

ON THE EPR SPECTRA OF HYDRAZYL AND HYDRAZOXYL RADICALS<sup>1</sup>

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Confusion regarding the nature of the radicals produced by photolysis of azocarboxylates and detected by epr spectroscopy appears to be growing.

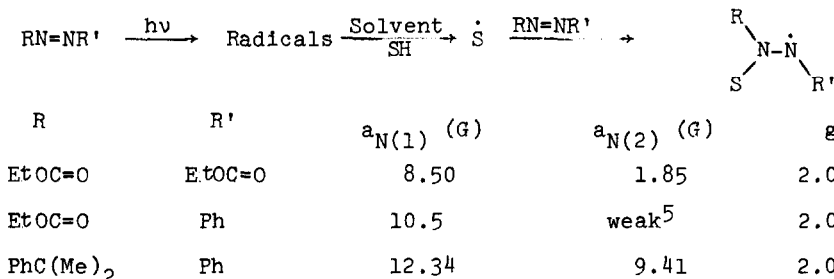
Stilbs et al<sup>3</sup> suggested that the radicals from symmetric azodicarboxylates were diazenyl radicals,  $RN=N^{\cdot}$

$$RN=NR \longrightarrow RN=N^{\cdot} + (R^{\cdot})$$

R	$a_{N(1)}$ (G)	$a_{N(2)}$ (G)	$a_H$ (G)	g
MeOC=O	8.56	1.78	0.38 (3H)	-
EtOC=O	8.50	1.85	0.39 (2H)	2.0063
Bu <sup>t</sup> OC=O	8.56	1.75	-	-

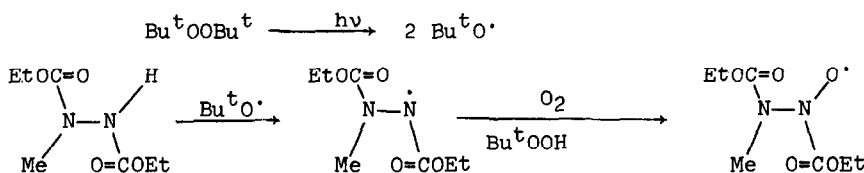
The radicals had half-lives of about 1 min. and did not react with oxygen. The possibility that the radicals were hydrazoxyls,  $RR'NN(O^{\cdot})R''$  (aminonitroxides) was considered and rejected because "it is difficult to envisage a reasonable structure of this type derived from the azoester". Difficult or not, we show in this Communication that these radicals are indeed hydrazoxyls.

Marnett et al<sup>4</sup> rejected Stilbs<sup>3</sup> diazenyl radical assignment and concluded from photolytic studies on unsymmetrical azo compounds that hydrazyl radicals are produced by addition of a solvent (isopentane: methylcyclohexane, 1:4) derived radical to the starting azo compound.



As we have already emphasized<sup>6</sup> the epr spectral characteristics for unequivocally derived hydrazyls invariable show strong coupling of the unpaired electron with the second nitrogen ( $a_{N(1)}/a_{N(2)}$  ca 1.0 to 1.5, generally)<sup>7</sup> and have g values of about  $2.0038 \pm 0.0003$ <sup>7</sup>. The third of Marnett's radicals listed above is clearly a hydrazyl but the other two are very unlikely to be. Unfortunately for Marnett et al, they used as an example of an "authentic hydrazyl radical" a species we have shown to be phenyl cumyl nitroxide<sup>6</sup>. The epr characteristics of Marnett's second radical and of Stilbs' three radicals are, as Stilbs pointed out, those of hydrazoxylys<sup>8</sup>. Furthermore, trialkylhydrazyls react with oxygen to yield hydrazoxylys that are relatively stable to oxygen<sup>12</sup>.

Proof that Stilbs' radicals (and presumably Marnett's second radical) are hydrazoxylys was simple. Repeating Stilbs' experiment with R = MeOC=O with the most careful degassing yielded a radical with  $a_{N(1)} = 8.83$ ,  $a_{N(2)} = 1.86$ ,  $a_H(3H) = 0.40$  G, and  $g = 2.00632$ , and a line width of 0.25G in isopentane: cyclohexane, 1:4, which is clearly Stilbs' radical (see Fig. 1). A radical with an epr spectrum identical in all respects to this species was obtained by photolysis of a mixture of 1,2-dicarboxyethyl-1-methylhydrazine and di-tert-butyl peroxide in the same solvent in the presence of oxygen or (for better resolution)<sup>14</sup> in the presence of tert-butyl hydroperoxide.



In the absence of oxygen or hydroperoxide a completely different spectrum is obtained (Fig. 2). This we assign to the hydrazyl,  $\text{EtO}_2\text{C}(\text{Me})\text{NN}\cdot\text{CO}_2\text{Et}$ , with

$a_{N(1)} = 13.5$ ,  $a_{N(2)} = 8.7$ ,  $a_H(3H) = 6.3$  G and  $g = 2.0038$ . The hydrazyl decays within the time constant of the instrument if the light is cut off and is therefore much shorter lived than the hydrazoxy.

