

OXIDATION OF CYCLIC N-(ARYLAMINO)IMIDES. AN EPR STUDY OF HYDRAZOXYL RADICALS*

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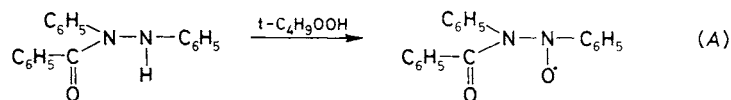
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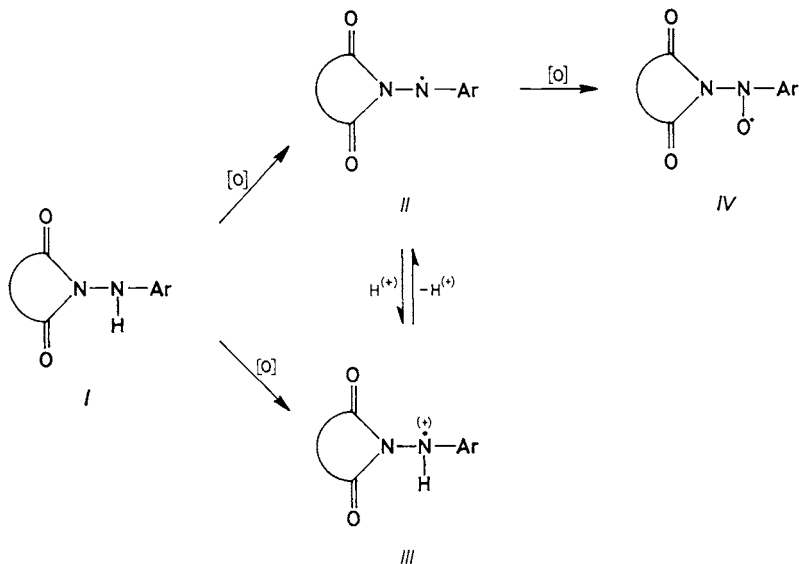
New types of hydrazoxyl radicals were identified by ESR spectroscopic method during oxidation of N-(arylamino)imides. The ESR parameters of radicals generated were obtained by a spectral simulation. The effect of substituents on the values of splitting constants of nitrogen atoms N¹ and N² is discussed. The splitting constants $a(N^1)$ well correlate with the σ -Hammett constants of substituents of the 1-phenyl group.

Oxidation of N-aryl substituted cyclic imides *I* with some oxidation reagents (MnO₂, PbO₂, diphenylpicrylhydrazyl, dibenzoyl peroxide, ditert. butyl peroxalate) afforded products the structure of which indicate the intermediates formation of a 1-aryl-2,2-diacylhydrazyl radical *II*, or a 1-aryl-2,2-diacylhydrazinium cation-radical *III* (ref.¹). If oxidation of type *I* compound is initiated with peroxy radicals a subsequent transformation of the hydrazyl radical *II* to a hydrazoxyl radical *IV* could be expected (Scheme 1). The hydrazyl radical *II* and the hydrazinium cation-radical *III* have hitherto not been reported. Although Forrester² succeeded to oxidize 1,2-diphenyl-1-benzoylhydrazine to the corresponding hydrazoxyl radical (Eq. (A)),



the analogous oxidation of N-anilinosuccinimide failed. 2,2-Diacylhydrazoxyl radicals were obtained by addition of diacylaminy radicals to 2-methyl-2-nitrosopropane³⁻⁷. Nevertheless, an attempt to prepare spin adducts with nitrosobenzene was unsuccessful. This paper is aimed to elucidate the structure of radicals formed by oxidation of imides *I* and to estimate the influence of substitution effect on the distribution of spin density.

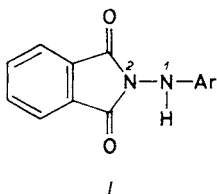
* Part VII in the series Radical Reactions of N-Heterocyclic Compounds; Part VI: see ref.¹.

