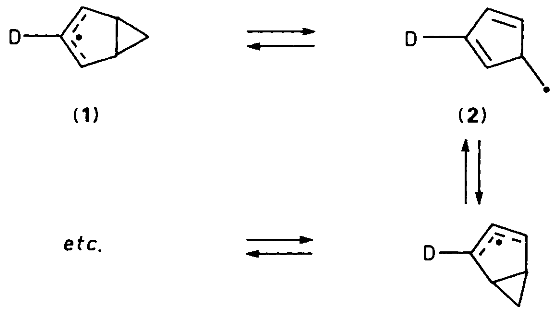
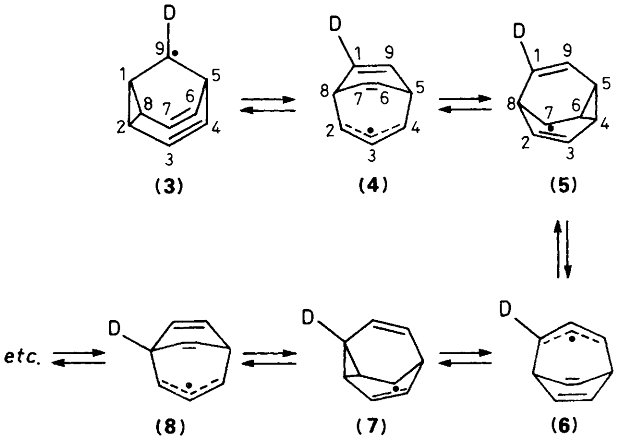
Structural Fluxionality in the Tricyclo[3.3.1.$0^{2,8}$]nona-3,6-dienyl and Bicyclo[3.2.2]nona-2,6,8-trienyl Radicals

John C. Walton
University of St Andrews, Department of Chemistry, St Andrews, Fife, KY16 9ST

E.s.r. observation of radicals derived from 9-bromotricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene, and related compounds, showed that they rearrange by β-scission to bicyclo[3.2.2]nona-2,6,8-trienyl radicals extremely rapidly; the latter radicals have hyperfine splittings similar to those of allyl radicals. 9-Deuterio- and 2-deuterio-9-bromotricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene were reduced with tributyltin hydride. The pattern of deuterium scrambling in the bicyclo[3.2.2]nona-2,6,8-triene and tricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene products showed that the intermediate radicals take part in a degenerate rearrangement sequence which makes them fully fluxional in three dimensions. The two radicals are in equilibrium at *ca.* 375 K, but the bicyclotrienyl species is more important by a factor of *ca.* 10^2. Neither the experimental results nor MNDO semiempirical calculations provided any evidence of additional thermodynamic stabilisation in the radical pair beyond that expected for allyl delocalisation.

The β-scission of cyclopropylmethyl radicals to give but-3-enyl radicals is extremely rapid and many examples of this type of process are known. The reverse reaction, cyclisation of but-3-enyl, is much slower[1] so that in normal solution-phase reactions only ring-opened products can be observed. However, if this structural unit is incorporated into a bi- or poly-cyclic system, the architecture can favour cyclisation. This occurs, for example, in the nortricyclyl to norbornenyl rearrangement which has an equilibrium constant of[2,3] 1.3 at 263 K, and is therefore nearly degenerate. Rearrangements which are degenerate, or nearly so, can lead, in appropriate molecules, to fluxional or even 'non-classical' behaviour. Many studies have shown that neutral free radicals do not exhibit 'non-classical' behaviour[4,5] but fluxionality, where the bonds of the basic structure undergo a process of continual making and breaking, seems entirely possible. One example of this, involving the cyclopropylmethyl to but-3-enyl rearrangement (CPM rearrangement), can be recognised in the behaviour of bicyclo[3.1.0]hexenyl radicals (1). Deuterium-substituted radicals were found to give products in which the deuterium atom was statistically distributed.[6] Effectively, the methylene unit undergoes 'circumambulation' about the five-membered ring by a process of successive β-scission of the CPM unit in (**1**) and cyclisation of the butenyl unit in (**2**).[6,7] Thus the basic structure is fluxional in two dimensions and alternates between the bicyclic structure (**1**) and the monocyclic structure (**2**).

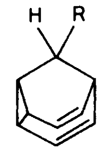




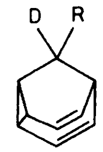
Scheme 1.

