Table I. Tetraaminoethylenes


Compd.	x	R	B.p., °C. (mm.)	Yield, %
1	0	CH_3	96–97 (8) (57ᵃ)	83
2	0	C_2H_5	136–138 (8) (48ᵃ)	82
3	0	CH_3 and C_2H_5	80–82 (0.25)	77
4	0	n-C_3H_7	108–110 (0.20)	75
5	0	n-C_4H_9	125–129 (0.20)	73
6	0	n-C_6H_{13}	185 (0.20)	77
7	0	$C_6H_5CH_2$	(162–164ᵃ)	100ᵇ
8	1	CH_3	104–105 (8.5)	34

	$(R_2N)_2C=C(NR_2)_2$		
Compd.	R_2N	M.p., °C.	Yield, %ᵇ
9	Pyrrolidinyl	91–93	98
10	Piperidino	59–61	89
11	Morpholino	170–171	41
12	N'-Methylpiperazinyl	79–80.5	53

ᵃ Melting point, °C. ᵇ Yield of crude product.

$\Delta^{2,2'}$-bis(imidazolidine) (14a).[7] The tetraaminoethylenes are exceptionally strong π bases, forming highly paramagnetic charge-transfer complexes with a variety of π acids.[8]

13

14a, Ar = C_6H_5
b, Ar = p-$CH_3C_6H_4$–
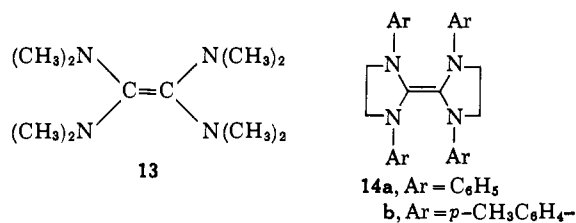
Wanzlick and co-workers have suggested that the ethylene 14a dissociates readily and reversibly into divalent carbon intermediates.[9] Lemal and his co-

14a
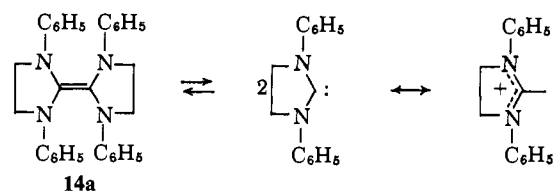
workers have presented evidence that the proposed equilibrium does not occur with ethylenes 14a and 14b.[10] The possibility of dissociation of the more reactive aliphatic peraminoethylenes to diaminocarbenes was tested in crossover experiments analogous to those of Lemal. Equal volume mixtures of 2 and 13 and of 2 and 5 were heated 1 hr. at 150° followed by 1 hr. at 175°. Gas chromatography of the two mixtures showed only the original components and no

(7) D. M. Lemal and K. I. Kawano, J. Am. Chem. Soc., 84, 1761 (1962).

(8) N. Wiberg and J. W. Buchler, Angew. Chem., 74, 490 (1962), prepared tetrakis(dimethylamino)ethylene complexes with electron acceptors.

(9) H. W. Wanzlick and H. Ahrens, Chem. Ber., 97, 2447 (1964), and earlier papers.

(10) D. M. Lemal, R. A. Lovald, and K. I. Kawano, J. Am. Chem. Soc., 86, 2518 (1964).

crossed products. Thus, the peraminoethylenes 2, 5, and 13 do not appear to be in equilibrium with the corresponding divalent carbon derivatives.[11] Reactions of the peraminoethylenes which might involve carbene intermediates more likely proceed by an electrophilic attack on the π-electron system as proposed by Lemal.[10] A number of such reactions of the aliphatic peraminoethylenes will be reported.

(11) This conclusion is in agreement with earlier work on tetrakis-(dimethylamino)ethylene (13) by N. Wiberg and J. W. Buchler, Chem. Ber., 96, 3000 (1963).

