the di-*p*-toluenesulfonate of ethylene glycol in a Carius tube.[42] The purified material melted at 235–237° (lit.[42] mp 233–234°).

Ethylenediamine-$^{15}N_2$ dihydrochloride was obtained by heating a suspension of 1,2-diphthalimidoethane-$^{15}N_2$ in 6*M* hydrochloric acid in a Carius tube at 180° for 3 hr. The crude product obtained from the filtrate and washings of the reaction mixture by freeze-drying was used in the next stage of the synthesis.

The ethylenediamine-$^{15}N_2$ dihydrochloride was allowed to react with sodium iodoacetate at 45° with concomitant addition of sodium hydroxide solution to keep the pH at 10 ± 0.3. When the reaction was complete, as judged by the fact that the pH no longer dropped on addition of base, the mixture was quickly cooled to about 5°, and hydrochloric acid was added rapidly to bring the pH to 1.2. The precipitate was removed by filtration, leached with water, and air dried. The ethylenediamine-$^{15}N_2$-tetraacetic acid so obtained melted at 232–235° (lit.[43] mp 242° dec).

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[42] E. J. Sakellarios, *Helv. Chim. Acta*, **29**, 1675 (1946).

[43] *Beilstein*, **4**, III 1187.

Nitrogen-Centered Free Radicals. VI. Electron Spin Resonance Studies of *N*-Alkoxy-*N*-alkylamino, *N*-Alkoxy-*N*-arylamino, and *N*-Alkoxy-*N*-carboethoxyamino Radicals in Solution[1]

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Abstract: A variety of substituted *N*-alkoxyamino radicals, RNOR′, have been generated and studied by esr spectroscopy. The oxygen substituent, R′, has been *tert*-butyl in most cases; the nitrogen substituent, R, categorizes the radical into one of three different classes. One such class, the *N*-alkoxy-*N*-alkylamino radicals (R = alkyl), is formed by photolysis of *tert*-butyl *N*-alkylperoxycarbamates, by hydrogen abstraction from appropriately substituted hydroxylamines, or by direct photolysis of solutions of these latter compounds. The ability of the alkoxy substituent to delocalize the unpaired electron is discussed; INDO calculations were performed on the *N*-methoxy-*N*-methylamino radical and the results were compared with experiment. Speculation as to the mechanism of N–O bond formation is also presented. A second category of paramagnetic species, the *N*-alkoxy-*N*-arylamino radicals (R = aryl), was also studied. A variety of these radicals with both electron-donating and -withdrawing substituents in the meta and para positions were generated from either the appropriate *tert*-butyl *N*-arylperoxycarbamate (electron-withdrawing substituents) or by photolysis of a solution of di-*tert*-butyl peroxide and the substituted aniline (electron-donating substituents). It was found that both para-electron-donating and para-electron-withdrawing substituents were effective in delocalizing the unpaired electron and that the *N*-alkoxy-*N*-arylamino radicals could be assigned to Walter's "class S" based on the nitrogen hyperfine coupling constant. The addition of a small amount of *tert*-butyl hydroxperoxide to solutions which normally afforded the alkoxyarylamino radicals produced, instead, the corresponding alkoxy aryl nitroxides. The nitrogen hfsc's in these radicals could be correlated with Hammett σ constants exhibiting the anticipated "class O" behavior. A final class of radicals, the *N*-alkoxy-*N*-carboethoxyamino species (R = carboethoxy), was generated and found to possess a Π-electronic ground state on the basis of the esr parameters.

Recent interest in neutral amino free radicals has led to several electron spin resonance (esr) investigations in this area.[1a,b,2–8] Photolysis of 2-tetrazenes directly in the esr cavity produced isotropic solution spectra of the simple dialkylamino radicals,[2] while the aziridino and azetidino radicals were formed by N–H abstraction from the parent heterocyclic amine by *tert*-butoxyl radicals.[3] Several amido radicals have been generated by the photolysis of *N*-chloramides.[1a] The anilino radical was prepared in an adamantane matrix by X-irradiation[4] while the 2,4,6-tri-*tert*-butylanilino species was produced by flash photolysis of 2,4,6-tri-*tert*-butylaniline.[5] Several alkylimino radicals have been prepared by the photoinduced decomposition of aminoalkyl radicals in an adamantane matrix[6,7] and two *N*-methoxyamino radicals were produced by hydroxyl radical addition to oxime *O*-methyl ethers.[8] During the course of this investigation, esr studies of *N*-*tert*-butylanilino[9] and *N*-*tert*-butoxyamido radicals[10] were reported which have a direct relationship to certain of the results herein.

In an earlier communication we reported that the photolysis of *tert*-butyl *N*-alkylperoxycarbamates pro-

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[1] (a) Part V: W. C. Danen and R. W. Gellert, *J. Amer. Chem. Soc.*, **94**, 6853 (1972). (b) Preliminary communication of part of this work: W. C. Danen and C. T. West, *ibid.*, **93**, 5582 (1971). (c) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant PRF No. 5579-AC4), and the Kansas State Bureau of General Research for support of this work.

[2] W. C. Danen and T. T. Kensler, *J. Amer. Chem. Soc.*, **92**, 5235 (1970).

[3] W. C. Danen and T. T. Kensler, *Tetrahedron Lett.*, 2247 (1971).

[4] R. V. Lloyd and D. E. Wood, *Mol. Phys.*, **20**, 735 (1971),

[5] N. M. Atherton, E. J. Land, and G. Porter, *Trans. Faraday Soc.*, **59**, 818 (1963).

[6] T. Richerzhagen and D. H. Volman, *J. Amer. Chem. Soc.*, **93**, 2062 (1971).

[7] D. E. Wood, R. V. Lloyd, and D. W. Pratt, *ibid.*, **92**, 4115 (1970).

[8] P. Smith and W. M. Fox, *Can. J. Chem.*, **47**, 2227 (1969).

[9] S. F. Nelsen, R. T. Landis, L. H. Kiehle, and T. H. Leung, *J. Amer. Chem. Soc.*, **94**, 1610 (1972).

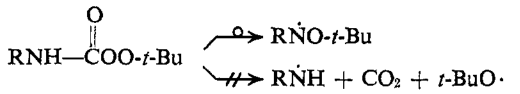
[10] T. Koenig, J. A. Hoobler, and W. R. Mabey, *ibid.*, **94**, 2514 (1972).

Table I. Hyperfine Splitting Constants and *g* Values for *N*-Alkoxy-*N*-alkylamino Radicals

Radical	a^N	$a^H{}_\beta$	$a^H{}_{OCH_2R}$	*g* value	Temp, °C	Method[a]
$CH_3\dot{N}OC(CH_3)_3$	14.47	21.51		2.0048	−90	B (−30), C
$CH_3CH_2\dot{N}OC(CH_3)_3$	14.28	24.95		2.0048	−120	B
	14.27	23.37			−80	B, C, D
	14.27	22.68			−60	B
	14.25	21.58			−20	A, B
	14.26	21.23			+20	A, B
$CH_3\dot{N}OCH_3$	14.30	21.85	2.62	2.0048	−90	B
$CH_3CH_2\dot{N}OCH_3$	14.00	24.20	2.62	2.0048	−90	B
$CH_3CH_2\dot{N}OCH_2CH_3$	14.31	24.30	2.50	2.0048	−90	B, C
$CH_3\dot{N}CH_3$	14.78	27.36		2.0044	−90	Ref 2

[a] Method of generation of radicals: (A) photolysis of *ca.* 10% *tert*-butyl peroxycarbamate in benzene; (B) photolysis of RNHOR′ with di-*tert*-butyl peroxide in cyclopropane; (C) photolysis of RNHOR′ in cyclopropane; (D) photolysis of RNHOR′ with azomethane in cyclopropane.

duced esr spectra of *N*-*tert*-butoxy-*N*-alkylamino radicals instead of the anticipated monoalkylamino radicals (eq 1).[1b] The latter species were expected since the



$$RNH{-}\overset{O}{\overset{\|}{C}}OO\text{-}t\text{-}Bu \begin{cases} \xrightarrow{\circ} R\dot{N}O\text{-}t\text{-}Bu \\ \not\longrightarrow R\dot{N}H + CO_2 + t\text{-}BuO\cdot \end{cases} \quad (1)$$

analogous *tert*-butyl peresters have been shown to give esr spectra of alkyl radicals when photolyzed at reduced temperatures.[11] Furthermore, arylamino radicals from the decomposition of peroxycarbamates have been postulated to initiate vinyl polymerization.[12,13]

We have expanded our studies of peroxycarbamates and presently wish to report the observation of *N*-*tert*-butoxy-*N*-arylamino radicals from the thermal decomposition of *tert*-butyl *N*-arylperoxycarbamates. In no instance were the simple anilino radicals observed. It also was found that certain *N*-*tert*-butoxy-*N*-arylamino radicals could be produced by the photolysis of a solution of the corresponding aniline with di-*tert*-butyl peroxide. The addition of a small amount of *tert*-butyl hydroperoxide to the solution yielded spectra of the corresponding nitroxide radical. The effect of substituents on *N*-*tert*-butoxy-*N*-arylamino radicals was investigated and it was found that these radicals can be assigned to Walter's "class S."[14] Several *N*-*tert*-butoxyamido radicals also have been observed and it was concluded that these species exist in a Π ground electronic state.