It seemed possible that this type of rearrangement could be incorporated into a tricyclic molecule where the degeneracy would lead to fluxionality in three dimensions. The most symmetrical example appeared to be the tricyclo[3.3.1.$0^{2,8}$]-nona-3,6-dienyl (barbaralanyl) radical (**3**). β-Scission of the C(1)–C(2) bond produces the bicyclo[3.2.2]nona-2,6,8-trienyl radical (**4**) which has four possibilities for cyclisation (see Scheme 1). Addition from C(4) to C(6) is shown to give (**5**) which has two possibilities for β-scission. The C(6)–C(5) scission gives (**6**) and repetition of this process leads in turn to (**7**), (**8**), *etc.* The structure alternates between the tricyclo type (**3**), (**5**), (**7**). *etc.* with a localised radical site, and the bicyclo type (**4**), (**6**), (**8**), *etc.* in which the unpaired electron experiences allyl-type delocalisation. At sufficiently fast exchange rates each C-atom occupies in turn every possible site and the unpaired electron moves in turn to every site. Thus, radicals (**3**) and (**4**) form a pair which renders the structure fully fluxional in three dimensions. It also seemed possible that the effective delocalisation of the unpaired electron over the whole surface of the radical might confer additional thermodynamic stabilisation on this species.

In the only previous study of the barbaralanyl radical (**3**), complete scrambling of the deuterium label was observed.[8] This was tentatively attributed to a type of non-classical structure which rendered the radical totally degenerate. In this paper



(9) a; R = OH
b; R = OSiMe$_3$
c; R = Br



(10) a; R = OH
b; R = Br

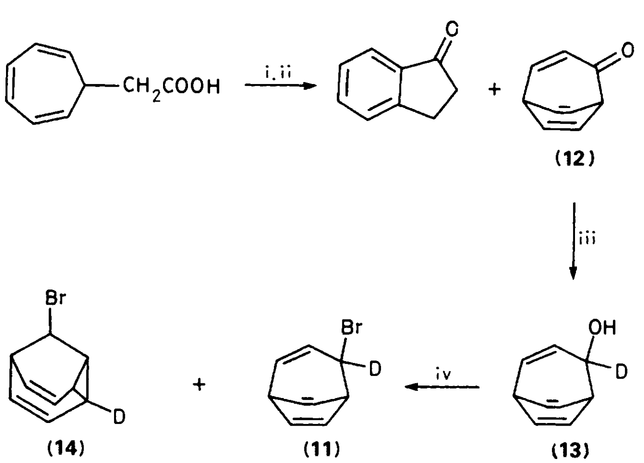
we report our study of barbaralanyl radicals using e.s.r. spectroscopy and deuterium labelling; part of this work has been published as a preliminary communication.[9]

Results and Discussion

Preparation of Radical Precursors.—Tricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-one (barbaralone) was prepared from the dianion of cyclo-octatetraene *via* bicyclo[4.2.1]nona-2,4,7-trien-9-one using the method of Shechter and co-workers.[10] The unlabelled compounds (**9a–c**) were made from the ketone using standard methods (see the Experimental section). The deuterium-labelled compounds (**10a, b**) were made by reduction of the ketone with sodium borodeuteride and secondly, treatment of the alcohol with phosphorus tribromide.

Attempts were also made to synthesise 3-bromobicyclo-[3.2.2]nona-2,6,8 triene (**11**). Ketone (**12**) was obtained, together with indan-1-one on treatment of cycloheptatrienylacetyl chloride with triethylamine. The ketone was purified by chromatography on silica and reduced to the deuterium-labelled alcohol (**13**) on treatment with sodium borodeuteride (Scheme 2). The alcohol (**13**) was then treated with phosphorus tribromide at 0 °C but, interestingly, this gave almost entirely rearranged bromide (**14**); even when the reaction was carried out at −78 °C only 13% of (**11**) was obtained. Previous work on the solvolysis of 4-bicyclo[3.2.2]nonatrienyl nitrobenzoates showed that the cation from (**13**) is rapidly transformed into the 9-barbaralyl cation;[11–13] the reaction of (**13**) with PBr_3 is evidently another example of this process. On the other hand, 9-barbaralanyl anions[11,13,14] and radicals (see below) preferentially rearrange to the bicyclo[3.2.2]nonatrienyl form.

