

Cyclopentane-1,3-diyl Radical Cation; ESR Evidence for its Intermediacy in the Radiolytic Oxidation of Bicyclo[2.1.0]pentane to the Cyclopentene Radical Cation in Freon Matrices

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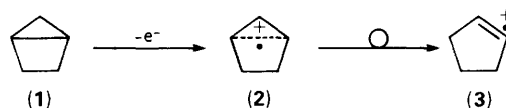
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The title radical cation (**2**) has been detected and characterized by ESR spectroscopy as the initial product of the radiolytic oxidation of bicyclo[2.1.0]pentane (**1**) in the CF₃CCl₃, CF₂ClCCl₂, CFCI₂CFCI₂, and CFCI₃ matrices at 77 K, its formation being accompanied by retention of C_s symmetry with the development of planar carbon centres at the original bridgehead positions; (**2**) undergoes subsequent isomerization to the cyclopentene radical cation (**3**) by intramolecular hydrogen transfer at ca. 100 K.

Recent ESR studies in Freon matrices have shown that in the radiolytic oxidations of hexa-1,5-diene^{1,2} and bicyclo[2.2.0]hexane,² the cyclohexane-1,4-diyl radical cation represents a common intermediate along the pathways to the cyclohexene radical cation. Pursuing our interest in extending this class of unusual radical cations, we noted that the neutral 1,3-diyls of cyclopentane³ and cyclobutane⁴ are well characterized as triplets in their electronic ground states, encouraging the idea that the corresponding radical cations might also represent stable intermediates. Our first approach to the title species (**2**) by the attempted cyclization of the penta-1,4-diene radical cation failed,⁵ so we resorted to the oxidation of bicyclo[2.1.0]pentane (**1**). Although a previous report⁶ indicated that the radical cation of (**1**) isomerizes in the CFCl₃ matrix to the cyclopentene radical cation (**3**) without the detection of (**2**) as an intermediate, even at 4 K, further examination of this reaction in other matrices appeared to be justified on the basis of previous experience,^{1,2} and here we report both ESR and chemical evidence for (**2**) (Scheme 1).

The clearest results were obtained with dilute solutions (<1 mol%) of (**1**) in CF₃CCl₃ (Figure 1). On annealing the γ -irradiated sample from 80 to 140 K, the initial spectrum (a) decayed rapidly above 90 K and was replaced by a wider spectrum (b) with a different hyperfine structure, the irreversible nature of this change being demonstrated by a comparison of spectra (a) and (c) recorded at the same temperature before and after annealing. Spectrum (b) matches perfectly with that obtained by the direct oxidation of cyclopentene in CF₃CCl₃,⁷ and it can therefore be unequivocally assigned to (**3**), the ESR parameters (Table 1) also agreeing closely with those originally reported for (**3**) in CFCl₃.⁸ Evidently the initial spectrum

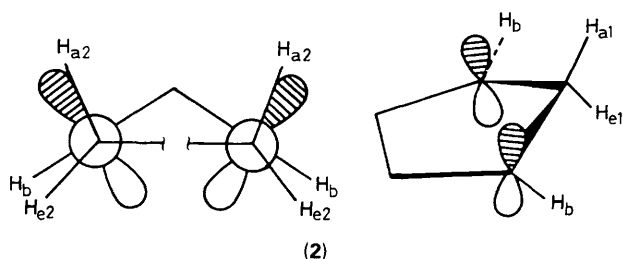


Scheme 1

Table 1. ESR parameters for the radical cations and neutral radicals generated by radiolytic oxidation of bicyclo[2.1.0]pentane in Freon matrices.

Radical cation or radical	Matrix or solvent	T/K	g_{iso}	Hyperfine couplings/G	Ref.
(2)	CF ₃ CCl ₃	90	2.0033	44.9 (1H _{a1}), 33.5 (2H _{a2}), 11.7 (2H _b)	This work
	CFCl ₂ CFCl ₂	80	2.0032	44.8 (1H _{a1}), 32.5 (2H _{a2}), 12.0 (2H _b)	This work
(3)	CF ₃ CCl ₃	140	2.0031	49.1 (4H _β), 10.0 (2H _α), 6.4 (2H _γ)	This work
	CF ₃ CCl ₃	110	2.0039	49.6 (4H _β), 10.5 (2H _α), 7.0 (2H _γ)	7
	CFCl ₂ CFCl ₂	110	2.0030	50.1 (4H _β), 8.4 (4H) ^a	This work
	CFCl ₃	140	2.0028	49.7 (4H _β), 8.8 (4H) ^a	This work
	CFCl ₃	130	— ^b	49.3 (4H _β), 9.8 (2H _α), 7.0 (2H _γ)	8
Cyclopent-3-en-1-yl	CFCl ₂ CFCl ₂	130	2.0023	36.8 (4H _β), 20.5 (1H _α)	This work
	CF ₂ CICFCl ₂	105	2.0030	37.6 (4H _β), 21.6 (1H _α)	This work
	(1) or <i>cis</i> -C ₃ H ₆ or C ₂ H ₄	113–373	2.00298	36.9 (4H _β), 21.2 (1H _α), 0.46 (2H _γ)	12

