

DIAZIRIDINYLS

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Interest in hydrazyls, for so long mainly confined to diphenylpicrylhydrazyl (DPPH),¹ has been stimulated recently by the detection (e.s.r.) of several mono-,² di-,^{3,4} and tri-⁵alkylhydrazyls and 6-, 5-, and 4-membered bicyclic⁶ hydrazyls. We now report the first detection and characterisation of 3-membered cyclic hydrazyls - the diaziridinyls.

Irradiation (1Kw, Hg-vapour high pressure lamp) of a solution of the diaziridine⁷ (1; R=H) in di-t-butyl peroxide at room temperature in the cavity of the e.s.r. spectrometer resulted in the detection of the spectrum shown in Fig. 1. This has been interpreted as arising from coupling with two nitrogen atoms $a_N = 14.2$ and 11.7 g and one proton $a_H = 45.7$ g. The corresponding dideuterodiaziridine gave a spectrum with $a_N = 14.1$ and 11.8 g and $a_D = 7.2$ g ($\frac{a_H}{a_D} = 6.3$) thus confirming our interpretation. Similar treatment of the N-alkyldiaziridines (1; R=Me and Et) gave spectra, e.g. Fig. 2, from which the coupling constants listed in the Table were derived. The spectra rapidly disappeared when the lamp was shuttered and could not be observed when the solutions were irradiated $<0^\circ$. Interestingly, no spectra were observed when 3,3-pentamethylenediaziridine was irradiated in di-t-butyl peroxide-chloroform.

The g-values and $\frac{a_{N1}}{a_{N2}}$ ratios clearly exclude diaziridinoxyl^{5,6,8} (3) and hydrazonoxyl⁹ (5) structures for the above radicals and are more consistent with hydrazyls²⁻⁶ (7) than hydrazonyls^{9,10} (4) (Table). Also, the $\frac{a_H}{a_N}$ ratio 3.7 or 2.5 for the radical derived from the diaziridine (1; R=H) is much larger than that which would be expected from the hydrazonyl (4; R=H) and the a_{CH_3} value for that derived from (1; R=Me) is too small to be due to the hydrazonyl^{9,10} (4; R=Me) (Table). Unfortunately, authentic spectra of (4; R=H and Me) could not be detected when the corresponding hydrazones with di-t-butyl peroxide were irradiated in the range 60° to -50° .

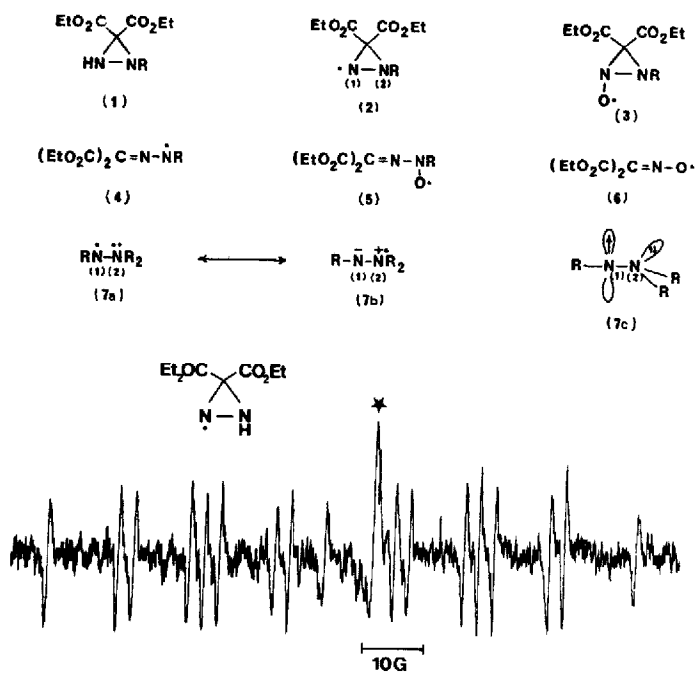


Fig. 1. Spectrum of (2; R=H): * indicates "quartz signal"

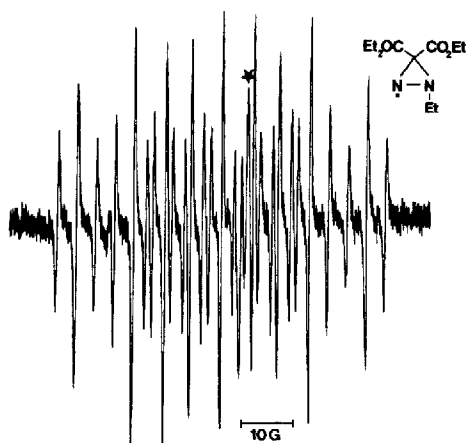


Fig. 2. Spectrum of (2; R=Et): * indicates "quartz signal"

Table

Hyperfine Coupling Constants (gauss) and g-Values of Diaziridinyls and Related Radicals