Electron Spin Resonance Study.—The bromide (**9c**), triethylsilane and di-t-butyl peroxide were dissolved in propane solvent, degassed, and photolysed in the cavity of the e.s.r. spectrometer. The photochemically formed t-butoxyl radicals abstract hydrogen from triethylsilane producing triethylsilyl radicals which preferentially abstract bromine from (**9c**). The e.s.r. spectrum showed a large triplet hyperfine splitting (hfs), doublet and quartet hfs, together with a second small triplet hfs, and was attributed to the bicyclo[3.2.2]nonatrienyl radical (**15a**). This identification was confirmed by direct generation of (**15a**) by hydrogen abstraction from bicyclo[3.2.2]nona-2,6,8-triene with t-butoxyl radicals. Essentially identical spectra were observed using these two routes. The spectra were unchanged, apart from minor variations in the hfs, in the temperature range 100–410 K. Where comparable, the hfs are closely similar to those of allyl radicals. Thus $a(H^{2,4})$ for (**15a**) (Table 1) is very similar to $a(H^{1,3}$, *anti*) in allyl (1.48 mT).[15] Under similar e.s.r conditions, unrearranged cyclopropylmethyl radicals can be observed at temperatures below *ca.* 150 K. The fact that only the fully rearranged radical (**15a**) was observed even at 100 K shows that scission of the three-membered ring in radical (3) occurs more rapidly than in the archetypal cyclopropylmethyl radical.



Scheme 2. *Reagents:* i, $(COCl)_2$, 0 °C: ii, Et_3N, 72 h; iii, $NaBD_4$–MeOH; iv, PBr_3, −78 °C.

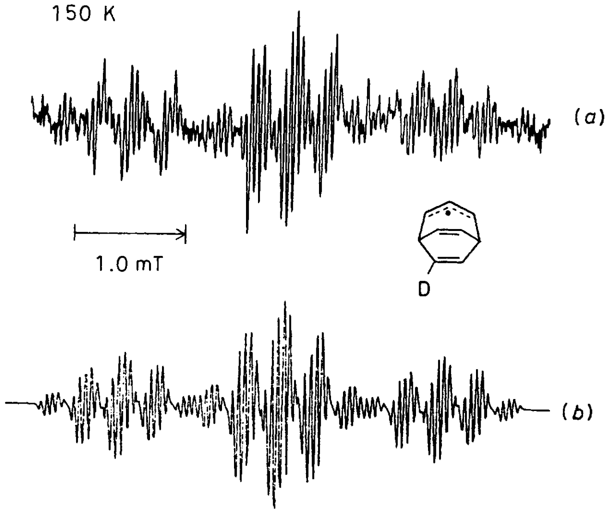
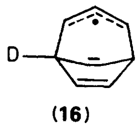


Figure 1. 9.4 GHz e.s.r. spectrum of radical (**15a**) in cyclopropane solution at 150 K. (*a*) experimental; (*b*) computer simulation.



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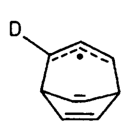

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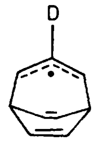
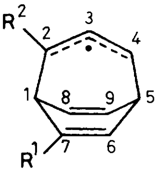


(18)

The e.s.r. spectrum obtained from the monodeuterio bromide (**10b**) at 150 K is shown in Figure 1. The initially formed 9-deuteriobarbaralanyl radical (3) can undergo two different β-scissions both of which produce the same type of radical, *e.g.* (**4**) with the deuterium substituent on one of the double bonds. The spectrum was readily analysed; the hfs are in Table 1 and the computer simulation is shown in Figure 1. If the sequence of cyclisations and β-scissions indicated in Scheme 1 were important, four different D-substituted radicals, *i.e.* (**4**) and (**16**)–(**18**) should be produced. At temperatures above *ca.* 200 K the spectrum weakened dramatically and became too complex to interpret. This behaviour is consistent with the onset of fluxionality above 200 K, because the mixture of four D-labelled radicals would produce just such a weak, complex spectrum. In contrast, the spectrum of unsubstituted radical (**15a**) remained strong even at 300 K and was detectable above 400 K, which strengthens the conclusion that rearrangement commences at *ca.* 200 K.