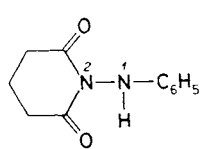


SCHEME 1

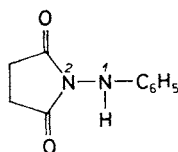
EXPERIMENTAL

The ESR spectra of hydrazoxyl radicals were taken with a Varian E-3 spectrometer at a 100 kHz modulation in the X-band at room temperature and their simulations were carried out by a Varian SS-100 computer. The reaction mixtures after oxidation were either nitrogen or argon saturated in order to obtain well resolved ESR spectra. The inert gases were deoxygenated in a column packed with copper splinters at 600°C prior to their use. Compounds Ia–Ik and V–VII were synthesized according to the method being published.

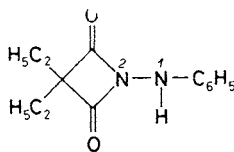
Ia, Ar = C₆H₅Ib, Ar = 4-CH₃-C₆H₄Ic, Ar = 3-CH₃-C₆H₄Id, Ar = 4-CH₃O-C₆H₄Ie, Ar = 2-CH₃O-C₆H₄If, Ar = 4-Cl-C₆H₄Ig, Ar = 4-NO₂-C₆H₄Ih, Ar = 2,4,6-NO₂-C₆H₂



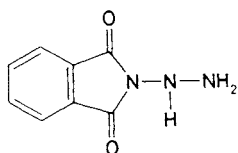
Ia



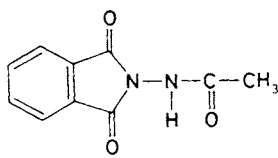
Ib



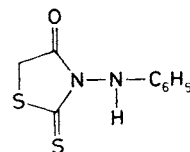
Ic



V



VI



VII

Oxidation of Compounds Ia–Ic, V–VII

A) To the respective compound dissolved in a $5 \cdot 10^{-2} \text{ mol l}^{-1}$ benzene solution of cobalt acetylacetonate ($\text{Co}(\text{acac})_2$, 2 ml) in a molar ratio substance: $\text{Co}(\text{acac})_2 = 5 : 1$, tert. butyl hydroperoxide (TBHP) was added with stirring in a molar ratio $\text{TBHP} : \text{Co}(\text{acac})_2 = 10 : 1$. Under these conditions a catalytic decomposition of TBHP in solution took place under formation of RO_2^{\cdot} and RO^{\cdot} radicals⁸; a sample of this mixture (0.3 ml) was withdrawn for ESR measurement.

B) Lead dioxide (10 mg) and TBHP (1 drop) were added to $10^{-2} \text{ mol l}^{-1}$ benzene solution of the respective compound (0.3 ml) in an ESR cell. During catalytical decomposition of TBHP with PbO_2 (ref.⁹) RO_2^{\cdot} radicals originated.

C) Lead tetraacetate (10 mg) was added to the $10^{-2} \text{ mol l}^{-1}$ benzene solution of the respective substance (0.3 ml) in an ESR cell.

RESULTS AND DISCUSSION

The oxidation systems A–C containing substances Ia–Ic generate radicals characterized by a high resolution ESR spectra of a great 1 : 1 : 1 splitting constant from the ^{14}N nucleus (Fig. 1). These radicals were found to be stable at room temperature for at least 1 h and represent the only type of radicals observed for this time period. Oxidation of compounds V–VII did not lead to any detectable radical forms under the same experimental conditions.