^a Separate couplings to 2H_α and 2H_γ could not be distinguished. ^b Unreported.



corresponds to the precursor of (3), and when recorded at the optimum temperature of 90 K, it shows a good fit to the pattern generated by computer simulation (Figure 2) of hyperfine interactions with 1H_{a1}, 2H_{a2}, and 2H_b in the order of decreasing couplings (Table 1), confirming a preliminary analysis by inspection. The relatively large line width (6 G) means, of course, that unresolved couplings of this magnitude may be present to additional hydrogens.

The hyperfine pattern and parameters of the initial signal carrier are naturally accommodated by the cyclopentane-1,3-diyl radical cation structure (2) with the single symmetry element (σ_h) in the C_s point group. First, the smallest resolved coupling of 11.7 G to 2H_b is readily identified with the 'bridgehead' (methine) hydrogens at the planar spin-bearing carbons, the corresponding α -hydrogens in the cyclohexane-1,4-diyl radical cation having a very similar coupling of 12.0 G.^{1,2} Secondly, the alternative planar (C_{2v}) structure is ruled out by the presence of only three strongly coupled β -hydrogens (1H_{a1} and 2H_{a2}). This finding is in accord, however, with the C_s model (2) in which these hydrogens occupy the 'axial' sites referenced to the axes of the neighbouring p orbitals containing the unpaired electron, the other three β -hydrogens (1H_{e1} and 2H_{e2}) residing in 'equatorial' sites with couplings of less than about 6 G. Indeed, a C_s envelope model using sp^2 -hybridized carbons at the 'bridgehead' positions with a maximum flap angle of *ca.* 40° gives $pC_\alpha-C_\beta-H_\beta$ dihedral angles close to 0° for 2H_{a2} and nearly 90° for H_{e1}, values which are certainly consistent with our results. The reason for the larger coupling to H_{a1} than to 2H_{a2} (Table 1) despite a less favourable angular factor is attributable to two considerations. First, the hydrogens in the single methylene bridge (H_{a1} and H_{e1}) can interact with both p orbitals on the adjacent α -carbons, and secondly, the coupling to H_{a1} can be further augmented by the well-known Whiffen effect,^{9,10} although the quantum mechanical enhancement factor may be significantly less than two in this case because the axes of the two p orbitals are not parallel to each other.

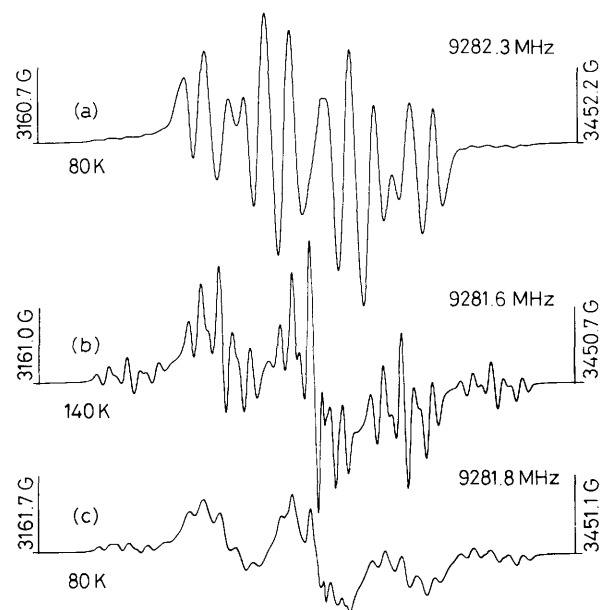


Figure 1. First-derivative ESR spectra of the radical products obtained by γ irradiation of a dilute solution (<1 mol %) of bicyclo[2.1.0]pentane in CF₃CCl₃ at 77 K, showing the effect of matrix annealing. The spectra were recorded consecutively (a) at 80 K, (b) at 140 K, and (c) on subsequent cooling to 80 K, using the same instrumental conditions.