Table 1. E.s.r. parameters of bicyclo[3.2.2]nonatrienyl radicals.[a,b]



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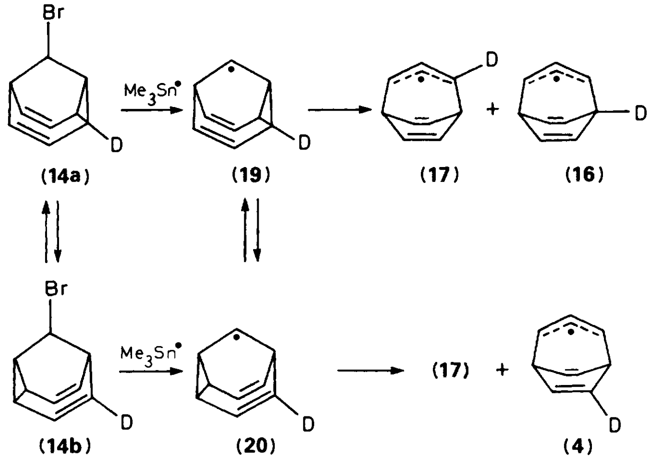
	Radical			hfs/mT				
	R^1	R^2	T/°C	$H^{2,4}$	H^3	$H^{6,9}$	$H^{1,5}$	H^{other}
(15a)	H	H	150	1.43	0.35	0.30	0.06	
(15a)	H	H	INDO[c]	[−1.31]	[0.64]	[0.53]	[0.07][c]	
(15b)	D	H	150	1.43	0.35	0.29	0.055	0.045 (D)
(15c)	H	D	150	1.42	0.35	0.29	0.06	0.24 (D)
(15d)	OH	H	250	1.46	0.38	0.35	*d*	
(15e)	$OSiMe_3$	H	270	1.46	0.38	0.34	*d*	
(15f)	H	OH	220	1.38	0.29	0.20	0.09	0.09 (OH)

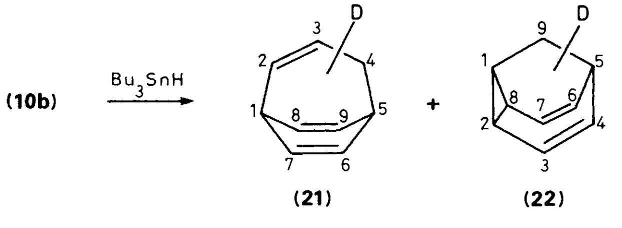
[a] Spectra at 9.3 GHz in hydrocarbon solution. [b] All *g* factors 2.003 ± 0.001. [c] Semiempirical INDO calculation with MNDO calculated geometry $\langle S^2 \rangle = 0.8166$ (see the text). [d] Line width too large for resolution.



Scheme 3.

The e.s.r. spectrum from the bromide (**14**) was rather complex even at 150 K. The reactant itself can undergo a divinylcyclopropane (Cope type) rearrangement to give the isomeric (**14b**) with the deuterium at a different position (Scheme 3). Radicals (**19**) and (**20**), produced by bromine abstraction, can each undergo two β-scissions so that a mixture of three radicals (Scheme 3) will be formed. Computer simulations were made for mixtures containing the pairs (**17**) + (**16**) and (**17**) + (**4**), but satisfactory agreement with experiment was only obtained if all three isomeric radicals were included. The free energy of activation for the divinylcyclopropane-type rearrangement in barbaralane[16,17] and derivatives[18] is *ca.* 8 kcal mol^{-1}.* This process will be very slow on the e.s.r. timescale at 150 K for both the bromide (**14**) and radicals (**20**) and (**21**). It is most probable that the reactant bromide (**14**), when handled at room temperature, gives a 50:50 equilibrium mixture of (**14a**) and (**14b**) (ignoring isotope effects) and the 46 MHz ^2H n.m.r. spectrum of (**14**) confirmed this (see the Experimental section). It is this room temperature equilibrium which leads to the formation of all three possible isomeric radicals at 150 K. Several substituted bicyclo[3.2.2]nonatrienyl radicals were generated by hydrogen abstraction from substituted barbaralanes and the e.s.r. parameters are in Table 1. As expected, the HO and Me_3SiO substituents at C(7) had little effect on the hfs. The hfs of the 2-hydroxy radical were slightly reduced; just as were the hfs of *anti*-1-hydroxyallyl radicals,[19] relative to the unsubstituted parent.