The ESR parameters following from simulation of experimental ESR spectra are listed in Table I; the spectra were ascribed to hydraoxyl radicals IVa–IVc. Comparison of the measured g -values ($g 2.0055$ – 2.0059), and the ratio $a(\text{N}^1) : a(\text{N}^2) > 5$ with the data reported for similar types of radicals of general formula VIII are in favour of this statement (Table II). Hydrazyl radicals and

TABLE I
ESR parameters of hydrazoxyl radicals *IV* generated by oxidation of N-(arylamino)imides *I*

Compound	Method	<i>g</i>	Splitting constant, mT					
			<i>a</i> (N ¹)	<i>a</i> (N ²)	<i>a</i> (H _o)	<i>a</i> (H _p)	<i>a</i> (H _m)	<i>a</i> (X)
<i>Ia</i>	<i>A, B</i>	2.0055	1.114	0.188	0.257	0.260	0.087	—
<i>Ib</i>	<i>A, B</i>	2.0055	1.125	0.190	0.259	0.275 ^a	0.085	—
<i>Ic</i>	<i>A, B</i>	2.0056	1.117	0.193	0.264	0.264	0.083 ^b	—
							0.087 ^a	
<i>Id</i>	<i>A, B</i>	2.0055	1.164	0.192	0.260	0.034 ^a	0.076	—
<i>Ie</i>	<i>A, B</i>	2.0056	1.225	0.185	0.234 ^b	0.252	0.071 ^b	—
							0.095 ^b	
<i>If</i>	<i>A, B</i>	2.0058	1.110	0.190	0.264	—	0.093	0.030 ^c
								0.025 ^d
<i>Ig</i>	<i>A, B</i>	2.0059	1.000	0.187	0.255	—	0.091	0.065 ^e
<i>Ih</i>	<i>C</i>	—	0.975	0.145	—	—	0.091 ^b	0.038 ^f
							0.100 ^b	0.044 ^e
<i>Ii</i>	<i>A, B</i>	—	1.162	0.181	0.261	0.261	0.086	—
<i>Ij</i>	<i>A, B</i>	2.0056	1.130	0.190	0.262	0.259	0.092	0.020 ^g
<i>Ik</i>	<i>A, B</i>	—	1.125	0.180	0.266	0.260	0.086	0.025 ^h

Splitting due to: ^a three hydrogen atoms; ^b one hydrogen atom; ^c ³⁵Cl atom; ^d ³⁷Cl atom; ^e nitrogen atom; ^f two nitrogen atoms; ^g (δ-H) of 4 hydrogen atoms of imide ring; ^h (ε-H) of 4 hydrogen atoms of ethyl groups.

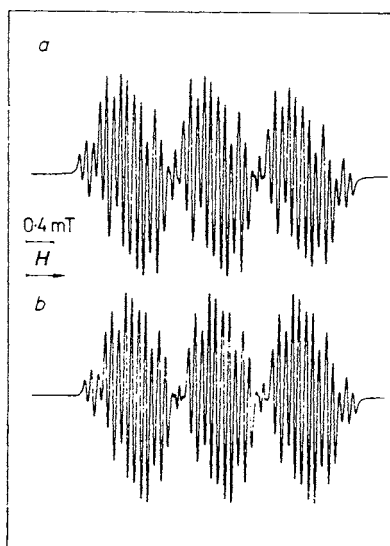
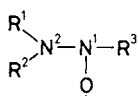


FIG. 1

Experimental (a) and simulated (b) ESR spectra of hydrazoxyl radical *IVa* prepared by oxidation of N-(arylamino)imide *Ia* by methods *A* and *B*



- VIII a*, $\text{R}^1 = \text{R}^3 = \text{C}_6\text{H}_5$; $\text{R}^2 = \text{CH}_3$
VIII b, $\text{R}^1 = \text{R}^3 = \text{C}_6\text{H}_5$; $\text{R}^2 = \text{COCH}_3$
VIII c, $\text{R}^1 = \text{R}^3 = \text{C}_6\text{H}_5$; $\text{R}^2 = \text{CHO}$
VIII d, $\text{R}^1 = \text{R}^2 = \text{CH}_3$; $\text{R}^3 = t\text{-C}_4\text{H}_9$
VIII e, $\text{R}^1 = \text{C}_6\text{H}_5$; $\text{R}^2 = \text{COCH}_3$; $\text{R}^3 = t\text{-C}_4\text{H}_9$
VIII f, $\text{R}^1 = \text{R}^2 = \text{COCH}_3$; $\text{R}^3 = t\text{-C}_4\text{H}_9$
VIII g, $\text{R}^1 = \text{C}_6\text{H}_{11}$; $\text{R}^2 = \text{H}$; $\text{R}^3 = t\text{-C}_4\text{H}_9$