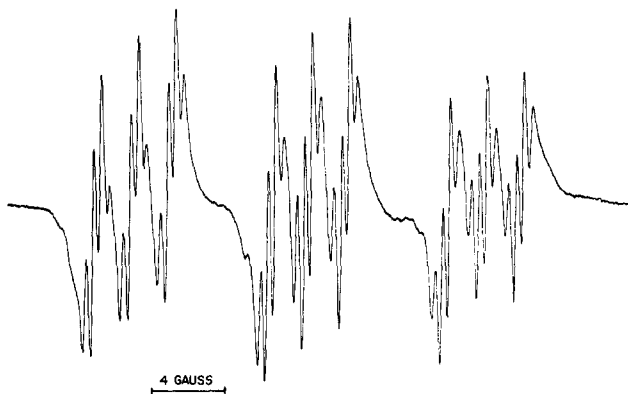


Fig. 1. Epr spectrum of N,N'-dicarboethoxy-N'-methylhydrazoxy

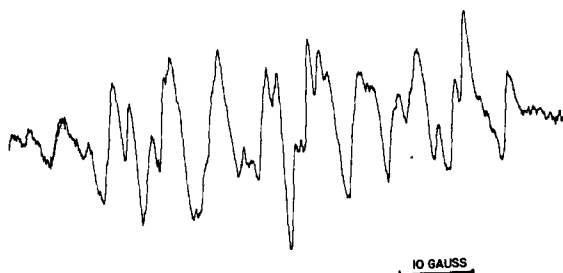
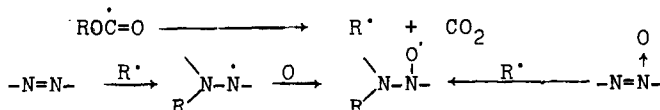
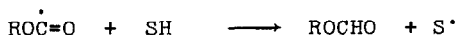


Fig. 2. Epr spectrum of N,N'-dicarboethoxy-N'-methylhydrazyl.

The mechanism by which hydrazoxyis are formed upon photolysis of azo-carboxylates remains a mystery<sup>15</sup> but of the fact that they are formed there can be no doubt. Furthermore, the alkyl fragment for which splitting is detectable is attached to the amino nitrogen and must be formed by decarboxylation of the carboxyalkyl radical<sup>17</sup> that itself is formed in the primary photochemical reaction.



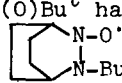
In good hydrogen donating solvents the hydrazoxyyl may contain a solvent derived radical on the amino nitrogen.



### Experimental

1,2-Dicarboxyethyl-1-methyl hydrazine was prepared (in 75% yield) from methyl hydrazine and ethyl chloroformate using a procedure analagous to that for the preparation of ethyl hydrazodicarboxylate<sup>16</sup>. Colorless oil, bp 105° at 0.02mm, nmr (in CDCl<sub>3</sub>, TMS as standard)  $\delta$  = 1.24 (6H, t, J = 7 cps.),  $\delta$  = 3.12 (3H,s),  $\delta$  = 4.16 (2H, q, J = 7 cps.),  $\delta$  = 4.18 (2H, q, J = 7 cps.),  $\delta$  = 7.4 (1H,s).

### References and Notes

- (1) Issued as NRCC No. 13341.
- (2) NRCC Postdoctoral Fellow 1972-73.
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- (5) "Weak couplings from one nitrogen nucleus and non-equivalent phenyl-group protons."<sup>4</sup>
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- (8) E.g., MeCO(Ph)NN( $\dot{O}$ )Ph has  $a_{N(1)}=11.62$ ,  $a_{N(2)}=1.67$ ,  $a_{H(o)}=2.73$ ,  $a_{H(m)}=0.89$  and  $a_{H(o,p)}=2.60G$  and  $g=2.0053$  in benzene<sup>9,10</sup>;  $[(CH_2)_8]NN(\dot{O})Bu^t$  has  $a_{N(1)}=16.1$ ,  $a_{N(2)}=1.24$ , and  $a_{H(4H)}=0.78G$  in aqueous dioxan<sup>11</sup>;  has  $a_{N(1)}=20.95$ ,  $a_{N(2)}=1.60$ ,  $a_{H(1H)}=3.98$ ,  $a_{H(2H)}=0.85 G$  and  $g=2.0060$ <sup>12</sup>;  $Bu^tCONCMe_2CMe_2NO\cdot$  has  $a_{N(1)}=12.25$ ,  $a_{N(2)}=1.72$ ,  $a_{H(6H)}=0.50G$  and  $g=2.0046$ <sup>13</sup>.
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- (13) E.F. Ullman, L. Call, and S.S. Tseng, J. Amer. Chem. Soc., 95, 1677 (1973).
- (14) An even stronger and better resolved signal is obtained by shaking a benzene solution of the hydrazine with lead dioxide.
- (15) It seems most likely that some azoxy compound, RN=N(O)R is present as an impurity in the azocarboxylate as normally prepared<sup>16</sup>. However, generation of an intermediate capable of oxidizing the hydrazyl radical via some minor photochemical pathway cannot be ruled out, e.g.  $EtO_2CN=NCO_2Et \xrightarrow{h\nu} 2 EtOC\equiv N+O$ .
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