

oxidation of TDE by some electronically activated intermediate transferring its energy to an original TDE molecule or by a different process in which a new TDE\* is generated.

The fluorescence quantum yield of TDE under 3660 Å. activation was obtained by comparison with fluorescein solutions of known efficiency. Pure TDE and its 1% solution in *n*-decane gave semiquantitative fluorescence quantum yields of 0.03 to 0.05. The over-all oxyluminescence quantum yield is about  $3 \times 10^{-4}$ , corresponding to about three photons emitted for 10,000 molecules of TDE oxidized. This was determined by measuring the total light emitted by 1 ml. of TDE floating on water. The fluorescence and oxyluminescence efficiencies indicate about 1% of the TDE molecules oxidized result in the production of TDE\*. This is in contrast to the 50% or more of luminol molecules that are oxidized to excited aminophthalate ions.<sup>2c</sup>

The oxyluminescence of TDE is profoundly affected by various protonic substances, including water and alcohols. In their absence, there is no significant reaction of TDE with air. The extreme sensitivity of the oxidation to traces of protonic agents can be shown readily by differential thermal calorimetry. Solutions of TDE in *n*-decane containing octyl alcohol as an impurity displayed large heats of reaction and bright oxyluminescence. Similar solutions of TDE in *n*-decane free of protonic agents developed no significant heat or light in the presence of dry air. Addition of a few parts per million of water to such solutions caused immediate oxyluminescence and heat generation.

Protonic agents used to induce oxyluminescence of TDE are consumed in the process. The concentration of agent required for optimum light emission is low and dependent on the agent. This results from the ease with which the oxyluminescence of TDE is quenched. For example, solutions of TDE in lower alcohols are not oxyluminescent. The oxyluminescence is also quenched by tetramethylurea and tetramethyloxamide, two of the oxidation products of TDE.

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Received December 21, 1964

## Tetraaminoethylenes

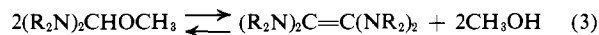
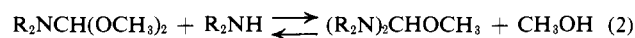
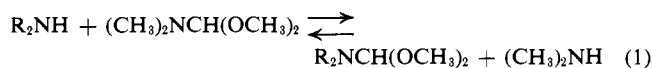
Sir:

A number of previously unavailable and unusually reactive tetrakis(dialkylamino)ethylenes have now been synthesized and their chemistry studied.<sup>1</sup> The new tetraaminoethylenes are obtained by the novel reaction of 1,1-dimethoxytrimethylamine<sup>2</sup> with appropriate aliphatic secondary amines. Under distillation conditions dimethylamine and methanol are eliminated with the intermediate formation of bis(dialkylamino)me-

(1) Previously known tetraaminoethylenes include tetrakis(dimethylamino)ethylene (13) first reported by R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3649 (1950), and aryl-substituted bis(imidazolidines) (14) reported by H. W. Wanzlick, F. Esser, and H. J. Kleiner, *Chem. Ber.*, **96**, 1208 (1963).

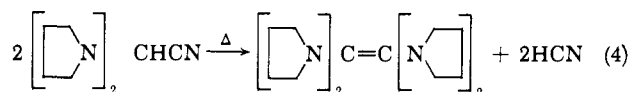
(2) H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Chem. Ber.*, **96**, 2671 (1963); M. Brown, U. S. Patent 3,092,637 (June 4, 1963).

thoxymethanes<sup>3</sup> which on further heating condense to the corresponding tetrakis(dialkylamino)ethylenes.



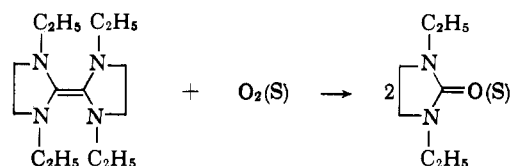
The reaction rates of the various equilibria are influenced by the basicity of the amine, increasing with increasing basicity, and by steric factors. Cyclic secondary amines, such as pyrrolidine and, particularly, *N,N'*-dialkylethylenediamines, are eminently suitable as intermediates to the ethylenes. The nature of the amine and the reaction conditions (temperature, time) dictate the relative proportions of the products.

In the coupling reaction (eq. 3) other stable anions besides methoxyl can serve as leaving groups, as is shown by the evolution of HCN on heating  $\alpha,\alpha$ -bis(*N*-pyrrolidinyl)acetonitrile with the formation of tetrakis(*N*-pyrrolidinyl)ethylene.