hydrazinium cation-radicals show lower values of the g value ($g\ 2.0035\text{--}2.0050$) and the proportion $a(\text{N}^1) : a(\text{N}^2)$ varies within 1–2 (refs^{18,19}). Substituents at atoms N^1 and N^2 influence in a distinguishable manner the splitting constants of all interacting nuclei (cf. Tables I and II). The electron-accepting acyl substituents at N^2 evidently reduce the splitting constant $a(\text{N}^1)$ by 0.2–0.3 mT (1-tert-butylhydraz-1-oxyls *VIII d*–*VIII g*, Table II), whereas the splitting constant $a(\text{N}^2)$ increases from 0.09 to 0.18 mT (compounds *VIII d*, *VIII f*; Table II). The same tendency was observed in the 1-phenylhydraz-1-oxyl radical series (compounds *VIII a*–*VIII c*, *IV j* Table II). The drop of the $a(\text{N}^1)$ splitting constant by 0.06–0.09 mT was accompanied by an increase of $a(\text{N}^2)$ splitting constant from 0.059 to 0.19 mT.

TABLE II
ESR parameters of some hydrazoxyl radicals *VIII* in benzene

Compound	Splitting constant, mT					Ref.
	$a(\text{N}^1)$	$a(\text{N}^2)$	$a(\text{H}_o)$	$a(\text{H}_p)$	$a(\text{H}_m)$	
<i>VIII a</i>	1.219	0.059	0.293	0.293	0.096	10
<i>VIII b</i>	1.161	0.167	0.260	0.273	0.089	11–14
<i>VIII c</i> ^a	1.176	0.125	0.260	0.260	0.089	14
<i>IV j</i> ^b	1.130	0.190	0.262	0.259	0.092	—
<i>VIII d</i>	1.890	0.090	—	—	—	15
<i>VIII e</i>	1.600	0.150	—	—	—	16
<i>VIII f</i>	1.600	0.180	—	—	—	5
<i>VIII g</i>	1.860	0.090	0.090 ^d	—	—	17
			0.090 ^e	—	—	

^a In pyridine; ^b cf. Table I, compound *I j*; splitting due to: ^c hydrogen atom of the CHO group;

^d hydrogen atom in R^2 ; ^e hydrogen atom of the cyclohexyl group.

The spin density value $\rho(\text{N}^2)$ could be calculated from the ESR data for 1-tert-butyl-2-cyclohexylhydraz-1-oxyl (compound *VIIIg*; Table II). From the simple McConnell equation employing values Q_{NH}^{H} 3.5 mT (ref.²⁰) and a_{H} 0.09 mT, the $\rho(\text{N}^2)$ equals 0.025. Obviously, a partial delocalization of the spin density on the carbonyl group is possible when attached to N^2 atom. The spin density value at carbon atom of the carbonyl group $\rho(\text{C})$ 0.13 was obtained employing Q_{CH}^{H} 2.4 mT (ref.²⁰) and $a_{\text{H}}^{\text{CHO}}$ 0.312 mT (compound *VIIIc*; Table II). Since the change of $a(\text{N}^1)$ splitting does not evolve a considerable difference of the $a(\text{N}^2)$ splitting constant value (compounds *VIIIb*, *VIIIe*; Table II), the significant contribution to the $a(\text{N}^2)$ value might stem from the spin density at carbonyl groups. The Q_{CN}^{N} values, however, considerably vary for various types of radicals (e.g. in radical ions Q_{CN}^{N} 0.17–1.38 mT, ref.²⁰). The contribution to the $a(\text{N}^2)$ splitting constant ranging from 0.019 to 0.034 mT seems to be possible when employing Q_{CN}^{N} 0.073–0.131 mT for neutral hydrazyl radicals²¹. The electron-accepting effect of the carbonyl group is also manifested at the aryl group attached to N^1 as evidenced by the lowered values of splitting constants of all protons of the aromatic ring (compounds *VIIIa*–*VIIIc*, *IVj*; Table II).

