ESR Studies of Phenoxyl Radicals Produced by the PbO_2 Oxidation of Hindered Polyphenols. III. *p*- and *m*-Phenylenebisgalvinoxyls, Stable Triplets

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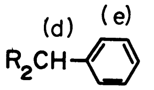
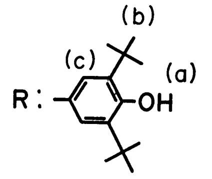
PbO_2 oxidation of two hindered polyphenols produced, in turn, primary, secondary, and ternary radicals. The ternary radicals are π-conjugated biradicals; the structures of the radicals were assigned to be *p*- and *m*-phenylenebisgalvinoxyls. Both zero field splitting parameters and hyperfine splitting constants were determined from ESR spectra.

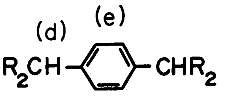
PbO_2 oxidation of 4-substituted 2,6-di-*t*-butylphenols in organic solvents produces the corresponding phenoxyl radicals, which are known as "hindered phenoxyls". The magnetic properties of these phenoxyls in solution have been extensively studied with the aid of the electron spin resonance (ESR) spectra.[1)]

The galvinoxyl radical is a well known stable phenoxyl radical, which can be separated as a pure solid with 100% radical concentration.[2–4)] This radical shows some anomalous magnetic properties in the solid state.[4,5)] Phenylgalvinoxyl (I-S) (see Fig. 1(a)) has an electronic structure similar to galvinoxyl, and exhibits a stability approaching that of galvinoxyl.[6)] These radicals can be prepared from their diphenylmethane precursors, 3,3′,5,5′-Tetra-*t*-butyl-4,4′-dihidroxydiphenylmethane and 3,3′,5,5′-Tetra-*t*-butyl-4,4′-dihydroxydiphenylphenylmethane (phenol (I)), by their PbO_2 oxidation in 2-MeTHF under vacuum or nitrogen gas.



I





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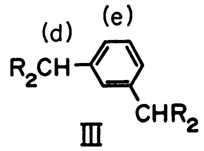

III

We have prepared two other *para*- and *meta*-phenylenebis(diphenylmethane) precursors (phenols (II) and (III)) which are related to phenol (I), and have succeeded in synthesizing the corresponding π-conjugated biradicals, *para*- and *meta*-phenylenebisgalvinoxyls (II-T) and (III-T) (see Figs. 1(b) and (c)).

The study of interelectronic interactions in organic π-conjugated biradicals has been of interest in recent years. However, the number of the stable π-conjugated biradicals reported are very limited: only about ten, as far as we know, including three of the phenoxyls.[7–9)]

Experimental

*3,3′,5,5′-Tetra-*t*-butyl-4,4′-dihydroxydiphenylphenylmethane (phenol (I)).* Phenol (I) was prepared according to the procedure used by Coffield *et al.*[10)] 2,6-di-*t*-butylphenol (0.1 mol, 20.6 g) and benzaldehyde (0.1 mol, 10.6 g) were dissolved in 20 ml of ethanol in a three-necked flask, and a solution of KOH (6.6 g in 15 ml of ethanol) was added gradually under an atmosphere of nitrogen. The deep green solution was stirred overnight at 20 °C, and the solids were filtered out. The crude product was then taken up in ether to remove the potassium benzoate. Removal of the ether left a white crystalline solid, and this was recrystallized twice from ethanol, mp 164.0—164.5 °C (lit, mp 161—163 °C); UV spectrum (λ_{max}=278 nm, log ε=3.54, λ_{max}=286 nm, log ε=3.53 in *n*-hexane); NMR spectrum ($H^a \delta$=4.92 ppm (2), H^b 1.39 (36), H^c 6.80 (4), H^d 5.26 (1), H^e 6.98, 7.06, 7.16, 7.23 (total 5); δ in CCl_4 with TMS as internal standard).

para-*Phenylene-bis(3,3′,5,5′-Tetra-*t*-butyl-4,4′-dihydroxydiphenylmethane) (phenol (II)).* 2,6-Di-*t*-butylphenol (15.2 g, 0.074 mol) and terephthalaldehyde (5.0 g, 0.037 mol) were dissolved under an atmosphere of nitrogen in 33 ml of ethanol under stirring, and a solution of KOH (4.8 g in 10 ml of ethanol) was added slowly. The color of the reaction mixture changed gradually from yellow to green at 30 °C. The reaction was continued overnight at 30 °C, and finally some white solids were precipitated in the viscous deep blue reaction mixture. The solids were filtered off and washed with ethanol. Then they were taken up in ethyl ether, washed with water, and dried over anhydrous sodium sulfate. After removal of the ethyl ether, the white solids were recrystallized first from benzene, second from *p*-xylene, and finally washed twice with acetone, mp 290—292 °C; Found: C, 83.07; H, 10.09%. Calcd for $C_{64}H_{90}O_4$: C, 83.24; H, 9.82%; UV spectrum (λ_{max}=278 nm, log ε=3.97, 284 nm; log ε=3.93 in tetrahydrofuran); NMR spectrum ($H^a \delta$=4.87 ppm (4), H^b 1.33 (72), H^c 6.80 (8), H^d 5.21 (2), H^e 6.94 (4); δ in CCl_4 with TMS as internal standard).

