Cope Rearrangement of the *endo*-5-Vinylbicyclo[2.2.1]hept-2-ene (*endo*-5-Vinylnorborn-2-ene) Radical Cation to the *cis*-Bicyclo[4.3.0]nona-3,7-diene (*cis*-3a,4,7,7a-Tetrahydroindene) Radical Cation at 100–150 K. A Matrix–isolation ESR Study

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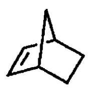
Radical cation 'fingerprinting' by ESR spectroscopy reveals that the radiolytic oxidation of *endo*-5-vinylbicyclo[2.2.1]hept-2-ene **2** leads to the formation of the *cis*-bicyclo[4.3.0]nona-3,7-diene radical cation $\mathbf{3}^{\cdot+}$ by a [3,3]sigmatropic shift at 100–150 K, whereas the neutral Cope rearrangement from **2** to **3** only occurs at 400–440 K.

Despite the growing importance of organic reactions initiated by single-electron transfer (SET),[1] the mechanistic role of the radical cation in such processes is frequently obscure.[2] Thus in photoinduced SET reactions, back electron transfer can occur rapidly to produce a second generation of reactive intermediates. One approach to this difficult problem is to form the radical cation of interest by radiolytic oxidation in a Freon matrix and study its intrinsic reactivity by ESR spectroscopy.[3] We now report evidence obtained in this way that the radical cation of an unsymmetrical 1,5-diene can undergo a [3,3]sigmatropic shift (Cope reaction) with remarkable facility at 100–150 K. This is the first complete demonstration of a normal Cope rearrangement at the radical cation stage, only the Cope-like cyclic transformation of the hexa-1,5-diyne radical cation having previously been reported.[4]



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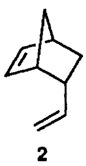

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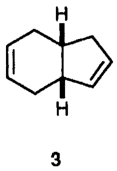


3

A recent study found that the positive hole in the 4-vinylcyclohex-1-ene radical cation is initially localized at the ene rather than the vinyl group.[5] Similarly, the ESR results in Fig. 1 demonstrate that the positive hole resides at the 2-ene group in the radical cations of both norborn-2-ene **1** and *endo*-5-vinylnorborn-2-ene **2**. First, the unresolved ESR spectra at 83–85 K from the oxidation of **1** and **2** are of comparable width (*ca.* 45–50 G; 1 G = 10^{-4} T), and secondly, the ten-line pattern of $\mathbf{1}^{\cdot+}$ resolved at 109 K is simulated by hyperfine couplings of 10.6 G ($2H_\alpha$) and 5.2 G ($2H_\beta$ and $3H_{exo-\gamma}$) in accord with the expected structure for a norborn-2-ene radical cation (Table 1).

On annealing the oxidised sample of **2** in $CF_2ClCFCl_2$ above 100 K, the ESR spectrum underwent an irreversible change to the wider signal form displayed in Fig. 2(*a*). Although this spectrum is contaminated by strong features from the neutral radical produced by bimolecular ion–molecule reactions involving the vinyl group in this mobile matrix,[6,7] careful examination reveals a hint of the same fine structure that characterizes the pattern in Fig. 2(*b*) generated from the corresponding oxidation of *cis*-bicyclo[4.3.0]nona-3,7-diene (*cis*-3a,4,7,7a-tetrahydroindene) **3**, the Cope rearrangement product of **2**.[8,9]

Table 1 ESR parameters for unsaturated bicyclic radical cations of interest

Radical cation	Matrix	T/K	g_{iso}	Hyperfine couplings/G	Ref.
$\mathbf{1}^{\cdot+}$	$CF_2ClCFCl_2$	109	2.0026(5)	10.6 ($2H_\alpha$), 5.2 (5H)[a]	This work
$\mathbf{3}^{\cdot+}$	$CF_2ClCFCl_2$	110	2.0025(5)	5.1 (3H),[b] 15.4 ($1H_\beta$), 30.0 ($1H_\beta$), 50.9 ($1H_\beta$)	This work
Bicyclo[3.2.0]hepta-2,6-diene$^{\cdot+}$	$CFCl_2CFCl_2$	133	2.0026(3)	4.5 ($2H_\alpha$),[c] 22.5 ($1H_\beta$), 31.6 ($1H_\beta$), 41.5 ($1H_\beta$)	*d*
Bicyclo[3.2.1]oct-2-ene$^{\cdot+}$	$CFCl_2CFCl_2$	135	2.0030(3)	5.9 ($2H_\alpha$), 9.6 ($1H_\gamma$),[e] 24.5 ($1H_\beta$), 27.6 ($1H_\beta$), 54.9 ($1H_\beta$)	5