Tin Hydride Reduction of (**9c**), (**10b**), *and* (**14**).—Reaction of the unlabelled bromide (**9c**) with tributyltin hydride under the usual free-radical conditions gave a mixture of bicyclo[3.2.2]nona-2,6,8-triene and barbaralane at all accessible temperatures, with the former in large excess. The 9-deuterio bromide (**10b**) was allowed to react in the same way, the two products (**21**) and (**22**) were separated by preparative g.l.c. and the distribution of the D label was monitored by n.m.r. spectroscopy. The ^2H and ^{13}C n.m.r. spectra of the bicyclotriene (**21**) showed that it consisted of a mixture of all seven possible isomers each containing one D atom at a different site. The reaction was carried out at a series of temperatures and the relative proportion of the D label at each site was determined by integration of the ^2H n.m.r. signal of the separated bicyclotriene. The results (Table 2) showed that for temperatures above *ca.* 375 K the D label was essentially statistically scrambled to every site. This confirms the occurrence of the degenerate rearrangement sequence described above and demonstrates the fluxionality of the pair of radicals (**3**) and (**4**).



That the series of β-scissions and cyclisations shown in Scheme 1 should lead to scrambling of the D label to every C atom in the limit of fast rearrangement is most easily seen from the analysis given in Scheme 4. The radical first generated from (**10b**) *i.e.* (**3**) rapidly undergoes β-scission to give either (**4**) or (**23**). In (**4**) cyclisation from C(9) gives localised radical (**24**); β-

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* 1 cal ≡ 4.18 J.

Table 2. Deuterium scrambling in bicyclo[3.2.2]nona-2,6,8-trienes (**21**) determined by 46 MHz ^2H n.m.r. spectroscopy.

Reactant	H or[a] D	T/K[b]	Site[c] C(6,9)	C(7,8)	C(2)	C(3)	C(1)	C(5)	C(4)
(**10b**)	SnH	stat.[d]	2	2	1	1	1	1	1
(**10b**)	SnH	434	[2.0]	2.0	0.90	0.96	1.04	1.02	0.88
(**10b**)	SnH	390	[2.0]	2.0	0.90	0.98	0.94	0.92	0.80
(**10b**)	SnH	348	[2.0]	2.0	0.62	0.98	0.74	0.60	0.80
(**10b**)	SnH	313	[2.0]	2.0	0.40	0.90	0.32	0.28	0.52
(**10b**)	SnH	273	[2.0]	2.0	0.28	0.68	0.12	0.12	0.44
(**10b**)	SnH	250	[2.0]	2.0	0.32	0.48	0.28	0.22	0.28
(**10b**)	SnD	stat.[d]	2	2	1	1	1	1	10
(**10b**)	SnD	377	[2.0]	2.0	1.05	1.05	1.05	1.02	9.93
(**14**)	SnH	stat.[d]	2	2	1	1	1	1	1
(**14**)	SnH	403	[2.0]	2.0	1.0	1.0	1.2	1.2	1.1

Deuterium scrambling in barbaralane (**22**)

			C(3,7)	C(2,4,6,8)	C(1,5)	C(9)
(**10b**)	SnD	stat.[d]	2	4	2	10
(**10b**)	SnD	377	3.1	4.2	[2.0][e]	11.3

[a] SnH; Bu_3SnH reduction, SnD; Bu_3SnD reduction. [b] Temperature of the tin hydride reduction. [c] Calculated from ^2H n.m.r. integral relative to the integral for the C(6,9) position. Error limits ±0.1. [d] Statistical ratio for complete scrambling. [e] Results relative to C(1,5) site; error limit ±0.8.