meta-*Phenylene-bis(3,3′,5,5′-Tetra-*t*-butyl-4,4′-dihydroxydiphenylmethane) (phenol (III)).* Phenol (III) was synthesized by condensation of 2,6-di-*t*-butylphenol with isophthalaldehyde in KOH–ethanol solution under an atmosphere of nitrogen at 35 °C, following a method similar to that used with phenol (II). The reaction was continued for three days under stirring. The white solids obtained were recrystallized first from ethanol and second from methanol–acetone, giving white silky needles, mp 223.0—224.0 °C; Found: C, 83.06; H, 10.10%. Calcd for $C_{64}H_{90}O_4$: C, 83.24; H, 9.82%. UV spectrum (λ_{max}=277nm, log ε=3.82; 285 nm, log ε=3.80 in *n*-hexane); NMR spectrum (H^a δ=4.86 ppm (4), H^b 1.31 (72), H^c 6.73 (8), H^d 5.20 (2), H^e 6.84, 6.98, 7.07, 7.14 (total 4); δ in CCl_4 with TMS as internal standard).

Measurements. All the ESR measurements were carried out using a JES-ME-3X spectrometer equipped with a Takeda-Riken microwave frequency counter. ESR hyperfine splittings and *g*-values were measured relative to those of $(KSO_3)_2$-

TABLE 1. HYPERFINE SPLITTINGS (in G), FINE STRUCTURES (D) (in G), AND g-VALUES OF PHENOXYL RADICALS

Radical	Primary (P)			Secondary (S)		Ternary (T)		
	a_{β}^{H}	a_{m}^{H}	g-value	a_{m}^{H}	g-value	a_{m}^{H}	g-value	D
I	8.44	1.71	2.0044_4	1.34	2.0044_0	—	—	—
II	8.53	1.67	2.0044_3	1.34	2.0044_3	0.69	2.0044_5	20.0
III	8.74	1.68	2.0044_4	1.33	2.0044_2	0.69	2.0044_3	26.1

NO ($a^{N}=13.05\pm0.03$ G; $g=2.0054$[11]).

The NMR spectra were taken on a JEOLCO 4H-100 (100 MHz) nmr spectrometer.

Magnetic susceptibility measurements were carried out using a Shimadzu MB-2 type magnetic torsion balance.

Results and Discussion

An initial slight oxidation of the phenols (I)—(III) with PbO_2 in 2-MeTHF in a sealed, degassed system gives ESR spectra consisting of a doublet-triplet splitting. We assign the spectra to primary phenoxyl radicals (I-P), (II-P), and (III-P) formed from the parent phenols by abstraction of a phenolic hydrogen atom. The large doublet splittings in the primary radicals are clearly due to the *para* methylene group and the triplet splittings are explained by the *meta* hydrogens. The values of hyperfine splittings are listed in Table 1.

The spectrum due to radical (I-P) changes rapidly with time. Almost as soon as it was observed, a further quintet due to a secondary radical (I-S) was seen growing in the center of the spectrum, and this, after further oxidation, dominated the spectrum. The phenols (II) and (III) show similar behavior. The structure of the secondary radical (I-S), named phenylgalvinoxyl, is shown in Fig. 1(a); those from phenols (II) and (III) are analogous to those from phenol (I). The spectrum of (I-S) is shown in Fig. 2(a). The quintet splitting of the secondary radicals ($a^{H}=1.33$—1.34 G)[12] may be explained by four equivalently interacting hydrogens in the *meta* position.*

