## Tricyclo[3.3.1.0<sup>2,8</sup>]nona-3,6-dienyl and Bicyclo[3.2.2]nona-2,6,8-trienyl; A Fluxional Radical Pair

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Tricyclo[3.3.1.0<sup>2,8</sup>]nona-3,6-dienyl and bicyclo[3.2.2]-nona-2,6,8-trienyl radicals form a pair which is rendered fluxional by a series of degenerate cyclopropylmethyl type rearrangements.

Degenerate rearrangements with two or more reaction pathways of equal, or almost equal, free energy are quite rare for free radicals, but are well known for pericyclic processes and carbo-cationic intermediates. One of the best known *reversible* free radical rearrangements is cyclopropylmethyl to but-3-enyl (cpm rearrangement). The equilibrium constant is  $1.3 \times 10^4$  at 298 K,<sup>1</sup> which shows that the ring opened radical is greatly favoured. However, the cyclised form can be important when the molecular architecture is favourable, as it is in polycyclic systems such as the nortricyclyl to norbornenyl rearrangement for which the equilibrium constant is 1.3 at 263 K.<sup>2,3</sup> It seemed possible that this type of rearrangement could be incorporated into an appropriate structure such that the degeneracy could be extended in three dimensions to give a fluxional free radical.

The most symmetrical example appeared to be the tricyclo[ $3.3.1.0^{2.8}$ ]nona-3.6-dienyl (barbaralanyl) radical (1). Scission of the C(1)–C(2) bond should produce the bicyclo[3.2.2]-nona-2.6.8-trienyl radical (2) which has four possibilities for cyclisation back to a radical of type (1) *i.e.* by addition from C(2) to C(1) or C(7) or by addition from C(4) to C(6) or C(9); each of the type (1) radicals so produced can then undergo two different  $\beta$ -scissions. That these rearrangements lead to equivalence of all the carbon atoms at the limit of fast exchange is most easily seen from the partial analysis shown in the Scheme. Thus, cyclisation of (2) occurs from C(4) to C(9) to give (3) which undergoes  $\beta$ -scission of the C(9)–C(5) bond to give (4). In turn (4) cyclises from C(7) to C(1) producing (5) and this process can be repeated until (1) is regenerated. Thus the rearrangement is equivalent to a

sevenfold pseudo-rotation about an axis perpendicular to the C(1)-C(9) bond which can occur in a clockwise or anticlockwise direction. One seventh of the pseudo-rotation is shown in Scheme 1. Cyclisation in the 'plane' of the seven-membered ring, *e.g.* from C(2) to C(7) in (2) (rather than out of the 'plane' as in Scheme 1) shifts the rearrangement into a different, but degenerate, pseudo-rotation in which two different atoms take the place of C(1) and C(9). By a succession of such pseudo-rotations the unpaired electron effectively moves over the whole surface of the structure. Thus (1) and (2) form a unique type of radical pair which should be fully fluxional in three dimensions.

To test this idea, bromide (6) was made from barbaralone<sup>4</sup> by reduction with sodium borohydride (or deuteride) and treatment of the resulting alcohol with phosphorus tribromide. Radical (1) was generated from (6a) by photochemical reaction with hexamethylditin in the cavity of an e.s.r. spectrometer. The spectrum showed only the allyl-type radical (2) throughout the whole temperature range 100-410 K [a(2H) = 1.435, a(1H) = 0.35, a(4H) = 0.30, a(2H) = 0.06 mTat 150 K]. This could indicate either that the proportion of (1)was too small for detection or that the cyclisation step is not viable. The mono-deuteriated material (6b) gave the spectrum of (7) below 200 K but at higher temperatures the spectrum became more complex and too weak for definitive analysis. This behaviour is however, consistent with the onset of fluxionality above 200 K and the consequent formation of a set of four radicals like (7) but with the D-label at each possible site *i.e.* this would produce a weak and complex mixture, as observed.



(9)

(8)

 $7 \underbrace{1}_{6} \underbrace{9}_{5} \underbrace{1}_{6} \underbrace{2}_{5} \underbrace{1}_{4} \underbrace{1}_{6} \underbrace{1}_{5} \underbrace{2}_{4} \underbrace{1}_{6} \underbrace{1}_{5} \underbrace{1}_{4} \underbrace{1}_{6} \underbrace{1}_{5} \underbrace{1}_{4} \underbrace{1}_{6} \underbrace{1}_{6}$ 

Scheme 1

Reduction of (6) with tri-n-butyltin hydride gave a mixture of (8) and (9) in the ratio 1 to 0.14 at 393 K. This is similar to the result obtained by Washburn in his previous study of this reaction.<sup>5</sup> The proportion of (9) increased with increasing temperature, as would be expected if the radical intermediates were in equilibrium. The reduction product from the monodeuteriated bromide (6b), *i.e.* deuteriated (8), had the deuterium label essentially statistically scrambled at 393 K as shown by the 46 MHz <sup>2</sup>H and 75 MHz <sup>13</sup>C n.m.r. spectra. The deuterium label was also distributed to every site in the barbaralane, (9) as had been observed previously.<sup>5</sup> These results confirm the occurrence of the degenerate rearrangement sequence described above and demonstrate the fluxionality of the pair.

The e.s.r. spectrum showed only radicals of type (2) even at the highest temperatures, thus no 'non-classical' state, in which the unpaired electron is delocalised over the whole surface of the structure, and interacts with nine equivalent hydrogens, is reached. This implies that delocalisation of this type does not confer any extra thermodynamic stabilisation on the radical. The fluxionality shown here for the neutral radical pair (1) and (2) is reminiscent of the fluxionality of bullvalene<sup>6,7</sup> but is based on the quite different cpm rearrangement. In bullvalene the fluxionality results from a series of degenerate Cope type rearrangements. Radical (1) can also undergo a degenerate Cope rearrangement, and this probably accompanies the pseudo-rotational process, but it can not lead to the type of deuterium scrambling observed here (see Scheme 1). Further work on the kinetics of the rearrangement and on other examples is in progress.

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