[a] Approximately equal couplings to C1-H_β, C4-H_β, C5-$H_{exo\text{-}\gamma}$, C6-$H_{exo\text{-}\gamma}$, C7-$H_{exo\text{-}\gamma}$. [b] Approximately equal couplings to C7-H_α, C8-H_α, and C5-$H_{exo\text{-}\gamma}$. [c] C2-H_α and C3-H_α. [d] G.-F. Chen, J. T. Wang, F. Williams, K. D. Belfield and J. E. Baldwin, *J. Am. Chem. Soc.*, 1991, **113**, 9853. [e] C7-$H_{exo\text{-}\gamma}$.

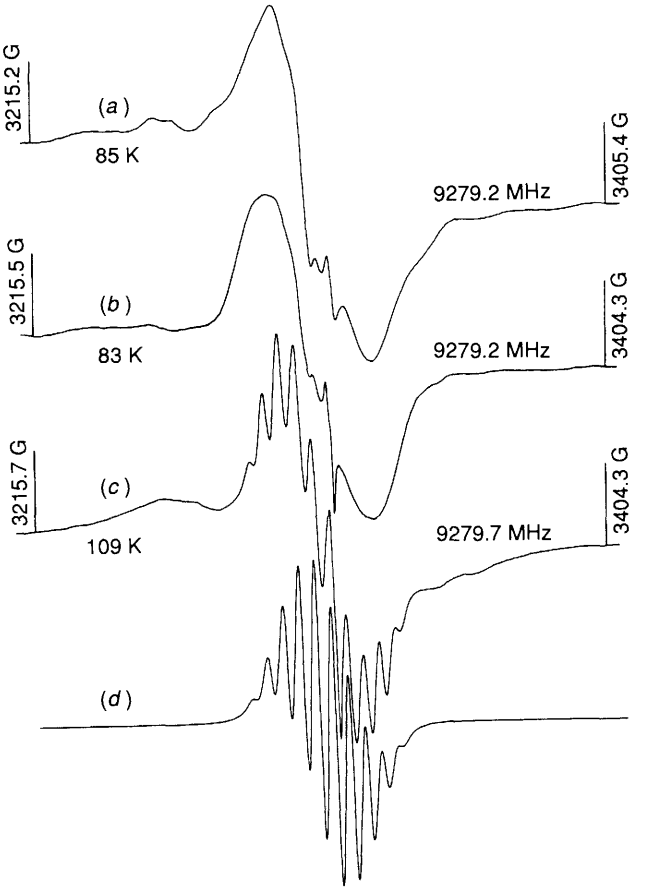


Fig. 1 First-derivative ESR spectra for *ca.* 0.05 mol % solutions of **2** [spectrum (*a*)] and **1** [spectra (*b*) and (*c*)] in $CF_2ClCFCl_2$ recorded at the indicated temperatures after γ irradiation (dose, *ca.* 0.3 Mrad) at 77 K. Spectrum (*a*) is assigned to $\mathbf{2}^{\cdot+}$ and spectra (*b*) and (*c*) to $\mathbf{1}^{\cdot+}$; spectrum (*d*) was simulated using the parameters for $\mathbf{1}^{\cdot+}$ in Table 1 and a linewidth of 3 G.