Results and Discussion

***N*-Alkoxy-*N*-alkylamino Radicals.** When approximately 10^{-1} *M* deoxygenated benzene solutions of *tert*-butyl *N*-alkylperoxycarbamates were photolyzed at temperatures greater than −30°,[15] it was apparent that the observed radicals exhibited no N–H hyperfine interaction as would be anticipated for a monalkylamino radical. When comparing the β-hydrogen hfsc of the dimethylamino radical[2] (27.36 G) and the radical derived from *tert*-butyl *N*-methylperoxycarbamate (21.51 G), it was immediately obvious that there was a rather effective unpaired electron-withdrawing substituent attached to nitrogen. Furthermore, there was no hyperfine interaction of the unpaired electron with the substituent. All of these observations were consistent with a *tert*-butoxy group attached to the nitrogen in these radicals. In order to prove that *tert*-butyl *N*-alkylperoxycarbamates formed *N*-*tert*-butoxy-*N*-alkylamino (alkoxyalkylamino) radicals upon photolysis, a number of *N*,*O*-dialkylhydroxylamines were synthesized and hydrogen abstraction reactions carried out directly in the esr cavity. Indeed, *N*-ethyl-*O*-*tert*-butylhydroxylamine and *N*-methyl-*O*-*tert*-butylhydroxylamine upon N–H abstraction showed identical esr spectra under identical experimental conditions with the spectra observed when the corresponding peroxycarbamates were photolyzed. The hfsc's and *g* values of the alkoxyalkylamino radicals are given in Table I.

The alkoxyalkylamino radicals were generated by several methods. In addition to photolysis of *tert*-butyl *N*-alkylperoxycarbamates (eq 1) and N–H abstraction from *N*,*O*-dialkylhydroxylamines by either photolytically produced *tert*-butoxyl radicals or methyl radicals (eq 2), esr signals exclusively of *N*-alkoxy-*N*-alkylamino radicals were observed simply by photolyzing *N*,*O*-dialkylhydroxylamines in cyclopropane solution (eq 3). Even though direct photolysis of *N*,*O*-dialkylhydroxylamines produced esr spectra of alkoxyalkylamino radicals, addition of di-*tert*-butyl peroxide or azomethane prior to photolysis increased the intensity of the observed esr spectra relative to the spectra in the absence of abstracting agents. In addition, the methyl radical was not observed when azomethane was photolyzed in the presence of *N*,*O*-dialkylhydroxylamines, whereas a strong esr signal due to the methyl radical was observed in the absence of the *N*,*O*-dialkylhydroxylamine under otherwise identical experimental conditions.

$$RNHO\text{-}t\text{-}Bu \xrightarrow[h\nu]{t\text{-}BuOO\text{-}t\text{-}Bu \text{ or } CH_3N{=}NCH_3} R{-}\dot{N}{-}O\text{-}t\text{-}Bu \quad (2)$$
$$R = CH_3, C_2H_5$$

$$RNHOR' \xrightarrow{h\nu} R\dot{N}OR' \quad (3)$$

From Table I it can be seen from the temperature dependence of the β-hydrogen hfsc that the *N*-*tert*-butoxy-*N*-ethylamino radical exhibited a barrier to rotation about the N–C bond. Increasing the temperature caused the rotation to approach or reach the free rotational limit of *ca.* 21.5 G at *ca.* +20°. Assessment of the energy barrier of rotation using the method de-

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[11] (a) J. K. Kochi and P. J. Krusic, *ibid.*, **91**, 3940 (1969); (b) R. O. C. Norman, *Chem. Soc., Spec. Publ.*, **No. 24**, 147 (1970).

[12] For a review of the decomposition of peroxycarbamates and their initiation of vinyl polymerization, see F. C. Baines, J. H. Grezlak, and A. V. Tobolaky, *J. Polym. Sci., Part A-1*, **7**, 3297 (1969).

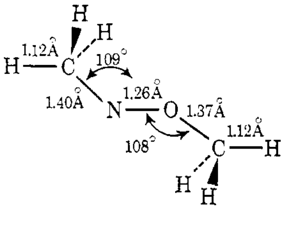
[13] E. L. O'Brien, F. H. Beringer, and R. B. Mesrobian, *J. Amer. Chem. Soc.*, **79**, 6238 (1957).

[14] R. I. Walter, *J. Amer. Chem. Soc.*, **88**, 1923 (1966).

[15] Solubility required temperatures to be maintained above −30°.

scribed by Kochi and Krusic[16] did not reproduce the experimental curve of β-hydrogen hfsc *vs.* temperature. Apparently the rotation about the N–C bond does not transverse a simple twofold barrier.

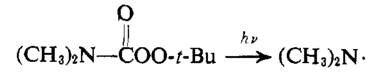
INDO calculations[17] predicted a trans coplanar structure for the *N*-methoxy-*N*-methylamino radical and yielded $a^{\mathrm{N}} = +11.3$ G, $a^{\mathrm{H}}{}_{\beta} = +23.6$ G, and $a^{\mathrm{H}}{}_{\mathrm{OCH_3}} = +0.5$ G in reasonable agreement with experiment. The spin densities in the nitrogen 2s and 2p orbitals for the INDO energy-minimized structure were calculated to be 0.0299 and 0.7789, respectively. The (X_{OR}) parameter calculated by Fischer's empirical method suggested a lower value for the 2p spin density than was obtained by INDO calculations.



Both INDO calculations and use of Fischer's method showed the spin density in the nitrogen 2p orbital in the alkoxyalkylamino radicals to be smaller than the nitrogen 2p spin density in the dimethylamino radical. It should be noted, however, that the nitrogen hfsc remained nearly the same in both radicals, indicating that the nitrogen 2s spin density must have remained nearly constant. This illustrates that π–σ spin polarization is not equally effective in these two types of radicals and that a common Q_{N} value cannot be utilized to accurately correlate the observed a^{N} with the nitrogen 2p spin density. Recent calculations from this laboratory on amino radicals using energy localized orbitals generated from INDO wave functions[18] indicated that spin polarization from the nitrogen 2p to the nitrogen 2s orbital was a function of 2p spin density, X–N–X bond angle, and the nature of the X–N σ bond. The calculations also indicated the major source of positive nitrogen 2s spin density was from the lone pair of electrons on nitrogen and that the bond pairs showed an overall negative nitrogen 2s spin density as a result of π–σ repulsions.

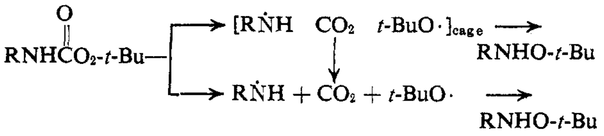
Qualitatively, more effective spin polarization upon replacing a methyl group with an alkoxy group on an amino radical could be the result of a higher s character of the nitrogen lone pair on the alkoxy substituted amino radical or more delocalization of β spin of a bonding pair to the alkoxy substituent. Both mechanisms would be consistent with the decreased nitrogen 2p spin density and increased a^{N} for the alkoxyamino radicals since the alkoxy substituent is more electronegative than a methyl substituent.