H. E. Winberg, J. E. Carnahan
D. D. Coffman, M. Brown
Contribution No. 1078, Central Research Department
E.I. du Pont de Nemours and Company
Wilmington 98, Delaware
Received March 8, 1965

Stable Phenoxy Radicals Derived from Phenols Related to Lignin[1]

Sir:

Recently, evidence has been presented for the existence of stable radical species in lignin.[2–4] Oxidized lignin preparations exhibit higher spin concentrations than native lignins. To determine what structural features favor the stabilization of radicals prepared by mild oxidation, we have dehydrogenated a variety of phenols derived from guaiacol and syringol. These products were examined by e.s.r. spectrometry. Stable phenoxy radicals were generated at room temperature from syringyl derivatives with an α-carbonyl side chain; these gave well-defined e.s.r. spectra.

When syringol derivatives in nonaqueous solvents were treated with a number of oxidants (Figure 1) at room temperature, strong e.s.r. signals were obtained at g = 2.0055. The average half-life of the radical species was 5 hr. in benzene. Resolution was best when benzene solutions of the phenols were dehydrogenated with PbO_2 (Figure 2), according to the method of Mueller.[5] On the other hand, no signal was detected when the following guaiacol derivatives were oxidized: vanillin, acetovanillone, 6-methyl-4-propylguaiacol, 5-nitro- and 5-bromovanillin. Weak e.s.r. signals were obtained from 5-formylvanillin, syringic acid, and sinapinic acid. The light green radical species was rapidly destroyed by aqueous or alcoholic solvents.

The hyperfine splitting patterns can be rationalized if one assumes interaction with six equivalent methoxyl protons and with two equivalent meta protons for all three phenoxy derivatives (Table I). For phenoxy radical (1) with all coupling constants identical, one would anticipate a nine-line spectrum with relative line intensities of 1:8:28:56:70:56:28:8:1. This is in good agreement with the experimental data. For the radical from acetosyringone (2), a slightly larger coupling constant for the two equivalent meta protons would account for the presence of shoulders on the principal

(1) Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(2) R. W. Rex, Nature, 188, 1185 (1960).

(3) C. Steelink, T. Reid, and G. Tollin, J. Am. Chem. Soc., 85, 4048 (1963).

(4) C. Steelink, Geochim. Cosmochim. Acta, 28, 1615 (1964).

(5) E. Mueller, R. Mayer, U. Heilmann, and K. Scheffler, Ann., 645, 67 (1961).

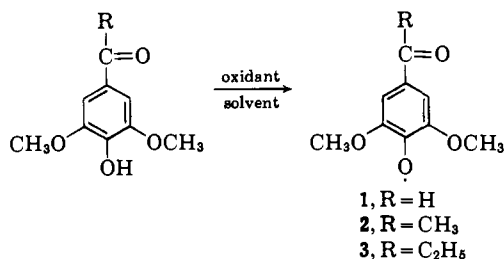Figure 1. Oxidation of model lignin phenols. Oxidants: (a) 0.3 M $K_3Fe(CN)_6$ in 2 M aqueous KOH; (b) 0.1 M $Ce(HSO_4)_4$ in 1 M aqueous H_2SO_4; (c) PbO_2, solid. Solvents: benzene, toluene, and dichloromethane.

Figure 2. First derivative e.s.r. spectra of radicals 1, 2, and 3.

lines. The propiosyringone radical (3) yields 17 lines, with intensities closely paralleling those predicted from the constants in Table I (e.g., 1:6:2:15:12:21:30:21:40:21:30:21:12:15:2:6:1); here, the *meta* proton coupling is 1.5 times that of the methoxyl proton. Theoretical spectra, calculated for each of the above, confirmed these assignments.[6] The values for the

Table I. Coupling Constants for Syringol Radicals

Syringol radical	No. of lines	$A^H_{OCH_3}$, gauss	A^H_{meta}, gauss
1	9	1.30	1.30
2	9	1.30	1.45
3	17	1.30	1.95

methoxyl and *meta* proton coupling constants are consistent with previously published values.[7,8]

The visible absorption spectra of all three radical species in solution are almost identical; principal bands appear at 420, 450, 470, and 750 mμ. Over a period of time, the 750 mμ band height decreases while the 470 mμ band height increases. A plot of the log height of the 750 mμ band vs. time is parallel to the plot of the log intensity of the e.s.r. signal vs. time, thus indicating that the radical species is represented by the green 750 mμ band.