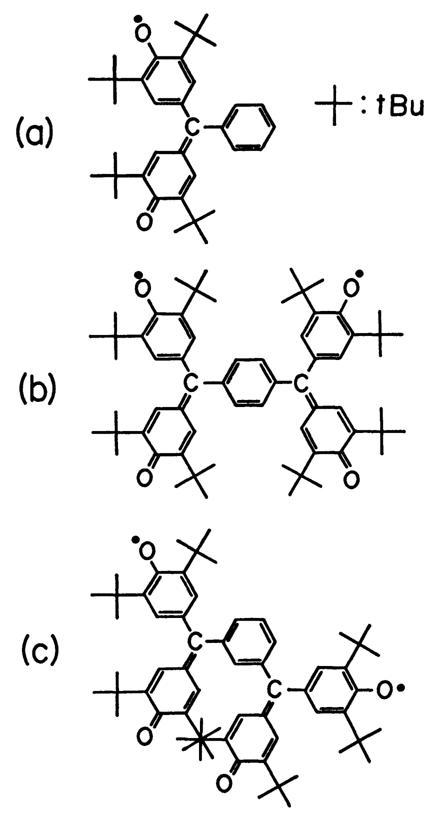

Fig. 1. Molecular structures of phenoxyl radicals.
(a) Phenylgalvinoxyl (I-S). (b) *para*-Phenylenebisgalvinoxyl (II-T). (c) *meta*-Phenylenebisgalvinoxyl (III-T).

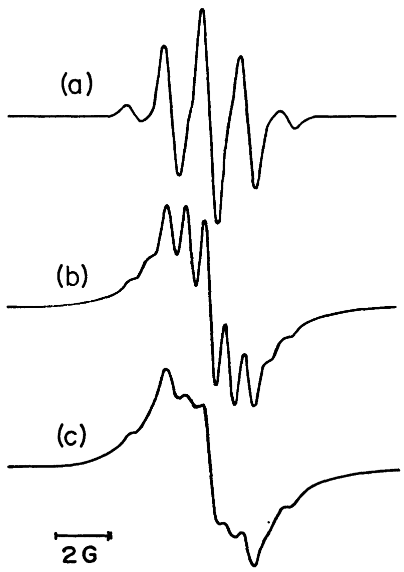

Fig. 2(a). First-derivative ESR spectrum observed for the monoradicals, (I-S), (II-S), and (III-S), produced by the PbO_2 oxidation of phenols (I-III) in 2-MeTHF.

Fig. 2(b) and (c). ESR spectra observed for the biradicals, (II-T) and (III-T), produced by the further oxidation of (II-S) and (III-S) in 2-MeTHF.

Phenylgalvinoxyl (I-S) is very stable and appears to be capable of existing for many days in 2-MeTHF in the absence of oxygen. The spectrum remains unchanged upon further oxidation. On the other hand, in the case of phenols (II) and (III), as the oxidation process proceeds, the five-line well resolved spectra of the secondary monoradicals begin to overlap with each other; finally, these are completely altered to a nine-line spectra with an equivalent splitting distance, as

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* In a recent ENDOR investigation, two kinds of hyperfine splittings due to *meta* ring protons are observed at −80 °C for this radical ($a^{H}_{m\text{-}1}=1.363$ G, $a^{H}_{m\text{-}2}=1.282$ G). T. Yamamoto, M. Kohno, T. Miyamae, K. Mukai, and K. Ishizu, *Chem. Lett.*, **1972**, 681.

shown in Fig. 2(b) and (c). These spectra, which consist of nine considerably overlapped lines, were unchanged at the lowest concentration at which they could be detected. Thus, they are thought to be due to the eight *meta* ring protons of phenoxyl biradicals, *p*- and *m*-phenylenebisgalvinoxyls ((II-T), $a_m=0.69$ G; (III-T), $a_m=0.69$ G). The structures of these biradicals are shown in Figs. 1(b) and (c).

When the solution containing the biradicals (II-T) and (III-T) is frozen into a rigid glass (77 K), one can observe some dipolar splittings, as are shown in Fig. 3(a) and (b). These spectra at 77 K can be interpreted on the basis of a randomly-oriented set of triplets with axial symmetry; thus the values of the dipolar splitting, D, are 20.0 G for the biradical (II-T) and 26.1 G for the biradical (III-T), as one half of the outer two lines' splitting.

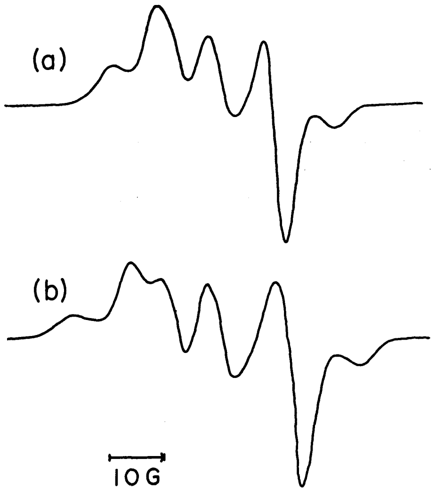

Fig. 3(a). ESR spectrum of the biradical (II-T) in 2-MeTHF at 77 K.

Fig. 3(b). ESR spectrum of the biradical (III-T) in 2-MeTHF at 77 K.