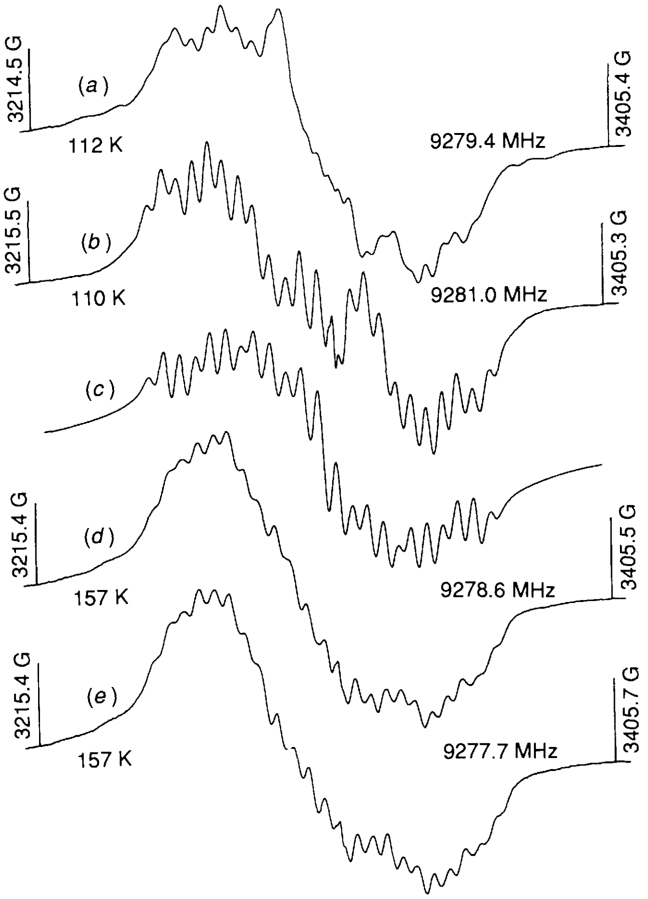
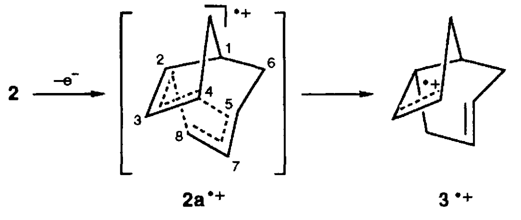


Fig. 2 First-derivative ESR spectra for *ca.* 0.05 mol % solutions of **2** in $CF_2ClCFCl_2$ [spectrum (*a*)] and in CF_2ClCCl_3 [spectrum (*d*)] recorded at the indicated temperatures after γ irradiation (dose, *ca.* 0.3 Mrad) at 77 K. Spectra (*b*) and (*e*) were similarly obtained from solutions of **3** in $CF_2ClCFCl_2$ and CF_2ClCCl_3, respectively, and are assigned together with spectrum (*d*) to $\mathbf{3}^{\cdot+}$; spectrum (*c*) was simulated using the parameters for $\mathbf{3}^{\cdot+}$ in Table 1 and a linewidth of 3 G.



Scheme 1

Convincing evidence for the rearrangement of $\mathbf{2}^{\cdot+}$ to $\mathbf{3}^{\cdot+}$ was obtained in the more rigid CF_2ClCCl_3 matrix. As shown in the lower part of Fig. 2, the 'fingerprint' ESR spectra (*d*) and (*e*) recorded at 157 K after the 77 K oxidation of **2** and **3**, respectively, constitute a perfect match. Moreover, the detailed hyperfine structure of these patterns is clearly the same as that obtained by the oxidation of **3** in $CF_2ClCFCl_2$ [Fig. 2(*b*)]. Accordingly, the signal carrier in each case can be assigned to $\mathbf{3}^{\cdot+}$, the input hyperfine parameters of the computer-simulated spectrum (*c*) being suitably concordant with values reported for radical cations of analogous bicyclic compounds (Table 1).

The [3,3]sigmatropic shift of $\mathbf{2}^{\cdot+}$ to $\mathbf{3}^{\cdot+}$ is likely to proceed through the distorted boat transition state $\mathbf{2a}^{\cdot+}$ shown in Scheme 1. This highly strained structure contrasts with the relaxed chair conformation of the *stable* cyclohexane-1,4-diyl radical cation produced by the oxidation of hexa-1,5-diene,[10,11] and also with the symmetrical boat structure of the *stable* bisallylic radical cation derived from the oxidation of semibullvalene,[12] the formation of these stable species in degenerate systems corresponding to a 'half-Cope' reaction in each case. Therefore, the completion of a radical cation Cope rearrangement along a nondegenerate reaction path seems to be facilitated by a constrained transition structure that fails to attain the stereoelectronic requirements for a stable diyl or bisallylic radical cation. This situation evidently allows the overall reaction to proceed at 100–150 K with only a low (<10 kcal mol^{-1}; 1 cal = 4.184 J) energy barrier, in contrast to the much higher free energy of activation ($\Delta G^{\ddagger}$ = 34 kcal mol^{-1}) for the neutral rearrangement observed at 400–440 K.[8,9]

This research was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy (Grant DE-FG05-88ER13852).

Received, 12th February 1992; Com. 2/00739H

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