.r. spectra were taken with a Varian A-60 spectrometer with $CDCl_3$ as solvent. Mass spectra were recorded at 70 eV with a Varian MAT CH-5 spectrometer.

The yields of phenoxyl radicals, (I)—(V) $(\overline{\text{ArO}}\cdot + 2\overline{\text{D}})/[\text{ArOH}]_0$, were measured as follows. The addition of an excess of hydrazobenzene to the radical solution leads to azobenzene formation. The quantity of azobenzene formed was measured [14] and thus the yield of radicals was calculated. Radical yields proved to be close to 100%. The concentration of $[\overline{\text{ArO}}^{\cdot}]$ was calculated from a comparison of the integral intensity of the e.s.r. spectra of the solutions and the standard (2,2,6,6-tetramethylpiperidin-1-oxyl); the error was 20%.

The absorption spectra of these solutions at the same temperature were recorded and extinction coefficients of the radicals are collected in Table 1. The spectral data for (IV) are in good agreement with the results of Dimroth *et al.*[9] The absorption maxima and extinction coefficients of the dimers were calculated from a comparison of the absorption spectra of the reactions (1) at different temperatures (Table 1).

Thermal Decomposition of 4-*Methoxy*-2,6-*diphenylphenoxyl* (I).—A solution of the dimer (5.0 g) of radical (I) [3] in *o*-

dichlorobenzene (50 ml) was heated at 120 °C. The green colour immediately formed slowly vanished. After 9 h, the light-brown solution was evaporated *in vacuo*. The residue was separated by column chromatography and the products were further purified through separation with the aid of high-pressure liquid chromatography on a semi-preparative scale. Column chromatography gave 2-methoxy-4-phenyldibenzofuran (VI) (0.4 g, 8%), m.p. 115°; 4-methoxy-2,6-diphenylphenol (VII) (1.76 g, 35%), m.p. 64°; product (VIII) (0.9 g, 18%), viscous oil; and product (IX) (0.7 g, 14%), viscous oil. All products were analysed with i.r., n.m.r., and mass spectrometry. Moreover 2-methoxy-4-phenyldibenzofuran (VI) was prepared by methylation of 2-hydroxy-4-phenyldibenzofuran.[15] Both compounds showed the same spectra and a mixed m.p. showed no depression. The same was observed for 4-methoxy-2,6-diphenylphenol (VII).

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