DIALKOXYAMINYL RADICALS

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NH-Dialkoxyamines [1, 2] readily form dialkoxyaminyl radicals (DR), RONOR', where R = R' = Me (I), R = Me, R' = i-Bu (II), R + R' = (CH₂)₂ (III), R + R' = CHMe(CH₂)₂ (IV) (Table 1), upon storage under ordinary conditions, photooxidation, and by the action of sterically hindered quinones, nitroxyl or aroxyl radicals in toluene. The aminyl structure of DR was established by the similarity of their hyperfine coupling and g-factor with RONR radicals [3] and marked difference from RO(R)NO· radicals [4]. The concentration of DR decreases upon cooling of the solution with their complete disappearance at from -80 to -100°C and increases upon heating to 120°C. This behavior is likely explained by reversible dimerization:

$2 \text{ RONOR'} \Rightarrow \text{RO(R'O)NN(OR')OR}$

The high stability of DR is a consequence of the dative—dative stabilization due to the two oxygen atoms. DR are also generated upon the action of the 2-cyanopropyl radical on N,N-dimethoxyamine and reacts with it to form N,N-dimethoxy-2-cyano-2-aminopropane (V), which indicates promise for the use of radical reactions in the chemistry of NH-dialkoxy-amines.

$$(MeO)_2NH + NCCMe_2N = NCMe_2CN \xrightarrow{C_0H_0} (MeO)_2NCMe_2CN$$

$$(V)$$

Aminopropane (V) was obtained in 26% yield, mp 35°C (1 mm). PMR spectrum in C_6D_6 at 400 MHz (δ , ppm, relative to TMS): 1.16 s (Me), 3.38 s (MeO). ¹³C NMR spectrum in $(CD_3)_2CO$ at 100 MHz (δ , ppm, J, Hz, relative to TMS): 23.10 (Me, ¹J = 130.9), ³J = 4.4), 62.16 (MeO, ¹J = 143.6), 62.72 (²J = 4.4), 119.65 (CN, ³J = 5.0).

TABLE	1.	ESR	Spectral	Parameters*
		DUL	OPCCLIGA	I GIGHC CCID

Radical	Spectral form	a _N , Oe	a _N , Oe	g-Factor
(I)	t. sept t. sext t. quint t.t	15.00	1,45	2,0046
(II)		15.00	1,25	2,0046
(III)		16.00	2,50	2,0046
(IV)		14,80	3,50 **	2,0059

*Taken on a Varian E-12 A spectrometer at about 20°C. **Hyperfine coupling observed only with the axial hydrogen atoms.

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