The observation of clean, moderately strong esr spectra of *N-tert*-butoxy-*N*-alkylamino radicals from the photodecomposition of *tert*-butyl peroxycarbamates apparently requires a rather efficient formation of the N–O bond.[19] To determine whether alkylamino radicals were formed initially upon photolysis of *tert*-butyl peroxycarbamates, *tert*-butyl *N,N*-dimethylperoxycarbamate was photolyzed in the esr cavity (eq 4). A weak spectrum of the dimethylamino radical was obtained indicating that amino radicals are probably formed prior to alkoxyalkylamino radicals in the case of *N*-alkylperoxycarbamates. Furthermore, it is reasonable to suspect



$$(CH_3)_2N\text{—}\overset{\overset{\displaystyle O}{\|}}{C}OO\text{-}t\text{-Bu} \xrightarrow{h\nu} (CH_3)_2N\cdot \qquad (4)$$

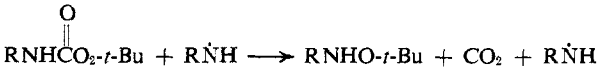
that the corresponding *N*-alkyl-*O-tert*-butylhydroxylamine may be formed as an intermediate followed by N–H bond scission. Several possibilities exist for the formation of such an intermediate including radical combination, an induced decomposition of peroxycarbamate by either the initially formed amino radical or even the amine itself, or an intramolecular rearrangement involving carboxy inversion in the starting material. Several of these pathways are shown in eq 5–8.



$$\mathrm{RNH}\overset{\overset{\displaystyle O}{\|}}{C}O_2\text{-}t\text{-Bu} \longrightarrow [\mathrm{R\dot{N}H}\ \ CO_2\ \ t\text{-BuO}\cdot]_{\text{cage}} \longrightarrow \mathrm{RNHO}\text{-}t\text{-Bu} \qquad (5)$$

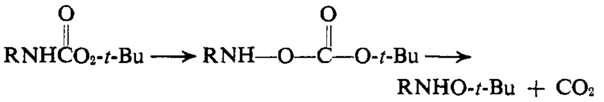
$$\mathrm{RNH}\overset{\overset{\displaystyle O}{\|}}{C}O_2\text{-}t\text{-Bu} \longrightarrow \mathrm{R\dot{N}H} + CO_2 + t\text{-BuO}\cdot \longrightarrow \mathrm{RNHO}\text{-}t\text{-Bu} \qquad (6)$$

radical combination



$$\mathrm{RNH}\overset{\overset{\displaystyle O}{\|}}{C}O_2\text{-}t\text{-Bu} + \mathrm{R\dot{N}H} \longrightarrow \mathrm{RNHO}\text{-}t\text{-Bu} + CO_2 + \mathrm{R\dot{N}H} \qquad (7)$$

radical-induced decomposition



$$\mathrm{RNH}\overset{\overset{\displaystyle O}{\|}}{C}O_2\text{-}t\text{-Bu} \longrightarrow \mathrm{RNH\text{—}O\text{—}}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O\text{-}t\text{-Bu} \longrightarrow \mathrm{RNHO}\text{-}t\text{-Bu} + CO_2 \qquad (8)$$

carboxy inversion

Geminate return in a cage process (eq 5) increases with solvent viscosity,[20] and it was found that as the solvent viscosity was increased the esr signal intensity increased in the photolytic decomposition of alkyl peroxycarbamates, implicating at least partial cage combination in the N–O bond forming process. In further support of this pathway, Pedersen[21] found that thermal decomposition of *tert*-butyl *N*-(*p*-nitrophenyl)peroxycarbamate formed *N*-(*p*-nitrophenyl)-*O-tert*-butylhydroxylamine as a major product. Although complete cage combination is not likely, such a process could still give rise to alkoxyalkylamino radicals since, even in the absence of abstracting agents, *N,O*-dialkylhydroxylamines show esr signals of alkoxyamino radicals.

Diffusion from the cage could lead to radical combination to form *N,O*-disubstituted hydroxylamine (eq 6), disubstituted hydrazines, and di-*tert*-butyl peroxide. The free radicals from diffusion could also undergo other reactions including induced decomposition with unreacted peroxycarbamate (eq 7) since radical-induced decompositions of peroxides are quite common.[22] Although a variety of peroxycarbamates exhibited first-order decomposition kinetics,[12,23] such studies were normally performed at more dilute concentrations (*ca.*

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[16] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

[17] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **90**, 4201 (1968).

[18] K. F. Purcell and W. C. Danen, *ibid.*, **94**, 7613 (1972).

[19] It must be borne in mind, however, that the esr spectrometer detects only paramagnetic species in adequate concentration under the experimental conditions and that these species may or may not be produced in a major reaction pathway.

[20] (a) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970); (b) T. Koenig, M. Deinger, and J. A. Hoobler, *ibid.*, **93**, 938 (1971).

[21] (a) C. J. Pedersen, *J. Org. Chem.*, **23**, 252 (1958); (b) *ibid.*, **23**, 255 (1958).

[22] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y. 1966, pp 82, 93.

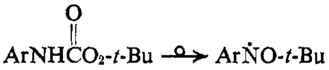
[23] E. L. O'Brien, F. M. Beringer, and R. B. Mesrobian, *J. Amer. Chem. Soc.*, **81**, 1506 (1959).

10^{-3} *M*) than the present esr investigation (*ca.* 10^{-1} *M*). Indeed, *tert*-butyl *N*-(α-naphthyl)peroxycarbamate has been shown to undergo a rather rapid induced decomposition.[13] In analogy to these results, the initially formed amino radical conceivably could cause induced decomposition of peroxycarbamate to produce the hydroxylamine (eq 7). Decomposition induced by the *tert*-butoxyl radical to produce the substituted hydroxylamine directly appears less feasible. Alternatively, reaction of the peroxycarbamate with the product aryl- or alkylamine formed by hydrogen abstraction (or disproportionation in the case of alkylamino radicals) is conceivable since amines are known to react with peroxides.[24]

The peroxycarbamate also could conceivably rearrange to an intermediate carbonic ester–anhydride which would lose CO_2 to form the hydroxylamine (eq 8).[25a] Finally, decomposition *via* a nitrene intermediate could occur in analogy to acyl carbamoyl peroxides.[25b] The actual mode of formation of the N–O bond was not investigated in detail since it was not considered pertinent to the objectives of this study.

***N*-Alkoxy-*N*-arylamino Radicals.** When *ca.* 10^{-1} *M* deoxygenated benzene solutions of *tert*-butyl *N*-arylperoxycarbamates were allowed to undergo thermal decomposition at room temperature, moderately intense esr spectra were observed which, upon analysis, indicated interaction of the unpaired electron with a nitrogen nucleus and the protons of the aromatic ring. As in the case of *tert*-butyl *N*-alkylperoxycarbamates, no N–H hfsc was observed, again consistent with a *tert*-butoxyl group attached to the nitrogen atom (eq 9a). Further, the ring hyperfine splittings of the radical produced from *tert*-butyl *N*-arylperoxycarbamates were smaller by about 25% than the anilino radical while the nitrogen hfsc's were larger than the anilino radical by about 14% which indicated the unpaired electron had become more localized on the nitrogen side chain than in the case of the anilino radical. The *g* values (2.0044 ± 0.0002) also suggested nitrogen radicals other than nitroxides ($g = 2.0059$[9]) or simple anilino radicals ($g = 2.0030$,[4] 2.0035[9]).

In addition, when aniline or *p*-chloroaniline was photolyzed in the presence of di-*tert*-butyl peroxide, esr spectra identical in hfsc and *g* value with those derived from *tert*-butyl *N*-phenyl- and *tert*-butyl *N*-(*p*-chlorophenyl)peroxycarbamates were observed (eq 9b).



$$\mathrm{ArNH\overset{\overset{O}{\|}}{C}O_2\text{-}\mathit{t}\text{-}Bu} \xrightarrow{\Delta} \mathrm{Ar\dot{N}O\text{-}\mathit{t}\text{-}Bu} \tag{9a}$$

$$\mathrm{ArNH_2} \xrightarrow[h\nu]{t\text{-BuOO-}t\text{-Bu}} \mathrm{Ar\dot{N}O\text{-}\mathit{t}\text{-}Bu} \tag{9b}$$

When approximately 1% *tert*-butyl hydroperoxide was included in the sample preparation of *tert*-butyl *N*-phenylperoxycarbamates, oxidation occurred to give esr spectra of *N*-*tert*-butoxy *N*-phenyl nitroxides. The hyperfine splitting constants for the nitroxide derived from *tert*-butyl *N*-phenylperoxycarbamate were identical within experimental error with the reported *N*-*tert*-butoxy *N*-phenyl nitroxide produced from the addition of *tert*-butoxyl radical to nitrosobenzene[26] and similar to the nitroxide produced upon photolysis of nitrobenzene in THF.[27,28] Table II gives the hyperfine splitting constants and *g* values of *N*-*tert*-butoxy-*N*-arylamino radicals.