The effect of substituents bound to N^1 is demonstrated by comparison of our data for radical *IVj* (Table II) with those, published for tert-butyl derivative⁶. The phenyl group in *IVj* was found to lower the $a(\text{N}^1)$ value by 0.46 mT, whereas the $a(\text{N}^2)$ value increases minutely. The same tendency is evident even with radicals *VIIIb* and *VIIIe*. Substituents at the aromatic ring influence the $a(\text{N}^1)$ splitting constant as expected: the electron-accepting groups decrease, whilst the electron-donating groups elevate the $a(\text{N}^1)$ value (Table I). The $a(\text{N}^1)$ splitting constants reveal a fair linear correlation with σ_p and σ_m Hammett constants²² (Fig. 2). The phthalimidoyl group linked to N^1 affords lower absolute ρ values (ρ 0.113) in comparison with

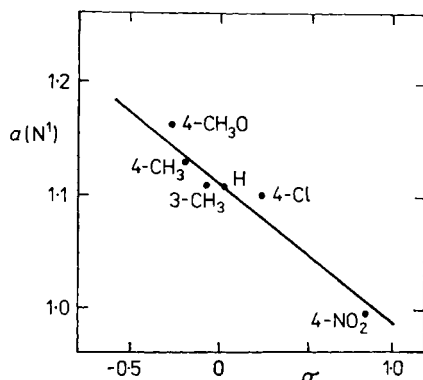


FIG. 2

Relationship between the splitting constant $a(\text{N}^1)$ and Hammett σ_p and σ_m constants in the series of hydrazoxyl radicals *IVa*–*IVh*. The σ Hammett constants were taken from literature²²

phenyl (ρ 0.1602, ref.²³), or N-acetyl-N-phenylamino group (ρ 0.1621, ref.¹⁴). This phenomenon could probably be associated with a more effective delocalization of the free electron pair of N² into the phthalimide ring. The $a(\text{N}^2)$ splitting constant only little changes with respect to various substituents at the phenyl ring. A considerable decrease of this value was observed with radical *IVh* only as a consequence of a strong electron-accepting effect of the picryl residue and a steric effect.

It has been observed that the $a(\text{N}^1)$ values of radicals *IVi*–*IVk* decrease with the magnitude of the imide ring, whereas the $a(\text{N}^2)$ ones were not influenced. This effect is evidently due to a different stage of mesomeric interaction of the carbonyl function with the lone electron pairs at nitrogen and the unpaired electron. The constant $a(\text{N}^2)$ value shows, however, that the system is quite complicated and its behaviour is difficult to anticipate. Delocalization of the unpaired electron density through carbonyl groups and the nitroxyl oxygen atom is responsible for the failure to obtain correlations between the $a(\text{N}^1) : a(\text{N}^2)$ ratio and the Hammett σ constants of 1-phenyl substituents of compounds *IVa*–*IVh*. This dependence, affording in addition a constant value of the sum $a(\text{N}^1) + a(\text{N}^2)$, was found in the series of hydrazyl radicals²⁴. The ESR spectra of hydrazoxyl radicals *IVj*, *IVk* also display very weak splittings $a(\text{H})$ 0.02 mT (Table I). High resolution spectra were obtained after addition of ethanol (0.05 ml) to the oxidation system *B*. This splitting originated with radical *IVj* as a consequence of interaction with methylene δ -hydrogen atoms of the imide ring with radical *IVh* due to interaction with ε -hydrogen atoms of ethyl groups of the substituted azetidone ring. So far, only (γ -H) splittings 0.056–0.089 mT were reported with hydrazoxyl radicals^{6,7,17,25}.

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Translated by Z. Votický.

Note added in proof: In formula V replace NH_2 group by H atom.