A number of conclusions may be drawn from these results: (a) The stability of the phenoxy radical is dependent on the presence of two o-CH_3O substituents, as well as a p-C=O function. Guaiacol derivatives, with a free *ortho* position, apparently dimerize or oxidize rapidly in preference to forming stable phenoxy radicals. (b) The stability of the radical from syringol is remarkable, in light of the fact that the vast majority of previously prepared phenoxyls have been substituted in the 2- and 6-positions by bulky groups, such as *t*-butyl. Mueller, however, did infer[9] that lignin model phenoxyls might be stable when he obtained a poor single line e.s.r. spectrum for a syringylacrylonitrile derivative. (c) Apparently, minor changes in the side chains of 1-3 (R = H, CH_3, C_2H_5) do affect the electron density at the two *meta* positions, giving rise to the different e.s.r. splitting patterns. (d) The slow decay
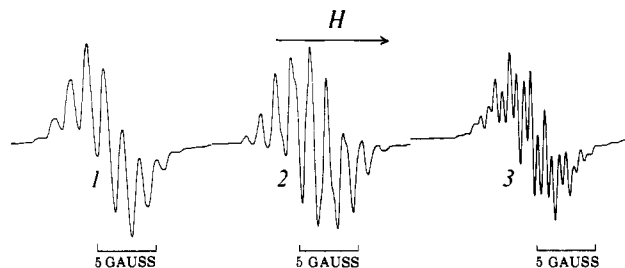
of these radicals to red species (probably o-quinones[10]) is of significance to lignin chemistry. Oxidation of lignins by biological systems or aqueous chemical systems could produce colored decay products, via intermediates such as 1, 2, and 3. These radical intermediates are stabilized temporarily by solvents such as benzene, or they may be indefinitely stabilized in the solid lignin matrix, thus contributing to the higher spin concentrations observed in solid, oxidized lignins.[3,4] The α-carbonyl syringyl moiety appears to be an inherent part of native lignin[11] and oxidized lignin[12] structures. Therefore, these well-characterized radicals from syringol constitute excellent models for a study of the course of dehydrogenation reactions of lignins. Such a study is currently in progress.

Acknowledgments. We are deeply grateful to Professor John Willard of the Department of Chemistry, University of Wisconsin, for the use of a Varian 4500 spectrometer (100 kc. field modulation), and to Professor John Harriman of the same department for his many helpful discussions of the e.s.r. spectra. We are also indebted to Mr. J. C. Pew of the Forest Products Laboratory for providing some of the model phenols used in this study.

(10) E. Adler, *Paperi Puu*, No. 11, 634 (1961).
(11) K. Freudenberg, *Holzforsch.*, 18, 3 (1964).
(12) J. Marton, *Tappi*, 47, 713 (1964).
(13) On sabbatical leave from the University of Arizona until Aug. 1965.

Cornelius Steelink[13]
Forest Products Laboratory
Forest Service, U. S. Department of Agriculture
Madison, Wisconsin

Magnetic Peroxyborates. The Pseudo-Superoxides

Sir:

We report that certain peroxyborates are paramagnetic; both static susceptibility and electron spin resonance (e.s.r.) measurements show many unpaired spins. To our knowledge there is no previous suggestion that peroxyborates could be paramagnetic.

Foerster[1] converted, by careful heating, sodium perborate monohydrate[2] to a material which briskly evolved oxygen on being placed in water; hydrogen peroxide is simultaneously formed. Menzel[3] and others[4] prepared similar perborate materials.

(6) We are indebted to Professor John Harriman of the Department of Chemistry, University of Wisconsin, for these computations.
(7) T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 4302 (1964).
(8) E. Mueller, H. Kaufmann, and A. Rieker, *Ann.*, 671, 61 (1964).
(9) E. Mueller, R. Mayer, H. D. Spanagel, and K. Scheffler, *ibid.*, 645, 61 (1961).

(1) F. Foerster, *Z. angew. Chem.*, 34, 354 (1921).
(2) Names and chemical symbols are those employed by peroxide chemists. They state only stoichiometry; structural implications are absent.
(3) H. Menzel, *Z. anorg. allgem. Chem.*, 167, 193 (1927).
(4) T. I. Taylor and G. G. Taylor, *Ind. Eng. Chem.*, 27, 672 (1935);