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N-(2,4,6-TRICARBOMETHOXYPHENYL)-ALKOXYAMINYLS,NEW PUSH-PULL STABLE NITROGEN FREE RADICALS

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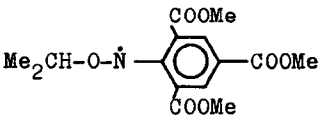
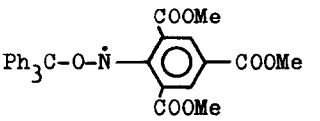
The preparation and detection, by ESR spectroscopy in static systems, of various nitrogen free radicals with one donor and one bulky acceptor group attached to the nitrogen atom [1-3] demonstrates that electronic as well as steric factors control the stability of such free radicals. The present paper reports the preparation and ESR spectra of N-(2,4,6-tricarbomethoxyphenyl)-isopropoxyaminyl (I) and of the related -triphenylmethoxyaminyl (II).



I



II

Isopropoxyamine [4] as well as trityloxyamine [5] react smoothly with 1-bromo-2,4,6-tricarbomethoxybenzene affording the corresponding N-alkoxyaniline derivatives. Oxidation with lead tetraacetate in 1,4-dioxane converts these alkoxyanilines into the free radicals I and II which have half-lives of about 30 minutes at room temperature in this solvent.

The ESR spectrum of I has twelve lines and is easily interpreted in terms of hyperfine coupling constants presented in table and figure. The ESR spectrum of II has nine lines and gives markedly different coupling constants. The aminyl formula results from the g-values, 2.0033 ± 0.0002. The table also presents for comparison data of two related free radicals,[6] whose details will be published later.

Radical II stands out by two features. The significant difference between its coupling constants and those of the other three radicals can be ascribed to a

sterically caused distortion of its molecule, taking the triphenylmethoxy group out of the plane and increasing thereby the amount of sigma character of the orbital containing the odd electron ; thus a_{m-H} is diminished and a_N is increased. Most interesting is the existence of radical II which shows no sign of dissociation into triphenylmethyl and a nitrosobenzene derivative (suggesting a possible alternative preparation of such radicals by spin trapping).

Table of hyperfine coupling constants (in Gauss) of radicals RO-N-$C_6H_2(COOCH_3)_3$

Formula	R	Alkoxy group	a_N	a_R^H	a_{m-H}^H
	Me	Methoxy	10.0	1.43	2.85
	Et	Ethoxy	9.76	1.39	2.80
I	i-Pr	Isopropoxy	10.0	2.0	2.0
II	CPh_3	Trityloxy	14.5	-	1.1

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