Several of the new tetraaminoethylenes synthesized by reaction of 1,1-dimethoxytrimethylamine with the appropriate secondary amine are listed in Table I.<sup>4</sup> The compounds 1-9, with the exception of 7, exhibit the unusual property of emitting visible light on air oxidation.<sup>5</sup> For example, when a small quantity of 2 is exposed to air, it chemiluminesces brightly, fumes, and is consumed in a short time. Solutions of 2 in inert aliphatic hydrocarbon solvents exhibit strong blue-green oxyluminescence, and exposure to only traces of air is sufficient to cause the luminescence. The fluorescence spectrum of a solution of 2 in cyclohexane under 3660 Å. activation coincides with the air-induced chemiluminescence spectrum of the same solution. The spectra are continuous with the maxima at 5060 Å. The known oxidation products of 2 do not fluoresce under these conditions, which suggests the oxyluminescence arises from electronically excited 2.

The ultimate oxidation product of 2 with air is the imidazolidinone; sulfur reacts similarly to form the corresponding thio analog. With bromine and iodine



the new tetraaminoethylenes give high yields of water-soluble bisquaternary salts analogous to those from tetrakis(dimethylamino)ethylene (13)<sup>6</sup> and tetraphenyl-

(3) H. Brederick, F. Effenberger, and G. Simchen, *Angew. Chem.*, **74**, 353 (1962); H. Brederick, F. Effenberger, and H. Botsch, *Chem. Ber.*, **97**, 3397 (1964).

(4) Satisfactory elemental analyses were obtained for all new compounds. Spectra characterizations including H<sup>1</sup> n.m.r. were consistent with the proposed structures. All manipulations involving peraminoethylenes were carried out under nitrogen.

(5) The strong oxyluminescence of tetrakis(dimethylamino)ethylene (13) was first observed by Pruett and co-workers, ref. 1. The aryl-substituted bis(imidazolidines) (14) do not oxyluminesce.

(6) N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3223 (1963).

Table I. Tetraaminoethylenes

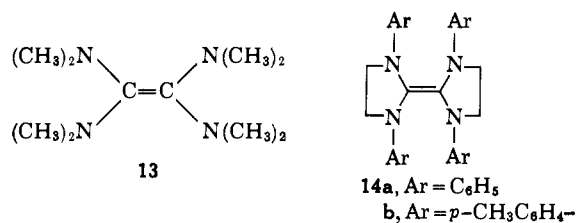
Compd. <i>x</i>	R	B.p., °C. (mm.)	Yield, %
1	0	96-97 (8) (57 <sup>a</sup> )	83
2	0	136-138 (8) (48 <sup>a</sup> )	82
3	0	80-82 (0.25)	77
4	0	108-110 (0.20)	75
5	0	125-129 (0.20)	73
6	0	185 (0.20)	77
7	0	(162-164 <sup>a</sup> )	100 <sup>b</sup>
8	1	104-105 (8.5)	34

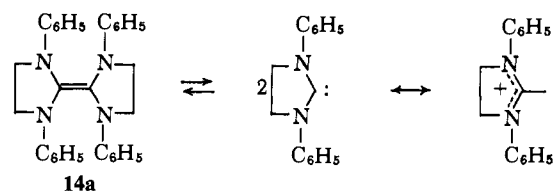
Compd.	(R <sub>2</sub> N) <sub>2</sub> C=C(NR <sub>2</sub> ) <sub>2</sub> R <sub>2</sub> N	M.p., °C.	Yield, % <sup>b</sup>
9	Pyrrolidinyl	91-93	98
10	Piperidino	59-61	89
11	Morpholino	170-171	41
12	N'-Methylpiperazinyl	79-80.5	53

<sup>a</sup> Melting point, °C. <sup>b</sup> Yield of crude product.

Δ<sup>2,2'</sup>-bis(imidazolidine) (**14a**).<sup>7</sup> The tetraaminoethylenes are exceptionally strong π bases, forming highly paramagnetic charge-transfer complexes with a variety of π acids.<sup>8</sup>



Wanzlick and co-workers have suggested that the ethylene **14a** dissociates readily and reversibly into divalent carbon intermediates.<sup>9</sup> Lemal and his co-



workers have presented evidence that the proposed equilibrium does not occur with ethylenes **14a** and **14b**.<sup>10</sup> 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.<sup>11</sup> 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.<sup>10</sup> 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).

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Received March 8, 1965

### Stable Phenoxy Radicals Derived from Phenols Related to Lignin<sup>1</sup>

Sir:

Recently, evidence has been presented for the existence of stable radical species in lignin.<sup>2-4</sup> 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<sub>2</sub> (Figure 2), according to the method of Mueller.<sup>5</sup> 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).