Oxaziridinyl Free Radicals

By Robert F. Hudson,* Alexander J. Lawson, and Keith A. F. Record
(*University Chemical Laboratory, Canterbury, Kent* CT2 7NH)

Summary The e.s.r. solution spectra of two 3,3-disubstituted oxaziridinyl free radicals are reported, and the isolation of a 2*H*-oxaziridine is described.

Although iminoxyls have been widely studied[1] in recent years, the isomeric oxaziridinyl free radicals remain unknown. We now report the generation of the 3,3-di-

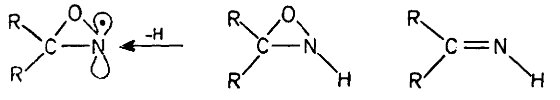
TABLE[a]

	g_{iso}	a_N	a_H	a_C		ν_{NH}/cm^{-1}	ν_{ring}[d]cm^{-1}	δ_C/p.p.m.[b,e]
(**1a**)	2·0041	1·16	c	0·7[e]	(**2a**)	3200	1260	80·1
(**1b**)	2·0041	1·21	0·035 (18H)	—	(**2b**)	3260	1257	84·7

[a] All values for solvent CCl_4 at room temperature except where noted. Splitting constants in mT. [b] Room temperature, C_6D_6. [c] Splittings unresolved. [d] Ring vibration in oxaziridines is at *ca.* 1250 cm^{-1} (ref. 5). [e] Assigned to the ring carbon atom.

substituted oxaziridinyls (**1**) by treatment with PbO_2 in CCl_4 of the corresponding oxaziridine (**2**), prepared itself by oxidation of the ketimine (**3**),† with *m*-chloroperbenzoic acid.

The oxaziridines (**2**) unsubstituted on nitrogen are not stable in the neat state;[2,3] thus (**2a**) is converted into benzophenone at room temperature, although (**2b**) may be isolated *ca.* 90% pure by high vacuum distillation and stored for several hours as a colourless oil without significant further decomposition to the principal contaminant, $Bu^t_2C{=}O$. Solution i.r. and n.m.r. spectra (Table) are fully consistent with the oxaziridine ring structure, while the e.s.r. parameters also listed in the Table exclude the possibility of the oxaziridinyl nitroxide for which an isotropic *g* value in the range of 2·005—2·006 would be expected, and are likewise consonant with the formulation (**1**) in which the unpaired electron occupies an orbital of principally nitrogen 2*p* character, as has been proposed for aziridinyl radicals.[4]



(1) (2) (3)

a; R = Ph
b; R = Bu^t

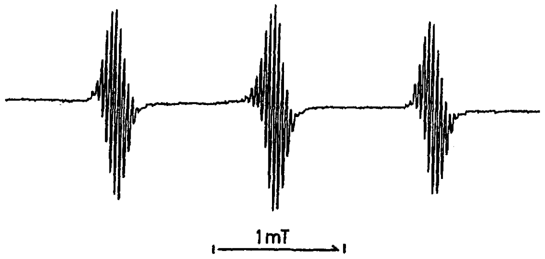


FIGURE. E.s.r. spectrum of di-t-butyloxaziridinyl radical in CCl_4 solution at 25 °C.

The radical (**1b**) (Figure) is particularly long-lived in solution‡ at room temperature, the e.s.r. signal intensity remaining unchanged over a period of 24 h, and this is clearly linked to the steric protection of the butyl groups;[1] a similar explanation for the increased stability of (**2b**) relative to (**2a**) is likely, in view of the apparent susceptibility of the ring system to rupture *via* dimerization through nitrogen.[3]

We thank Mr. Robert P. Orford for assistance.

(*Received*, 20*th February* 1975; *Com.* 214.)

---

† Peracid oxidation as a route to oxaziridines is generally used for *N*-substituted imines only. The original, alternative preparation for compounds of type (**2**) is described in ref. 2.

‡ The 3,3′-diphenyl radical (**1a**) decays over a period of 1 h at 50 °C, and a strong signal of the corresponding oximino-radical appears. We are investigating the mechanism of this rearrangement.

[1] G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, 1973, **95**, 2963.
[2] E. Schmitz, R. Ohme, and S. Schramm, *Tetrahedron Letters*, 1965, 1857.
[3] E. Schmitz, R. Ohme, and S. Schramm, *Angew. Chem. Internat. Edn.*, 1963, **2**, 157.
[4] W. C. Danen and T. T. Kensler, *Tetrahedron Letters*, 1971, 2247.
[5] K. Shinzawa and I. Tanaku, *J. Phys. Chem.*, 1964, **68**, 1205.