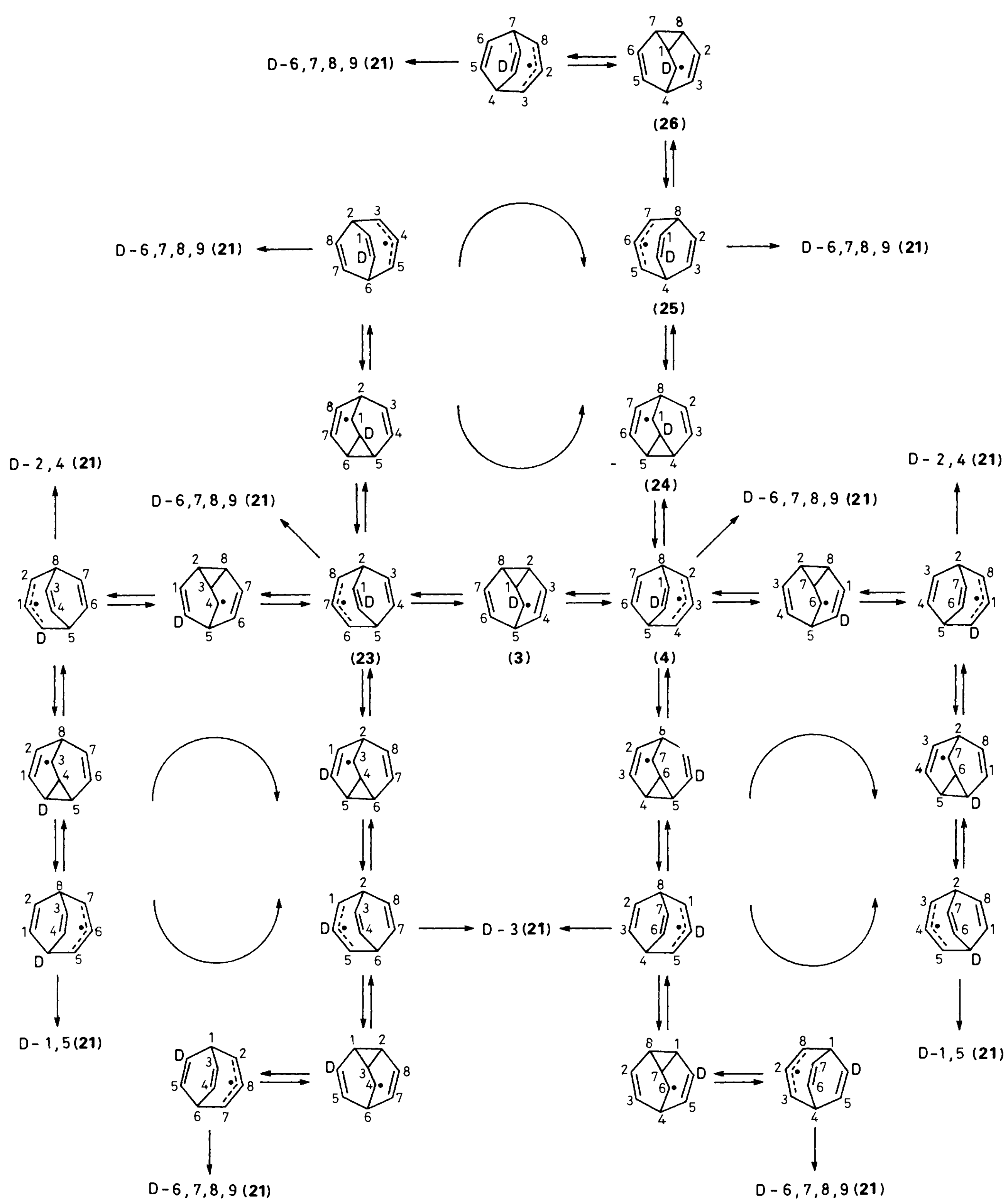
scission of C(5)–C(9) in (**24**) leads to radical (**25**) which can cyclise by addition from C(7) to C(1) to give (**26**). This process can be repeated until (**3**) is regenerated and is thus equivalent to a sevenfold pseudo-rotation about an axis perpendicular to the C(1)–C(9) bond. Part of this pseudo-rotation is shown in the upper cycle in Scheme 4. Cyclisation from C(2) to C(7) in (**4**) leads to the start of a second sevenfold pseudo-rotation about an axis perpendicular to the C(6)–C(7) bond (Scheme 4). Similarly a third pseudo-rotation about an axis perpendicular to the C(3)–C(4) bond is shown. Each allyl type radical can take part in two pseudo-rotations so that every possible pair of atoms forms the rotation axis in turn. Radicals (**4**) and (**23**) are formed first by the extremely rapid β-scission of (**3**) so that the D label can appear at C(6) to C(9) irrespective of any fluxional behaviour. C(7) and C(8) are equivalent, as are C(6) and C(9) (except when the D label is at C(4): but the difference was not resolvable by ^2H n.m.r. spectroscopy in this case) and these were taken as the reference sites for the data in Table 2.