Table II. Hyperfine Splitting Constants for *N*-*tert*-Butoxy-*N*-arylamino Radicals[a]

X	a^N	$a^{H}{}_{o}$	$a^{H}{}_{m}$	$a^{H}{}_{p}$	$a^{H}{}_{o}$	a^X	g^b
H	10.95	4.67	1.55	5.06			2.0044
p-Cl	10.62	4.54	1.43				2.0046
p-NO_2	9.95	4.38	1.41			1.51	2.0046
p-CH_3	10.74	4.34	1.42			6.20	2.0042
p-$OCH(CH_3)_2$	10.73	4.58	1.40				2.0042
p-OCH_3	10.75						2.0042
p-$C(O)CH_3$	10.10	4.37	1.60				2.0046
m-NO_2	10.78	4.80	1.50	4.90	4.15		2.0043
m-CH_3	11.00	4.55	1.58	5.03	4.35	1.58	2.0043
m-$C(O)CH_3$	10.87	4.80	1.55	5.00	4.20		2.0043
m-Cl	10.88	4.75	1.52	5.05	4.36		2.0042
m-$OCH(CH_3)_2$	11.00	4.58	1.58	5.15	4.35		2.0043

[a] For para substituents the ring couplings were arbitrarily assigned on the basis of ring couplings in nitrobenzene anion radicals. For meta substituents the ring couplings were arbitrarily assigned except for the meta proton. Satisfactory computer simulations were obtained for all radicals the assignment of which was not immediately obvious. Hfsc's are accurate to an estimated 0.05 G except in the case of the *m*-isopropoxy substituent, the lines of which were too broad for analysis to an accuracy greater than 0.1 G. [b] Accuracy of $g = \pm 0.0001$.

An esr spectrum purportedly due to the *N*-hydroxy-*N*-phenylamino radical has been observed[29,30] but the hyperfine splitting constants reported for this radical are more analogous to phenyl nitroxides[31,32] rather than the alkoxyanilino radicals reported here, suggesting a misassignment of radical structure by previous workers.

Interestingly, no spectra were observed when anilines with electron-withdrawing substituents ($-NO_2$ or $-CN$) in the para or meta position were photolyzed in the presence of di-*tert*-butyl peroxide in contrast to anilines with electron-donating substituents which gave strong esr signals. Since *tert*-butyl *N*-arylperoxycarbamates with electron donating substituents could not be prepared[29] there were available two routes to the *N*-*tert*-butoxy-*N*-arylamino radicals which included a full range of substituents.

The formation of the N–O bond in the reaction of anilines with di-*tert*-butyl peroxide could result from a simple radical combination but more probably occurs *via* either a homolytic (eq 10) or ionic (eq 11) pathway.

$$\mathrm{Ar\dot{N}H} + t\text{-}\mathrm{BuOO}\text{-}t\text{-}\mathrm{Bu} \longrightarrow \mathrm{ArNHO}\text{-}t\text{-}\mathrm{Bu} + t\text{-}\mathrm{BuO}\cdot \tag{10}$$

$$\mathrm{ArNH_2} + t\text{-}\mathrm{BuOO}\text{-}t\text{-}\mathrm{Bu} \longrightarrow \mathrm{ArNHO}\text{-}t\text{-}\mathrm{Bu} + t\text{-}\mathrm{BuOH} \tag{11}$$

The latter mechanism is reminiscent of the related reaction of substituted anilines with peracetic acid in which electron-withdrawing substituents on the aniline re-

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(24) Reference 22, p 98.

(25) (a) Reference 21b, footnote 8, and references cited therein; (b) R. Okazaki and O. Simamura, *Chem. Commun.*, 1308 (1969).

(26) A. Mackor, A. J. W. Wajer, and Th. J. deBoer, *Tetrahedron Lett.*, 385 (1967).

(27) R. L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963).

(28) E. G. Janzen and J. L. Gerlock, *J. Amer. Chem. Soc.*, **91**, 3108 (1969).

(29) K. Maruyama, T. Otsuki, and T. Iwao, *J. Org. Chem.*, **32**, 82 (1967).

(30) J. C. Baird and J. R. Thomas, *J. Chem. Phys.*, **35**, 1507 (1961).

(31) T. A. J. Wajer, A. Mackor, and T. J. DeBoer, *Tetrahedron Lett.*, 1941 (1967).

(32) G. A. Russell, E. J. Geels, F. J. Smentowski, K. Y. Chang, J. Reynolds, and G. Kaupp, *J. Amer. Chem. Soc.*, **89**, 3821 (1967).

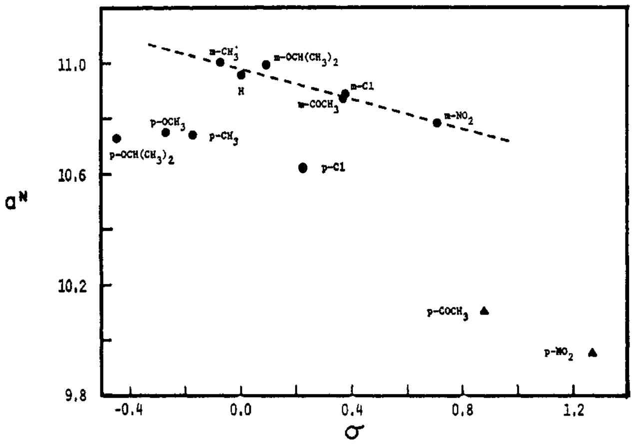
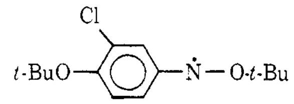


Figure 1. Attempted correlation of a^N of substituted *N-tert*-butoxy-*N*-arylamino radicals with σ constants (● = σ; ▲ = σ^-). The dashed line correlates the values for the meta substituents (see text for details).

tarded the rate as was qualitatively observed in the present work.[33]

The lifetimes of the alkoxyarylamino radicals were quite long in some cases. If the photolysis lamp was shut off during an experiment with a substituted aniline and di-*tert*-butyl peroxide the radical persisted for *ca.* 5–10 min and in the case of *p*-isopropoxyaniline the signal intensity remained nearly constant for at least 20 min. In contrast, spectra from *tert*-butyl *N*-(*m*-nitrophenyl)peroxycarbamate were less intense than spectra derived from peroxycarbamates with less powerful electron-withdrawing substituents. The latter case may be due to a difference in the rate of formation of the alkoxyarylamino radical but also may reflect the stability of the radicals produced since photolysis of anilines with electron-withdrawing substituents with di-*tert*-butyl peroxide produced no esr signals.

The *m*-chlorophenyl peroxycarbamate did not behave in the normal fashion. No radicals were detected by esr when 0.5–10% by weight solutions were warmed to room temperature or heated to 75°. When the solution was photolyzed with a 2000-W mercury lamp, a strong esr signal appeared which slowly changed with time to produce a mixture of at least two radicals with identical *g* values. After approximately 30 min of continuous photolysis, only one radical component was apparent which was different from the radical formed initially. The final radical was assumed to be *N-tert*-butoxy(*m*-chlorophenyl)anilino (Table II) since the hfsc's were quite similar to other meta-substituted *N-tert*-butoxyanilino radicals. The spectral parameters for the initially formed radical (a^N = 10.55, a^H = 1.62 (1 H), a^H = 4.57 (2 H), *g* = 2.0042) suggested that it was probably a substituted alkoxyarylamino radical but that one of the ring protons had been replaced with an esr-inactive group. The spectral parameters were consistent with the *N-tert*-butoxy-*N*-(*p-tert*-butoxy-*m*-chloro)anilino radical presumably formed by attack of a *tert*-butoxyl radical on the *m*-chlorophenyl peroxycarbamate initially present in relatively high concentration.



The ability to generate a wide variety of substituted *N-tert*-butoxy-*N*-arylamino radicals allowed an esr investigation of the effect of substituents on this class of radicals. Anilino radicals are unique in the sense that the nitrogen atom possesses both an unpaired electron and a nonbonding pair of electrons either of which is available for delocalization. Two limiting cases can be envisioned for the effect of substituents on such radicals. The first case would be described by both electron-donor and electron-acceptor substituents delocalizing the unpaired electron. In terms of Walter's criteria[14] for radical behavior, this case would exhibit class S behavior. That is, both donor and acceptor substituents have the "same" effect on the radical site, namely, to decrease the spin density at the nitrogen atom.

