An Electron Spin Resonance Study of the Cyclobutylhydroxymethyl Radical: Its Conformation, and Its Ring Opening Followed by 1,6-Transfer of Enolic Hydrogen

By Peter M. Blum, Alwyn G. Davies,* and Richard A. Henderson
(*Chemistry Department, University College London, 20 Gordon Street, London* WC1H 0AJ)

Summary The e.s.r. spectra show that in fluid solution the cyclobutylhydroxymethyl radical adopts a staggered conformation like that of cyclopropylmethyl radicals; in adamantane, cyclobutylhydroxymethyl radicals undergo ring-opening followed by 1,6-transfer of enolic hydrogen to give penten-1-oxyl radicals.

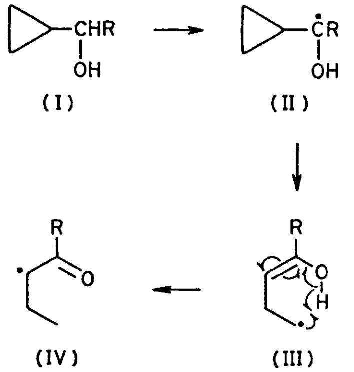
TABLE. E.s.r. characteristics of radicals

Radical	Solvent[a]	$a(H_\alpha)$/G[b]	$a(H_\beta)$/G[b]	g	T/°C
$\mathrm{CH_3CH_2\dot{C}HCHO}$	C_3H_6	18·4(1)	19·8(2)	*ca.* 2·0047	+16[c]
	$C_{10}H_{16}$	18·5(1)	14·0(2)	2·0047	+20
$\mathrm{CH_3CH_2\dot{C}HCOCH_3}$	C_3H_6	18·9(1)	20·8(2)	2·0045	−35[c]
	$C_{10}H_{16}$	18·5(1)	11·0(2)	2·0045	−40
$\mathrm{\overline{CH_2CH_2CH_2CH}\dot{C}HOH}$	C_3H_6	16·0(1)	11·5(1)	2·0029	−40
$\mathrm{\overline{CH_2CH_2CH_2CD}\dot{C}HOH}$	C_3H_6	16·0(1)	1·8(1)[d]	2·0029	−40
$\mathrm{(CH_3)_2CH\dot{C}HOH}$	Iso-C_8H_{18}	14·9(1)	22·0(1)	2·0032[e]	+27[f]
$\mathrm{\overline{CH_2CH_2CH}\dot{C}H_2}$	C_3H_6	20·7(2)	2·55(1)		−140[g]
$\mathrm{\overline{CH_2CH_2CH_2CH}\dot{C}H_2}$	C_3H_6	21·3(2)	12·7(1)	2·0026	−80[h]
$\mathrm{\overline{CH_2CH_2CH_2CH_2CH}\dot{C}H_2}$	C_3H_6	21·3(2)	21·3(1)		−90[i]
$\mathrm{(CH_3)_2CH\dot{C}H_2}$	C_3H_6	22·0(2)	31·8(1)		−90
$\mathrm{CH_3CH_2CH_2\dot{C}HCHO}$	$C_{10}H_{16}$	18·0(1)	13·5(2)	2·0047	+20
$\mathrm{CH_3CH_2CH_2\dot{C}DCHO}$	$C_{10}H_{16}$	2·8(1)[d]	13·5(2)	2·0047	+20

[a] C_3H_6 = liquid cyclopropane; $C_{10}H_{16}$ = solid adamantane. [b] Number of coupling hydrogens atoms in parantheses. [c] Ref. 3. [d] Deuterium coupling. [e] g-value in water (R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1966, **44**, 1245). [f] J. Q. Adams, *J. Amer, Chem. Soc.*, 1968, **90**, 5363. [g] Ref. 5. [h] M.-W. Tse, unpublished work. [i] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1969. **91**, 3940.