These small splittings may be explained by the large separation between the two galvinoxyl rings and the small unpaired spin density on the centered phenylene ring and the two carbon atoms bonded to the ring.**

The observed increase in the splitting constants, $D(\text{III-T})>D(\text{II-T})$, is consistent with the structure. Using a model of two-point dipoles, that is, the relation $D=(3/2)g\mu_B r^{-3}$, the average interelectronic distances in the biradicals (II-T) and (III-T) are calculated to be 11.2 Å and 10.2 Å, respectively. The relative intensity of the central singlet varied with the samples, that is, with the radical concentration of the samples. A zero-field splitting of $D=110$ G has been reported for the bisgalvinoxyl biradical.[8] The calculated average interelectronic distance, using a model of two point dipoles, is about 6.3 Å. The comparison of the average interelectronic distances of 6.3 Å for bisgalvinoxyl and 11.2 Å for *p*-phenylenebisgalvinoxyl indicates that the two point dipole model is still acceptable for bisgalvinoxyl, because the length of the centered-phenylene ring is about 4.3 Å.

The ESR results for a 2-MeTHF solution of the secondary radicals (I—III-S) obtained from phenol (I—III) at room temperature consist of a five-line, well-resolved ($a_m{}^H=1.33$—1.34 G) spectra. On the other hand, the ESR measurements of the two phenoxyl biradicals in a rigid solution at 77 K indicate that a triplet state exists in these radicals. If there is a strong scalar exchange interaction, J, between the two electrons such that $J\gg a_m{}^H$, the spectrum will consist of 9 lines separated by $a_m{}^H/2$, corresponding to an interaction with 8 equivalent protons.[13] In fact, the ESR spectra of the phenoxyl biradicals (II-T) and (III-T) in 2-MeTHF show nine lines of equivalent hyperfine splittings ($a_m{}^H=0.69$ G), respectively. The poorer resolution in the biradical (III-T) with respect to the biradical (II-T) may be due to a larger dipolar interaction in the former. These circumstances are very similar to those of verdazyl[14—16] and tetrazolinyl[17] biradicals, which have a π-electron system related to that of *p*- and *m*-phenylenebisgalvinoxyl radicals; each of them has π-conjugated monoradical halves linked by ***para*** and ***meta*** positions of a central phenylene π-bridge, and shows comparatively small zero-field splittings (about 38—53 G).

Recent studies of magnetic susceptibilities of *p*- and *m*-phenylenebisverdazyl biradicals have showed the presence of a triplet ground state ($S=1$) in these biradicals.[18] The intramolecular positive exchange integrals, J/k, of these biradicals are much greater than 300 K. The magnetic susceptibility of Yang's biradical, known as a stable phenoxyl radical and possessing three-fold symmetry, follows the Curie-Weiss law with a paramagnetic Curie constant of 1.0 K·emu/mol and a Weiss constant of −4 K.[19] This susceptibility also suggests that an intramolecular pure triplet approximation is reliable in the temperature region below 300 K. On the other hand, the results of the paramagnetic shift of the bisgalvinoxyl show that this radical has a singlet ground state with a negative exchange integral of 93 K.[20] The comparison of the electronic structures in *para* and *meta* phenylenebisverdazyls and bisgalvinoxyls and the smaller dipole-dipole interaction in the latter suggest a smaller exchange interaction in the latter.

Phenyl-galvinoxyl is rather stable and Ley *et al.*[6] succeeded in isolating it as a solid with an 85% spin concentration. In an attempt to clarify the level scheme of the spin system of these biradicals, preliminary experiments were performed for making the biradical solids of (II-T) and (III-T) by the PbO_2 oxidation in THF and in ethyl ether, respectively, under nitrogen gas, following the method of Kharasch and Joshi.[2] Spin concentrations were obtained from the results of the paramagnetic susceptibility measurements at room temperature, after correcting for the diamagnetic contribution calculated by the Pascal method. The values were 64% for (II-T) and 68% for (III-T) as $S=1/2$, $N=2N_0$, assuming the Curie law. These low observed concentrations are probably due to both

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** The orbital containing the unpaired electron of phenylgalvinoxyl has, at least in the Hückel approximation, a node in the phenyl ring. Ref. C. Besev, A. Lund, T. Vänngård, and R. Håkansson, *Acta Chem. Scand.*, **17**, 2281 (1963).

diamagnetic and monoradical impurities in the individual samples, since it is difficult to oxidize these hindered polyphenols until the final biradicals, owing to their insolubility in ordinary solvents. In addition, these radicals are not as stable as galvinoxyl. Despite the low concentrations, at least the presence of two unpaired electrons per molecule has been confirmed for these radicals from the susceptibility measurements.

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