Radical	g-value	$a_{N(1)}$	$a_{N(2)}$	Other a-values	Ref.
(2; R=H)	2.0038	14.2	11.7	$a_{H}^{NH} = 45.7$	This work
(2; R=D)	2.0037	14.1	11.8	$a_{D}^{ND} = 7.2$	This work
(2; R=Me)	2.0039	18.1	11.2	$a_{H}^{CH_3} = 2.6(3H)$	This work
(2; R=Et)	2.0038	17.7	11.2	$a_{H}^{CH_2} = 3.75(2H)$	This work
(2; R=COPh)	2.0038	11.0	9.6	-	This work
$CH_3\dot{N}NH_2$	2.0038	14.0	7.9	$a_{H}^{CH_3} = 17.7(3H)$, $a_{H}^{NH} = 2.8$ and 1.3	2
$Pr^i\dot{N}NHPr^i$	2.0038	12.7	9.5	$a_{H}^{NH} = 1.2$, $a_{H}^{CH} = 5.0$, $a_{H}^{CH} = 10.5$	5
$Me\dot{N}NMe_2$	2.0038	11.7	10.5	$a_{H}^{NMe_2} = 17.6(3H)$, $a_{H}^{NMe_2} = 5.9$ and 8.2	5
$\dot{N}NMe_2$	2.0038	9.6	11.5	$a_{H}^{NH} = 13.7$, $a_{H}^{NMe_2} = 6.9(6H)$	3
$Me\dot{N}N=CPhBu^t$	2.0037	12.0	4.4	$a_{H}^{CH_3} = 19.2(3H)$	10
$MeO_2CN(\dot{O})NMe(CO_2Me)$	2.0063	8.83	1.86	$a_{H}^{Me} = 0.40(3H)$	8
$PhN(\dot{O})N=C Bu_2^t$	2.0047	12.1	2.7	$a_{H} = 2.9(3H)$	9

Assignment of the a_N values of hydrazyls is best achieved by ^{15}N labelling² although with symmetrical 1,2-dialkylhydrazyls, e.g. (1; R=H), even this may not yield an unequivocal result. In the absence of such labelled substrates we, like others,^{1,5} must argue by analogy. In hydrazyls the divalent nitrogen $N_{(1)}$ normally has the larger a_N value unless $N_{(2)}$ carries substituents which make (7b) more favourable than (7a). Thus the parent hydrazyl $\dot{N}HNH_2$, and all 1-mono-, 1,2-di- and tri-alkylhydrazyls have $a_{N(1)} > a_{N(2)}$ but for 2,2-dialkylhydrazyls the reverse is true (Table). Hence, for the diaziridinyls we provisionally attribute the larger a_N value to $N_{(1)}$.

Hydrazyls are generally considered⁶ to be π -radicals with the unpaired electron in a predominantly 2p orbital on $N_{(1)}$ and the unshared pair on $N_{(2)}$ in a hybrid orbital as indicated (7c). However, this model has not been fully substantiated by MO calculations which at present cannot reproduce all of the observed coupling constants.⁴ Significantly, the $a_{N(1)}$ values of the diaziridinyls are larger than those of di- and tri-alkylhydrazyls⁵ (Table)

oxaziridinyls¹¹ (12.1 g) and aziridinyls¹² (12.52 g) which suggests that the spin-bearing orbital has correspondingly more s-character, i.e. $N_{(1)}$ is more pyramidal,¹³ than in these related radicals. The origin of the abnormal peak heights observed in the spectra of (2; R=Me and Et) (Fig. 2), almost certainly some molecular motion of the radical, is under investigation. The large a_H^{NH} value of (2; R=H), like the $a_H^{CH=N}$ value of aldiminyls,¹⁴ must arise by efficient hyperconjugative interaction with the electrons of the favourably disposed (small dihedral angle) N-H bond (cf. ref. 13).

The a_N values of the benzoyldiaziridinyl (2; R=PhCO) are smaller than those of the unsubstituted radical (R; R=H) but, surprisingly, the $\frac{a_{N1}}{a_{N2}}$ ratio is little affected. Too few acylalkylhydrazyls have yet been generated to appreciate the significance of this result.

Our attempt to generate diaziridinoxyls (3) by irradiating the diaziridine (1; R=Me) in di-t-butyl peroxide in the presence of oxygen or t-butylhydroperoxide^{6,8} gave only weak complex spectra arising from more than one species. On prolonged irradiation of the diaziridine (1; R=Me) in di-t-butyl peroxide or on irradiation of (1; R=Et) in di-t-butyl peroxide with oxygen present the iminoxyl¹⁵ (6) ($a_N = 31.8$ g, $g = 2.0046$) was detected. Several routes to this radical can be formulated none of which has yet been confirmed. However, at present this is our only evidence for photolytic/oxidative ring opening of the diaziridine ring (cf. oxiranyl- α -ketoalkyl rearrangements¹⁶).

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