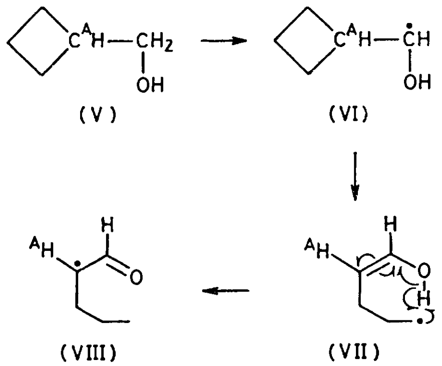
THERE is increasing interest in the kinetic behaviour of matrix-isolated radicals because, under these conditions, slow unimolecular reactions can take place which in fluid solution are precluded by more rapid bimolecular processes. We report here a comparative study by e.s.r. spectroscopy of the behaviour of cyclopropylhydroxymethyl and cyclobutylhydroxymethyl radicals in fluid and solid solution and show that, in an adamantane matrix, cyclobutylhydroxymethyl radicals undergo ring-opening followed by a 1,6-transfer of enolic hydrogen from oxygen to carbon.

In cyclopropane solution, t-butoxyl radicals react with cyclopropylmethanols (I) to give the cyclopropylhydroxymethyl radicals (II) which undergo rapid ring-opening at −120 °C to show the e.s.r. spectra of the hydroxybutenyl radicals (III).[1] At about −50 °C, 1,5-transfer of enolic hydrogen occurs, and the spectra of the buten-1-oxyl radicals (IV) are observed.[2,3]



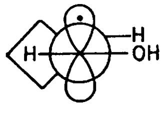
(I) (II) (III) (IV)

The same reactions occur in an adamantane matrix. The methanols (I; R = H or Me) were irradiated in adamantane with X- or γ-rays, then examined by e.s.r. spectroscopy. A strong spectrum of the appropriate buten-1-oxyl radical (IV) was observed, although the β-coupling constants were different from those in solution, and were more temperature-dependent. This effect of the matrix on hyperfine coupling constants has been observed previously.[4] Details of the spectra are given in the Table.



(V) (VI) (VII) (VIII)

Photolysis of di-t-butyl peroxide in the presence of cyclobutylmethanol or ([1-^{2}H]cyclobutyl)methanol (V, ^{A}H = ^{1}H or ^{2}H) in cyclopropane solution led to the spectrum of the cyclobutylhydroxymethyl radical (VI); the potential ring opening of (VI) is much slower than that of the cyclopropyl analogue (II), and is now precluded by the rapid removal of the radicals (VI) from solution by bimolecular self-reaction.



(IX)

The value of $a(H_\beta)$ in (VI) is much lower than that in the equivalent acyclic radicals [*e.g.* $\mathrm{(CH_3)_2CH\dot{C}HOH}$, see Table], and indeed a smooth progression is observed in the β-coupling constant in the series $\mathrm{\overline{CH_2CH_2CH}\dot{C}H_2}$, $\mathrm{\overline{CH_2CH_2CH_2CH}\dot{C}H_2}$, $\mathrm{\overline{CH_2CH_2CH_2CH_2CH}\dot{C}H_2}$, and $\mathrm{(CH_3)_2CH\dot{C}H_2}$ (see Table).[5]†

This implies that at low temperature the cyclobutylmethyl radicals (VI) adopt the staggered conformation shown in formula (IX); in the cyclopropylmethyl radicals

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† The spectra of cyclopropylhydroxymethyl radicals (II) have not been observed because the ring-opening (II) → (III) occurs too rapidly.

the preference for a similar staggered conformation has been ascribed to overlap of the singly occupied *p*-orbital with an anti-bonding ring orbital.[5]

After radiolysis in an adamantane matrix, cyclobutylmethanol (V) showed a strong spectrum of a radical with e.s.r. parameters (particularly the high *g*-value; see Table) which can reasonably be ascribed only to the penten-1-oxyl radicals (VIII, ^{A}H = ^{1}H or ^{2}H). We conclude that, in the matrix where the bimolecular removal of the radicals (VI) is not possible, the slow ring-opening to the pentenyl radicals (VII) can take place, and that this is followed by the first example to be recognised of a 1,6-transfer of enolic hydrogen from oxygen to carbon.

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