## E.S.R. OF HYDRAZOXYL RADICALS: EVIDENCE FOR CONFORMATIONAL ISOMERS.

ANGELO ALBERTI\*

Istituto dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni, C.N.R., Via Tolara di sotto 89, 40064-0ZZANO EMILIA, Italy

AND

ANDREW HUDSON" School of Molecular Sciences, University of Sussex, BRIGHTON, BN1 9QJ, U.K.

<u>ABSTRACT</u>. Thermolysis of azocarboxylates has been investigated by e.s.r. Experimental evidence for the existence of conformational isomerism in acylnitroxides has been obtained.

Initial confusion concerning the identity of free radicals produced by photolysis of azocarboxylates was resolved by Malatesta and Ingold<sup>1</sup> who showed that the species detected by e.s.r. were hydrazoxyl radicals (*i.e.* aminonitroxides)  $RO_2C(X)NN(\dot{O})CO_2R$  (1), rather than the expected hydrazyls  $RO_2C(X)N\dot{N}CO_2R$  (2). It was subsequently demonstrated by Roberts and Winter<sup>2</sup> that hydrazyls produced by reaction (*i*) can also be readily detected by e.s.r.

We have been investigating the thermolysis of azocarboxylates and have observed a number of previously unreported features in the e.s.r. spectra of hydrazoxyls. When a sample of di-*t*-butylazocarboxylate (3), either neat or dissolved in biphenyl, was melted in the cavity of a Bruker ER 200 e.s.r. spectrometer at  $ca.100^{\circ}$ C, the spectrum shown in figure 1 was obtained; a degassed sample

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gave the same result. The basic pattern of large (9.6 G) and small (1.8 G) couplings to <sup>14</sup>N nuclei and the *g*-factor (2.0060) are characteristic of hydrazoxyls and we assign the spectrum to (1),  $R = B_U^t$ ,  $X = B_U^t$ . It is clear under high resolution, however, that in fact two overlapping spectra are present and this is confirmed by the computer simulation. The coupling constants for the two radicals A and B, are given in the table. The ratio of their concentration is temperature dependent. The thermal decomposition of azocarboxylates is known to follow reactions (ii) and (iii) and Roberts and Winter<sup>2</sup> were able to ob-

$$RO_2CN=NCO_2R$$
  $\longrightarrow$   $N_2 + 2 \cdot CO_2R$  (*ii*)

 $\cdot CO_2 R \longrightarrow CO_2 + R \cdot (iii)$ 

serve both the expected hydrazyls (2,  $\chi = B_U^t$  and  $\chi = CO_2 B_U^t$ ) by working at low temperatures. The fact that we observe instead a hydrazoxyl, as did Malatesta

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R	X	Ţ(°c)	A/B	a (N)	a	'(N')	a	other	g
CMe <sub>3</sub>	CMe3	80	1.35	(A) 9.65 (B) 9.76	1	.80			2.00596 2.00611
CMe <sub>3</sub>	SiPh <sub>3</sub>	50	5,51	(A) 9.29 (B) 9.54	1 0	26 ).96			2.00605 2.00615
CMe <sub>3</sub>	GePh <sub>3</sub>	50	4.35	(A) 9.17 (B) 9.41	1 1	.41	 		2.00578 2.00600
Et	Et	28	2.27	(A) 9.10 (B) 9.13	1 1	83 78	0 0	.39(2H) .51(2H)	2.00609 2.00626
Et	GePh <sub>3</sub>	25	4.62	(A) 8.84 (B) 8.92	1	42 32	0 0	.40(2H) .52(2H)	2,00586 2,00607

and Ingold, can be attributed to the presence of an impurity in the azocarboxylate, most probably the azoxy compound. Support for this view is given by our results from a sample of di-ethylazocarboxylate (4) which gave no detectable rad icals when heated to 100°C. However, the hydrazoxyl radical (1), ( $R = \chi = Et$ ), was obtained on photolysis of (4) in di-*t*-butyl peroxide. The spectrum could again be simulated in terms of two overlapping species with closely similar coupling constants and g-factors. A small splitting from two equivalent protons was resolvable in addition to the coupling to two nonequivalent  $^{14}N$  nuclei.<sup>3</sup> A



number of other nitroxides were prepared by photolysing (3) or (4) in the presence of di-t-butyl peroxide and  $Ph_3SiH$  or  $Ph_3GeH$ ; their coupling constants are included in the table. In each case two species were present. The low field group of lines of the spectrum of (1, R = Et, X = GePh\_3), is shown together with a computer simulation in figure 2. The presence of a small triplet splitting, similar to that found for the radical with X = Et, indicates that this originates from one of the carboethoxy groups rather than from the adduct X.

The most interesting new feature to emerge in our investigation of hydrazoxyls is the recognition that in each case two distinct species are present. These have very similar e.s.r. parameters and we assign them to the *trans* and cis conformers [ and []. Previous discussion on the conformational properties



of N-acyl nitroxides have concluded <sup>4,5</sup> that a *trans*-conformation is preferred around the CO-N bond and attempts to detect a second conformer have proved unsuccessful. The *trans* isomer is believed to be more stable because it minimises steric interactions between the substituents, in our case OR and  $N(X)CO_2R$ , on the acyl and nitroxyl groups. If we assume that isomer A is *trans* and B is *cis*, the increase in the ratio of A to B when X is GePh<sub>3</sub> or SiPh<sub>3</sub> can be rationalised in terms of the greater steric requirements of these groups.

The thermolysis, or photolysis, of the systems we have been investigating provides further interesting results when performed at elevated temperatures. For example the thermolysis of (3) in molten biphenyl, which at 90°C gives the spectrum shown in figure 1, yields an additional species which replaces the hydrazoxyl at higher temperatures. The new spectrum has  $a_{(N)} = 12.18$  G,  $a_{(N')} = 8.38$  G and g = 2.00393 at 120°C and we assign it<sup>6</sup> to the hydrazyl (2,  $X = R = BU^t$ ). The remaining hydrazoxyl radicals in the table are also replaced by hydrazyls when the e.s.r. spectra are recorded at higher temperatures. When (3) in molten biphenyl is heated to 150°C a further, as yet unidentified, species is formed. This has the e.s.r. parameters:  $a_{(N)} = 9.76$  G,  $a_{(N')} = 5.21$  G, a doublet splitting of 6.89 G and g = 2.00402 characteristic of another hydrazyl radical. The other systems also give presently unidentified radicals at elevated temperatures.

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## REFERENCES AND NOTES.

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- 3) This spectrum is very similar in appearance to the spectrum of N,N'-dicarboethoxy-N'-methylhydrazoxyl published by Malatesta and Ingold.<sup>1</sup> They assigned the small splitting to a quartet, but some assymmetry is apparent in their spectrum and computer simulation suggests that the fine structure is better accounted for in terms of triplets from two overlapping species.
- 4) E. Flesia, J.-M. Surzur, and P. Tordo, Org. Magn. Res., 1978, <u>11</u>, 123.
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- 6) Roberts and Winter<sup>2</sup> report  $a_{(N)} = 12.6$  G,  $a_{(N')} = 7.8$  G and g = 2.0040 at 70°C.

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