The second case would be described by unpaired electron delocalization to donor substituents and nonbonding electron pair delocalization to acceptor substituents. By Walter's criteria the second case would exhibit class O behavior where donor and acceptor substituents would have "opposite" effects on the radical site. The spin density at nitrogen is decreased by spin delocalization onto donor substituents and increased by spin localization at nitrogen due to delocalization of the nonbonding pair of electrons onto acceptor substituents. Paired electron delocalization from a p orbital would result only if the difference in delocalization energy of two electrons and one electron would be greater than the promotional energy of an electron in the hybrid nonbonding orbital to the spin bearing p orbital.

Although the substituted anilino radicals could conceivably belong to either class S or class O, Walter favored the latter classification ("possibly class O").[14] Walter listed $Ar_3\dot{N}^+$, $Ar_3C\cdot$, $Ar_3B\cdot^-$, and $Ar_2N\text{-}\dot{N}^+Ar_2$ as class S radicals although Janzen believed that there was not sufficient esr data to warrant creating a new classification of radicals.[34]

Numerous esr studies have been carried out on substituted aryl nitroxides and nitrobenzene anion radicals all of which have demonstrated Hammett behavior. The correlation of nitrogen hfsc with σ (or σ^-) has been interpreted as being due to an interaction of the substituent with a dipolar form of the radical;[34] these types of radicals all exhibited class O behavior.

The alkoxyarylamino radicals of the present study do not correlate with σ values and constitute a possible example of Walter's class S; electron-donating and electron-withdrawing substituents exhibit the "same" effect on nitrogen hfsc with the result that the unsubstituted radical exhibits the largest nitrogen splitting.[35] An attempt to correlate a^N with σ constants is shown in Figure 1.

It can be seen from Figure 1 that the effect of all para substituents is to decrease the nitrogen hyperfine splitting as required for a class S series of radicals. However, it is plausible that the effect of substituents in the *tert*-butoxy-*N*-arylamino radicals might be not only to delocalize the unpaired electron but also to exert a polar effect and influence the relative importance of the con-

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(33) K. M. Ibne-Rasa and J. O. Edwards, *J. Amer. Chem. Soc.*, **84**, 763 (1962).

(34) For a thorough review of substituent effects on esr spectra, see E. G. Janzen, *Accounts Chem. Res.*, **2**, 279 (1969).

(35) During the course of this investigation, S. F. Nelsen and coworkers observed that para-substituted *N-tert*-butylanilino radicals also belong to Walter's class S.[9]

tributing resonance form **2**. We believe, however, that

1 2

such polar contributions to a^N are, at most, of secondary importance and that the magnitude of a^N is determined predominately by the extent of direct unpaired electron delocalization onto the substituent. Three types of evidence support this conclusion. First, a^N is quite insensitive to the nature of the meta substituents. Direct delocalization of the unpaired electron onto such substituents is not possible but such substituents are fully capable of exerting an inductive stabilization of the resonance contributing structure **2**. Second, the a^N values are not very solvent dependent whereas the nitrogen coupling in a nitroxide radical is quite dependent upon the polarity of the solvent as a result of preferential solvation of the charge-separated polar resonance form.[36] Changing from benzene to 10% aqueous *tert*-butyl alcohol has no effect within experimental error (± 0.05 G) on the nitrogen coupling constant for *N*-*tert*-butoxyanilino radical, whereas a^N for the nitroxide derived from 2,2,6,6-tetramethyl-4-piperidone is increased by 1.5 G in changing from benzene to water. Finally, Walter suggested that the correlation of a^N with σ constants should break down completely for free radicals which belong to class S since, according to a molecular orbital treatment by Dewar, the effect of substitution should be approximately proportional to $\sigma/2$ for $\sigma < 0$, and proportional to $-\sigma$ for $\sigma > 0$. The $\sigma/2$ term utilized for electron-donating substituents indicates that the effectiveness of a given donor substituent should be about half as great in stabilizing a radical as in stabilizing a cation. Although a highly precise correspondence of the observed a^N values with "σ" ("σ" $= \sigma/2$ for $\sigma < 0$, $-\sigma$ for $\sigma > 0$) was not anticipated, it was demonstrated that a reasonable correlation existed lending further credence to the assignment of the *tert*-butoxyanilino radicals to class S.

It may be noted from the data in Table II that the strongly electron-withdrawing groups (p-NO_2 and p-CH_3CO) are more effective at removing unpaired electron density from the nitrogen atom than even the moderately electron-donating alkoxy substituents (CH_3O and i-PrO). This is in agreement with an LCAO–MO treatment of nitro and methoxy substituted aromatic radicals[37] but contrasts somewhat the effect of such substituents to delocalize spin density in simple substituted alkyl radicals.[38,39] These latter studies have employed the experimentally determined β-hydrogen hyperfine splitting constant of an attached methyl as a measure of spin density at a carbon center, and an apparently self-consistent set of substituent parameters relating the ability of a substituent group to delocalize unpaired electron density has been obtained. More recent work has shown, however, that there is a strong dependence of $Q^H_{CCH_3}$ on charge and that caution must be exercised when utilizing β-hydrogen hyperfine splitting constants as a measure of spin density.[40]

Further support for unpaired electron delocalization is evident when the ortho hydrogen hfsc's of para-substituted arylalkoxyamino radicals are compared to the unsubstituted case. It is found that the ortho hydrogen hfsc's are all smaller for the substituted radicals which indicates the spin density had decreased at the ortho position with all the para substituents. This behavior is expected from a resonance effect[41] and unlike the behavior expected for radicals exhibiting inductive effects on nitrogen hfsc.[34] It is concluded, then, that class S behavior of the arylalkoxyamino radicals is primarily a result of the spin delocalization onto the aromatic ring and substituents rather than a result of inductive effects.

A somewhat more quantitative delineation into resonance and polar effects of the change in a^N is also possible. From Figure 1 it is observed that the nitrogen hfsc *vs.* σ for the meta substituents describes a straight line with a slope of -0.28 G and a correlation coefficient of 0.956 while the nitrogen hfsc for para substituents showed no linear correlation with σ. Since σ is a constant which describes the effect of a substituent at a polar reaction site, the linear correlation of nitrogen hfsc of meta substituents *vs.* σ indicates the meta substituents exert a polar effect on the nitrogen hfsc. The observed nitrogen hfsc for a given para substituent can then be viewed as a composite of a polar and resonance effect as described by eq 12, were $a^N{}_{obsd}$ is the observed

$$a^N{}_{obsd} = a^N{}_{Ph} - \Delta_{sub} \pm \Delta_0 \qquad (12)$$

nitrogen hfsc, $a^N{}_{Ph}$ is the nitrogen hfsc of the *N*-*tert*-butoxy-*N*-phenylamino radical, Δ_{sub} is the amount the nitrogen hfsc decreased due to spin delocalization onto the para substituents, and Δ_0 is the amount the nitrogen hfsc changed due to the inductive effects of the substituents which tend to stabilize or destabilize structures such as **2**.

The decrease (or increase) of the nitrogen hfsc due to the inductive effects of the substituents was obtained by using the plot of nitrogen hfsc of meta substituents *vs.* σ. It was assumed that the inductive effect on the nitrogen hfsc of the para substituents would be described by the same line as for the meta substituents so that the position of the para substituents on the line was defined by σ constants. For the p-acetyl and the p-nitro substituents, σ^- constants were used since the negative charge on nitrogen introduced as a result of spin delocalization onto oxygen could be delocalized directly onto the acetyl or nitro substituent. The magnitude of Δ_0 for the para substituents was assumed to be the difference of $a^N{}_{Ph}$ and the nitrogen hfsc derived from the linear correlation line in Figure 1. The Δ_{sub} values were obtained using eq 12 and the Δ_0 values. The values of Δ_{sub} and Δ_0 are given in Table III.

The percent spin delocalization onto oxygen is given by $\Delta_0/(\Delta_{sub} + \Delta_0) \times 100$ and has a mean of 23.1 and a mean deviation of 5.3. It can be concluded that even though both spin delocalization onto oxygen and para substituents is in operation, spin delocalization onto para substituents is predominant.

***N*-*tert*-Butoxy *N*-Aryl Nitroxides.** The presence of

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(36) R. Briene, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3273 (1965).

(37) R. I. Walter, *J. Amer. Chem. Soc.*, **88**, 1930 (1966).

(38) H. Fischer, *Z. Naturforsch. A*, **20**, 428 (1965).

(39) G. A. Russell and J. Lokensgard, *J. Amer. Chem. Soc.*, **89**, 5059 (1967).

(40) G. R. Underwood and V. L. Vogel, *J. Chem. Phys.*, **51**, 4323 (1969).

(41) B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, **89**, 5172 (1967).