Similar oxidative studies in two other haloethane matrices (CF₂CICFCl₂ and CFCl₂CFCl₂) also provided ESR evidence for the initial formation of (2) from (1), although the transformation of (2) to (3) on annealing could not be followed as clearly in these more mobile matrices because of the onset of bimolecular reactions¹¹ to produce the neutral cyclopent-3-en-1-yl radical¹² (Table 1). Finally, Figure 3 shows the ESR spectra from a corresponding study in the CFCl₃ matrix. It now becomes clear that a mixture of (2) and (3) is produced initially in this case, and that (2) is again converted to (3) on annealing to 110 K.† Given the complexity

† In contrast, it was recently reported that the radical cation derived from bicyclo[1.1.0]butane does not isomerize to the cyclobutene radical cation even at 160 K in CFCl₃: F. Gerson, X.-Z. Qin, C. Ess, and E. Kloster-Jensen, *J. Am. Chem. Soc.*, 1989, **111**, 6456. This difference suggests that the isomerization of (2) to (3) is more likely to be controlled by a 1,3- rather than a 1,2-hydrogen transfer.

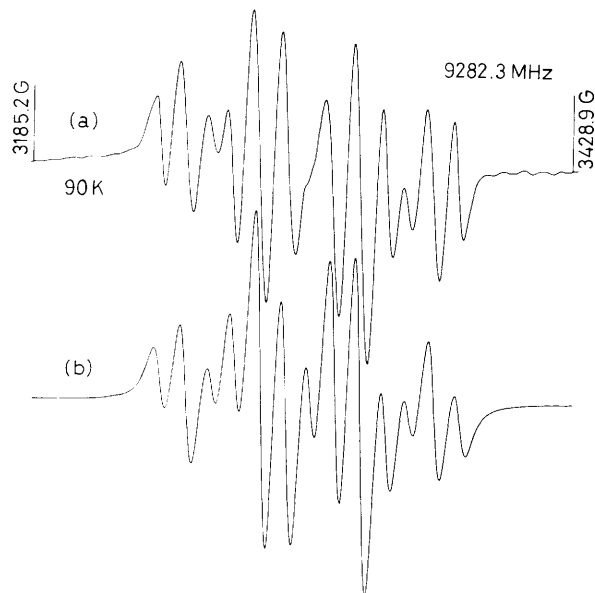


Figure 2. Comparison of the experimental ESR spectrum (a) assigned to the cyclopentane-1,3-diyl radical cation in the CF_3CCl_3 matrix at 90 K (see text) with the computer-simulated spectrum (b) obtained using the parameters in Table 1 and a line width of 6 G.

in the central part of spectrum (a) resulting from the strong overlap between the ESR signals of (2) and (3), it is not surprising that (2) was not previously detected in the CFCl_3 matrix.⁶

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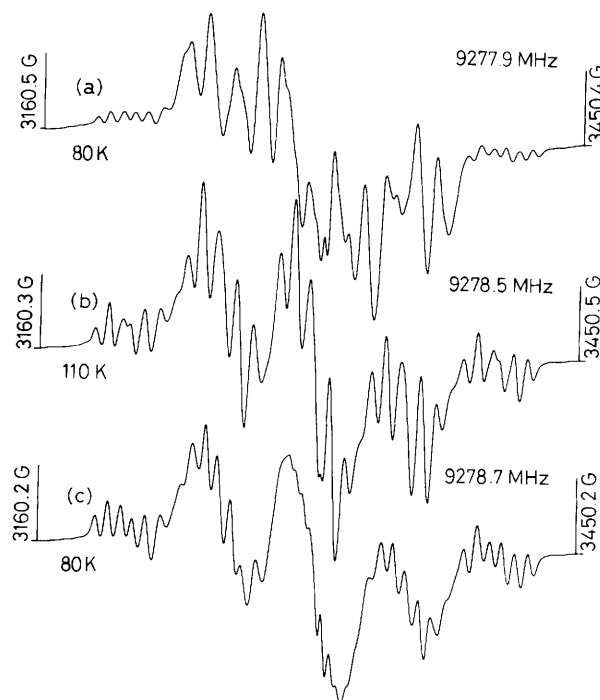


Figure 3. First-derivative ESR spectra of the radical products obtained by γ irradiation of a dilute solution (<1 mol %) of bicyclo[2.1.0]pentane in CFCl_3 at 77 K, showing the effect of matrix annealing. The spectra were recorded consecutively (a) at 80 K, (b) at 110 K, and (c) on subsequent cooling to 80 K, using the same instrumental conditions.

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