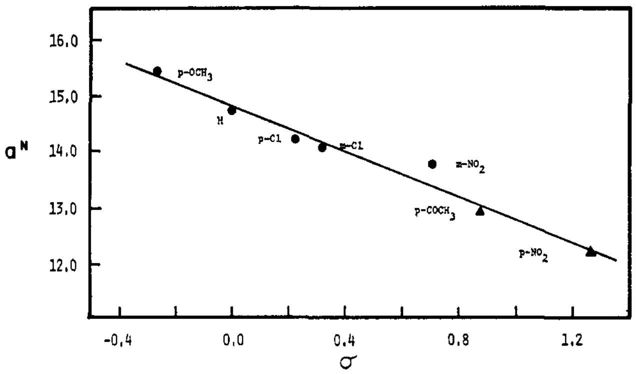


Figure 2. Correlation of a^N of substituted *N*-*tert*-butoxy *N*-aryl nitroxides with σ constants (● = σ; ▲ = σ⁻).

Table III. Spin Delocalization Parameters of Arylalkoxyamino Radicals

Substituent	Δ_{sub}	Δ_0	$\Delta_0/(\Delta_{sub} + \Delta_0) \times 100$
p-OCH(CH$_3$)$_2$	0.36	0.14	28.0
p-OCH$_3$	0.29	0.09	23.6
p-CH$_3$	0.27	0.06	18.2
p-Cl	0.29	0.04	12.1
p-C(O)CH$_3$[a]	0.64	0.21	24.7
p-NO$_2$[a]	0.68	0.32	32.0
Mean			23.1 ± 5.3

[a] σ^- values used in analysis.

a small amount of *tert*-butyl hydroperoxide in solutions which normally afforded the *N*-*tert*-butoxyanilino radicals produced instead corresponding nitroxides; results are reported in Table IV. The nitroxides were evident from the reduced ring hfsc, increased nitrogen hfsc, and increased g value (2.0048 ± 0.0002). Although the g values were significantly lower than that normally observed for dialkyl or alkyl aryl nitroxides (typically *ca.* 2.006), they were close to that reported for alkyl alkoxy nitroxides (2.0052)[42] and nitrobenzene radical anions (2.0044,[43] 2.0047[44]). Our hyperfine couplings agree well with those reported for a similar series of aryl alkoxy nitroxides observed by ultraviolet photolysis of nitrobenzenes in tetrahydrofuram.[45] The lower g value observed for aryl alkoxy nitroxides as compared to aryl nitroxides must result primarily from a greater deviation from planarity about the nitrogen in the alkoxy nitroxides. If the geometries about the nitrogens were similar for the two types of radicals, it would be anticipated that the alkoxy nitroxides would exhibit a larger g value because a greater portion of spin density must reside on oxygen and nitrogen atoms.

Table IV. Hyperfine Splitting Constants and g Values for *N*-*tert*-Butoxy *N*-Aryl Nitroxides[a]

XArN($\dot{O}$)-OC(CH$_3$)$_3$	a^N	$a^H{}_o$	$a^H{}_m$	$a^H{}_p$	$a^N{}_{NO_2}$	g^b
H	14.70	3.03	0.94	3.03		2.0047
p-Cl	14.20	2.98	1.33			2.0050
p-NO$_2$	12.20	2.97	0.90		0.90	2.0050
p-OCH$_3$[c]	15.42	3.04				2.0047
p-C(O)CH$_3$	12.90	2.90	1.07			2.0051
m-Cl	14.10	2.96	1.14	2.96		2.0046
m-NO$_2$	13.81	2.96	1.00	2.96		2.0048

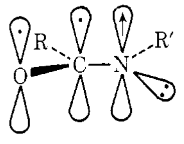
[a] Hfsc's are reported in gauss and have estimated accuracies of ±0.5%, except where noted. [b] Estimated accuracy ±0.0001. [c] Estimated accuracy ±1%.

It was anticipated that the aryl alkoxy nitroxides would exhibit class O behavior, and the least-squares plot of nitrogen hfsc *vs.* σ (σ⁻ for *p*-nitro and *p*-acetyl groups) gave a linear correlation with a slope of −2.01 G and a correlation coefficient of 0.984. Using the reported data of Sleight and Sutcliffe[44] for their related series of nitroxides, a least-squares plot of a^N *vs.* σ gave a slope of −2.15 G with correlation coefficient of 0.951, results nearly identical with those reported here.

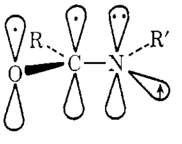
The nitroxides are structurally and electronically similar to the nitrobenzene anion radicals. The slopes of a^N *vs.* σ of the similar nitrobenzene anion radicals in DMSO[44] and acetonitrile[34] were −2.9 and −3.2 G, respectively, in agreement with the assertion that charged radicals are more sensitive than uncharged radicals to substituent effects.[46]

Another point of interest is that, even though the ring hfsc's were nearly the same for the nitrobenzene anion radicals and the aryl alkoxy nitroxides, the nitrogen hfsc's were larger by *ca.* 6 G in the aryl alkoxy nitroxides. This, presumably, results from the alkoxy oxygen being less effective in removing spin density from the nitrogen than the oxygen in nitrobenzene anion radicals since an additional charge-separated resonance structure must be invoked. Furthermore, any deviation from planarity about nitrogen in the aryl alkoxy nitroxides would place the unpaired electron directly in an orbital on nitrogen with a finite amount of s character.

***N*-Alkoxy-*N*-carboethoxyamino Radicals.** There has been considerable interest in determining whether amido radicals, RCO$\dot{N}$R′, are best classified as Π or Σ radicals (*cf.* **3** and **4**). Recent results from this laboratory suggest that simple *N*-alkylamido radicals possess a Π-electronic ground state.[1a,47] Prior to our work, the experimental evidence relating to the electronic structure of amido radicals had been confusing with reports of both Π and Σ structures. The basic question, of course, is whether the difference in energy resulting from resonance delocalization of a pair of electrons (*cf.* **4**) over a single electron (*cf.* **3**) in a p orbital would be sufficiently great to overcome the promotional energy of an electron in a hybrid orbital to a p orbital.



3 (Π)



4 (Σ)

Spectral parameters for two *N*-alkoxy-*N*-carboethoxy-

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[42] M. McMillan and R. O. C. Norman, *J. Chem. Soc. B*, 590 (1968).

[43] A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, **83**, 1852 (1961).

[44] W. C. Danen and C. T. West, *Tetrahedron Lett.*, 219 (1970).

[45] R. B. Sleight and L. H. Sutcliffe, *Trans. Faraday Soc.*, **67**, 2195 (1971).

[46] E. T. Strom, A. L. Bluhm, and J. Weinstein, *J. Org. Chem.*, **32**, 3853 (1967).

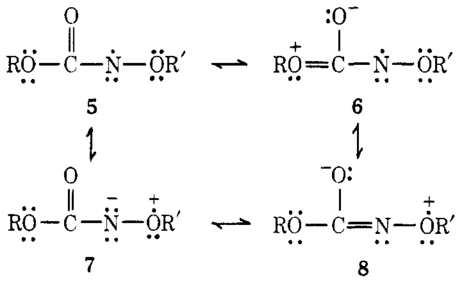
[47] INDO calculations by T. Koenig and coworkers predict three possible electronic configurations for the formamido radical, Π, Σ_N, and Σ_O. The Π configuration is most likely but it is not possible at the present time to unequivocally rule out a Σ_N configuration for substituted amido radicals. The authors wish to thank Professor Koenig for communicating his results to us prior to publication.

amino radicals, $C_2H_5OCO\dot{N}OR$, are reported in Table V. The radicals were generated by photolysis of benzene or toluene solutions of the ethyl *N*-ethoxy- or *N*-*tert*-butoxycarbamate in the presence of di-*tert*-butyl peroxide to effect N–H abstraction. The parameters are quite similar to those observed by Koenig, *et al.*, for a series of *N*-alkoxyamido radicals.[10,48] The nitrogen hyperfine coupling constants are significantly smaller than those observed for alkylamido radicals (*ca.* 15 G)[1a] consistent with considerable delocalization of the unpaired electron in the *N*-alkoxy-*N*-carboethoxyamino radicals. We conclude that these radicals probably possess a Π-electronic ground state similar to the simple amido radicals. However, the added oxygen-containing substituents of the *N*-alkoxy-*N*-carboethoxyamino radicals are anticipated to favor the Π ground state by reason of the following contributing resonance structures. Structure **5** undoubtedly is the best single representation but contribution of form **6** effectively reduces the electron-withdrawing capability of the carbonyl group. Moreover, the unpaired electron should occupy a 2p orbital on nitrogen to effectively overlap and interact with the 2p lone pair electrons on the noncarbonyl oxygen as represented by **7**. This latter interaction is reinforced by delocalization of the lone pair onto the carbonyl group as depicted in **8**. Thus, although the substituted amido radicals examined in this study indeed appear to possess a Π ground state, it cannot be claimed that these species are truly representative of simple amido radicals.

Table V. Spectral Parameters of *N*-Alkoxy-*N*-carboethoxyamino radicals

Radical	a^N	$a^H{}_{OR}$	$a^H{}_{C(O)OR}$	g^a
$CH_3CH_2OCO\dot{N}OCH_2CH_3$	10.80	4.23	1.33	2.0056
$CH_3CH_2OCO\dot{N}OC(CH_3)_3$	10.80		1.4^b	2.0057

[a] Estimated accuracy ±0.0001. [b] Estimated accuracy ±10% due to poor resolution of this line.


5 6 7 8

Experimental Section

Sample Preparation. All esr spectra were obtained on a Varian Model 4502 X-band spectrometer equipped with a dual cavity and standard variable-temperature apparatus. Hyperfine splitting constants (hfsc) and *g* values of the radicals were obtained by comparing with the hfsc and *g* value of Fremy's salt taken to be 13.09 ± 0.04 G and 2.00550 ± 0.00005, respectively.[49,50] Samples were prepared in Suprasil quartz sample tubes (3.5 mm i.d.). All samples were deoxygenated in the sample tubes by at least three freeze–pump–thaw cycles utilizing standard vacuum line techniques.

All photolyses were carried out using a 2000-W high-pressure mercury capillary lamp (PEK A-1-B or AH6-2B) located outside the magnet and focused on the sample by means of a series of suprasil lenses.

The esr spectra were obtained with experimental samples in the front cavity modulated at 100 kHz and an aqueous Fremy's salt solution in the rear cavity modulated at 200 or 400 Hz. Spectra of experimental samples and Fremy's salt were recorded simultaneously on a Varian G-22 dual channel recorder. Hyperfine splitting assignments in spectra with overlapping lines and broad line widths were verified by computer simulation.

Aryl Peroxycarbamates. Aryl peroxycarbamates were dissolved in dry benzene (*ca.* 10% by weight solution), then transferred to the sample tubes by a long pipet. The samples were deoxygenated, sealed, and then stored at −196° until used.

Alkyl Peroxycarbamates. Alkyl peroxycarbamates were dissolved in dry benzene (*ca.* 10% by weight solution), then transferred to the sample tubes by a long pipet and deoxygenated. For experiments run at temperatures below 0° an equivalent amount of cyclopropane or benzene was deoxygenated and transferred to the sample by trap-to-trap distillation. The sample tubes were sealed and stored at −196° until used.

***N*,*O*-Dialkylhydroxylamines.** For abstractions using di-*tert*-butyl peroxide, an approximately 3:1 (volume) solution of di-*tert*-butyl peroxide to *N*,*O*-dialkylhydroxylamine was prepared and transferred by a long pipet to the sample tubes. These solutions were deoxygenated and diluted with an equivalent volume of deoxygenated cyclopropane. The sample tubes were sealed and stored at −196° until used. Abstractions using azomethane in place of di-*tert*-butyl peroxide were prepared in the same manner with the exception that azomethane was trap-to-trap distilled into the sample tube. For direct photolysis of the *N*,*O*-dialkylhydroxylamines, approximately 10% (volume) solution of *N*,*O*-dialkylhydroxylamine in cyclopropane was prepared and deoxygenated. The sample tubes were sealed and stored at −196° until used.

Anilines. Samples were prepared by making 20% (volume) solutions of the substituted aniline in di-*tert*-butyl peroxide and sufficient benzene to afford dissolution if required and transferring the solution to the sample tube by a long pipet. The samples were deoxygenated, sealed, and stored at −196° until used.

***N*-Aryl *N*-Alkoxy Nitroxides.** The *N*-aryl *N*-alkoxy nitroxides were generated by the *tert*-butyl hydroperoxide oxidation of thermally decomposed aryl peroxycarbamates. Samples were prepared by adding about 1% (volume) of *tert*-butyl hydroperoxide to a 10% benzene solution of aryl peroxycarbamate. The solutions were transferred to esr tubes by a long pipet, deoxygenated, sealed, and stored at −196° until used.

The alkoxy nitroxide of *p*-isopropoxyaniline was generated by first photolyzing a 20% (volume) deoxygenated solution of *p*-isopropoxyaniline in *tert*-butyl peroxide–benzene (radical lifetime is greater than 20 min), then syringing 5 μl of *tert*-butyl hydroperoxide through a side arm fitted with a serum stopper.

Generation of Radicals. Aryl peroxycarbamates were usually decomposed in the esr cavity at room temperature. Radical concentrations could be increased for a short period of time by raising the sample temperature or by photolysis.

Alkyl peroxycarbamates were decomposed photolytically at −30 to +20° directly in the esr cavity.

Hydrogen abstractions from *N*,*O*-dialkylhydroxylamines were carried out directly in the esr cavity at −120 to +20° by photolytically produced *tert*-butoxyl radicals or methyl radicals.

N,*O*-Dialkylhydroxylamines were decomposed photolytically at −90° directly in the esr cavity.

Chemicals. Methyl isocyanate, ethyl isocyanate, *p*-nitrophenyl isocyanate, *m*-nitrophenyl isocyanate, aniline, *p*-chloroaniline, *p*-anisidine, *m*-anisidine, *p*-toluidine, *m*-toluidine, and *tert*-butyl hydroperoxide were commercially available and purified by either distillation or recrystallization before use. Commercially available ethyl chloroformate, ethyl iodide, methyl iodide, dimethylcarbamoyl chloride, phenyl isocyanate, and *p*-chlorophenyl isocyanate were used as received.

Syntheses. ***tert*-Butyl *N*-methylperoxycarbamate** was prepared by a method similar to that of *tert*-butyl *N*-ethylperoxycarbamate as described by Pedersen.[21a] A 3.0-g portion of freshly distilled methyl isocyanate was dissolved in 30 ml of benzene and 4.9 g of *tert*-butyl hydroperoxide and 6 drops of triethylamine were added. The stirred reaction mixture was cooled with an ice bath. The ice was

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(48) These workers report a^N = 11.95 G for $C_2H_5OCO\dot{N}OC(CH_3)_3$ in *tert*-butyl alcohol. We generated this radical by our technique in *tert*-butyl alcohol and observed a^N = 10.98 which is very similar to a^N in benzene (Table V). The reasons for the discrepancy in a^N between their laboratories and ours are not apparent at the present time. (Footnote 8 of ref 10 incorrectly refers to the *N*-*tert*-butoxypropionamido radical instead of the *N*-*tert*-butoxy-*N*-carboethoxyamino radical.)

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(50) J. Q. Adams and J. R. Thomas, *ibid.*, **39**, 1904 (1964).

allowed to melt and the reaction mixture slowly came to room temperature. Stirring was continued for 24 hr at room temperature after which time the benzene was removed *in vacuo* leaving mushy amber crystals which were crystallized from petroleum ether giving 1.12 g of pure material: mp 33.5–34.0°; ir (CCl_4) 3.05, 2.95, 3.42, 5.78, 6.62, 8.18, 8.40, 9.04 μ; nmr (CCl_4) 1.16 (9 H, s), 2.81 (3 H, d, $J = 5$ Hz), and 6.62 ppm (1 H, broadened singlet).

***tert*-Butyl *N*,*N*-dimethylperoxycarbamate** was prepared in 51% yield as described by Pedersen.[21a] Final purification was achieved by passing the peroxycarbamate through a Florisil column using pentane as the eluent since distillation at reduced pressure resulted in decomposition: ir (neat) 3.40, 5.75, 7.25, 8.70 μ; nmr (CCl_4) 1.24 (9 H, s) and 2.86 ppm (6 H, s).

***tert*-Butyl *N*-Ethylperoxycarbamate.** The synthesis of *tert*-butyl *N*-ethylperoxycarbamate was achieved in 86% yield according to the procedure of Pedersen,[21a] mp 42.5–43.0° (lit.[21a] 39–40°).

***tert*-Butyl *N*-Phenylperoxycarbamate and Related Compounds.** In a modification of the method of O'Brien, Beringer, and Mesrobian,[23] several drops of triethylamine were added to a stirred solution containing 2.0 g (0.0155 mol) of phenyl isocyanate in 30 ml of petroleum ether held at 0° by an ice–water bath. A 1.5-g (0.0155 mol) portion of *tert*-butyl hydroperoxide was slowly added to the stirred solution. Precipitation of *tert*-butyl *N*-phenylperoxycarbamate occurred within several minutes and reaction was allowed to continue for 20 min. The precipitate was filtered, washed several times with ice-cold petroleum ether, and recrystallized from petroleum ether to give *tert*-butyl *N*-phenylperoxycarbamate in 72% yield, mp 90.0–90.5° dec (lit.[23] mp 83° dec).

The following aryl peroxycarbamates were prepared in a similar manner: *tert*-butyl *N*-(*p*-chlorophenyl)peroxycarbamate, 93% yield, mp 79.5–80.0° dec (lit.[23] 71–72°); *tert*-butyl *N*-(*p*-nitrophenyl)peroxycarbamate, 90% yield, mp 95.5–96.0° dec (lit.[23] 93-94°); *tert*-butyl *N*-(*m*-nitrophenyl)peroxycarbamate, 89% yield, mp 79.0–80.5° dec (lit.[23] 80°).

In obtaining melting points of the peroxycarbamates, the temperature of the block was brought to within 5° of the final melting point before crystals were placed on the block. When this method was employed melting points obtained were sharper and at higher temperatures than when crystals were heated slowly from room temperature to the melting point.

***N*-Methyl-*O*-methylhydroxylamine.** Hydroxyurethane was prepared in 83% yield by condensing ethyl chloroformate and hydroxylamine hydrochloride as described by Jones.[51] *N*,*O*-Dimethylhydroxyurethane was synthesized by dimethylating hydroxyurethane following this same author, bp 153–155° (lit.,[51] bp 150–155°).

N-Methyl-*O*-methylhydroxylamine was prepared in 88% yield by KOH hydrolysis of *N*,*O*-dimethylhydroxyurethane as described by Major and Fleck.[52] The clear liquid obtained had a boiling point of 44–45° (lit.[52] 42–43°).

***N*-Ethyl-*O*-methylhydroxylamine.** Hydroxyurethane (see above) was methylated with methyl iodide as described by Jones[51] to give *O*-methylhydroxyurethane in 25% yield, bp 186–188° (lit.[51] bp 186–188°).

N-Ethyl-*O*-methylhydroxyurethane was prepared by the method of Jones and Major[53] in which *O*-methylhydroxyurethane was ethylated with ethyl iodide in ethanol. *N*-Ethyl-*O*-methylhydroxyurethane was obtained in 46% yield: bp 164°; ir (neat) 3.41, 5.85, 7.91, 8.68, 9.43 μ; nmr ($CDCl_3$) 1.17 (3 H, t, $J = 3.3$ Hz), 1.30 (3 H, t, $J = 3.8$ Hz), 3.55 (2 H, q, $J = 3.3$ Hz), 3.70 (3 H, s), 4.22 ppm (2 H, q, $J = 3.8$ Hz).

A 1.93-g sample of *N*-ethyl-*O*-methylhydroxyurethane was added to a solution of 3.5 g of 85% KOH in 20 ml of 50:50 ethanol–water. This solution was refluxed for 4 hr, then distilled into an HCl solution. Volatile materials in the HCl solution were removed under reduced pressure to give an oil, presumably the hydrochloride salt of *N*-ethyl-*O*-methylhydroxylamine. The oil was added to 2–3 ml of a frozen saturated KOH solution. Slow warming resulted in neutralization and the pure product was distilled from the saturated KOH to give *N*-ethyl-*O*-methylhydroxylamine in 63% yield: bp 59.5–60.0°; ir (neat) 3.13, 3.45, 6.85. 9.58, 10.35 μ; nmr ($CDCl_3$) 1.10 (3 H, t, $J = 3.8$ Hz), 2.98 (2 H, q, $J = 3.8$ Hz), 3.57 (3 H, s), 5.57 ppm (1 H, bs).

***N*,*O*-Diethylhydroxylamine.** *N*,*O*-Diethylhydroxyurethane was prepared by a modification of the method described by Major and Fleck.[52] A 17.8-g portion of ethyl iodide was added to a stirred solution consisting of 6 g of hydroxyurethane, 7.5 g of 85% KOH, and 40 ml of ethanol. The solution was stirred for 24 hr, then filtered to remove precipitated KI. Ethanol was removed by distilling under reduced pressure. The residue was taken up in ether, filtered, extracted three times with 25-ml portions of 10% NaOH, and dried over anhydrous Na_2SO_4. Ether was removed by distilling under reduced pressure. Vacuum distillation of the residue gave 26% yield of *N*,*O*-diethylhydroxyurethane, bp 88.5° (32 mm) (lit.[52] 107–112° (70 mm)).

N,*O*-Diethylhydroxylamine was obtained from *N*,*O*-diethylhydroxyurethane in 60% yield as described by Major and Fleck,[52] bp 78–79° (lit.[52] bp 83°).

***N*-Methyl-*O*-*tert*-butylhydroxylamine.** Ethyl azidoformate was prepared in 66% yield by the method of Lwowski and Mattingly,[54] bp 43.5° (37 mm) (lit.[54] bp 39–41° (~30 mm)).

O-*tert*-Butylhydroxyurethane was obtained in 25% yield by refluxing a solution of ethyl azidoformate in *tert*-butyl alcohol (20:1 *M*) for 2 days under a stream of deoxygenated nitrogen. The *tert*-butyl alcohol was distilled at atmospheric pressure and the residue vacuum distilled to give *O*-*tert*-butylhydroxyurethane: bp 113° (22 mm); ir (neat) 3.1, 3.4, 5.75, 6.78, 8.05, 8.95 μ; nmr ($CDCl_3$) 1.23 (12 H, m, overlapping *tert*-butyl and methyl), 4.23 (2 H, q, $J = 3.2$ Hz), 7.45 (1 H, s).

N-Methyl-*O*-*tert*-butylhydroxyurethane was prepared by adding 4.5 g of *O*-*tert*-butylhydroxyurethane to a stirred solution of sodium ethoxide (0.68 g of sodium reacted with ethanol) in 25 ml of ethanol. A 4.2-g portion of methyl iodide was slowly added. Stirring at room temperature was continued for 30 hr, then solvent was removed under vacuum. The residue was taken up in water and extracted three times with 20-ml portions of ether. The combined ether fractions were extracted with 20 ml of 20% NaOH, then dried over anhydrous Na_2SO_4. The ether was removed under vacuum to give 5.4 g of *N*-methyl-*O*-*tert*-butylhydroxyurethane which was used without further purification.

N-Methyl-*O*-*tert*-butylhydroxylamine was obtained pure in 42% yield from crude *N*-methyl-*O*-*tert*-butylhydroxyurethane by the same method used in obtaining *N*-ethyl-*O*-methylhydroxylamine from *N*-ethyl-*O*-methylhydroxyurethane: bp 87°; ir (neat) 3.10, 3.42, 6.60, 7.48, 8.43, 11.40 μ; nmr (CCl_4) 1.16 (9 H, s), 2.60 (3 H, broadened doublet), 4.75 ppm (1 H, bs).

***N*-Ethyl-*O*-*tert*-butylhydroxylamine.** *N*-Ethyl-*O*-*tert*-butylhydroxyurethane was prepared in 86% yield (crude) by ethylating *O*-*tert*-butylhydroxyurethane with ethyl iodide as described in the preparation of *N*-methyl-*O*-*tert*-butylhydroxyurethane. The material was used without purification.

N-Ethyl-*O*-*tert*-butylhydroxylamine was prepared in 59% yield from KOH hydrolysis of *N*-ethyl-*O*-*tert*-butylhydroxyurethane as described in the preparation of *N*-methyl-*O*-*tert*-butylhydroxylamine. A small amount of unknown impurity could not be removed by simple distillation; however, enough was purified and collected by glpc for spectral analysis and esr samples. Physical and spectral properties are: bp 97°; ir (neat) 3.13, 3.42, 6.93, 7.38, 8.33, 11.50 μ; nmr (CCl_4) 1.04 (3 H, t, $J = 3.8$ Hz), 1.18 (9 H, s), 2.93 (2 H, q, $J = 3.8$ Hz), 4.55 ppm (1 H, bs).

***p*-Isopropoxylaniline** was prepared in 24% overall yield from *p*-nitrophenol by the method of Tsatsas, *et al.*,[55] bp 141–142° (15 mm) (lit.[55] bp 128° (11 mm)).

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