On the basis of Scheme 4 we predict that the D label should be equally distributed at C(6) to C(9) even before the onset of fluxionality because no cyclisation steps are involved and because hydrogen abstraction from Bu_3SnH by the allyl type radical will be essentially equally probable at either end of the delocalised system. Table 2 shows that this is the case at temperatures down to 250 K. A minimum of one cyclisation step is required for formation of the 2- and 4-deuterio derivatives and for the formation of the 3-deuterio derivative (Scheme 4). We would expect incorporation at these sites to occur next and Table 2 shows that as the temperature increases D incorporation at C(2) and C(4) increases to roughly the same extent. D incorporation at C(3) outpaces that at C(2) and C(4) probably because a statistical factor of two favours the former. The minimum number of cyclisation steps from radical (3) required for formation of 1-and 5-deuterio derivatives is two (Scheme 4) hence we expect D incorporation to be slowest at these sites and Table 2 shows that the extent of D incorporation is indeed least at these two sites at the lower temperatures.

The monodeuterio bromide (**10b**) was also reduced with tributyltin deuteride and the pattern of incorporation of deuterium was again measured from the ^2H n.m.r. spectrum of the isolated bicyclotriene. As Table 2 shows, the experimental result at 377 K is close to the statistical prediction based on Scheme 4. In the reductions with Bu_3SnH the yield of barbaralane (**22**) was only about 1% that of the bicyclotriene (**21**). The ^1H n.m.r. spectrum indicated extensive D scrambling, but the isolated material was insufficient for ^2H n.m.r. spectra. However, in the Bu_3SnD reductions the yield of (**22**) was greater and the ^2H n.m.r. spectrum was obtained on the material isolated from the 377 K reaction. In product (**22**) the divinylcyclopropane-type rearrangement is fast at the temperature of the n.m.r. probe and hence C(1) and C(5) are effectively equivalent, as are C(2), C(4), C(6), and C(8). The error limits on the deuterium proportions were large in this case because of the weak sample but Table 2 shows that the experimental D distribution is close to statistical. As a cross check the monodeuterio bromide (**14**) was also reduced with Bu_3SnH and the products examined as before. Table 2 shows that the experimental pattern of D incorporation was again close to statistical at 403 K. Overall, the experimental results show that although there is some deuterium scrambling even at 250 K, the radical pair does not become fully fluxional until about 375 K.

The (**21**)/(**22**) concentration ratio was measured from a series of reductions of both the undeuteriated bromide (**9c**) and the 9-deuterio bromide (**10b**) at different temperatures and the results are shown graphically in Figure 2. At lower temperatures where cyclisation is unimportant the ratio [(**21**)]/[(**22**)] is proportional to the rate constant ratio[20] k_f/k_H where k_f refers to the rate of β-scission of (**3**) and k_H is the rate constant for hydrogen abstraction from Bu_3SnH by radical (**21**). A steep increase in [(**21**)]/[(**22**)] with increasing temperature is therefore expected and Figure 2 shows this in the range 200–300 K. The results at the lowest temperatures do not show the expected monotonic trend. This is probably an experimental artifact because the reactants partly crystallised from solution during the long photolysis times necessary at these temperatures. The graph passes through a maximum in the range 300–370 K, due to the onset of the cyclisation step, before setting into a decreasing trend above *ca.* 375 K where fluxionality is fully established and the two radicals are in equilibrium. This corresponds well with the conclusions reached from the deuterium labelling experiments. In this high-temperature region the product ratio is given by equation (1), where k_c is the rate constant for the cyclisation

$$[(\mathbf{21})]/[(\mathbf{22})] = k_f/(k_c + k_H[Bu_3SnH]) \qquad (1)$$



Scheme 4.

step. A rough estimate of k_c may be obtained by making the reasonable assumption that k_H is the same as that of primary and secondary alkyl radicals.[21] The e.s.r. spectra showed radical (**3**) to be fully ring-opened at 100 K, hence the activation energy for β-scission, E_f, must be ≤ 5 kcal mol^{-1}. For most ring-fission reactions of radicals[22] $\log(A_f/s^{-1}) = 13$ and if this data is used in the above equation with the [(**21**)]/[(**22**)] value from Figure 2 then k_c (380 K) $\geq 1.3 \times 10^8$ s^{-1} is obtained. As expected, this is considerably greater than the rate constant for but-3-enyl cyclisation which is[1,2] 1.3×10^5 s^{-1} at 380 K, but is gratifyingly close to the known rate constant for cyclisation of the norbornenyl radical[3] *i.e.* 2×10^8 s^{-1} at 380 K.

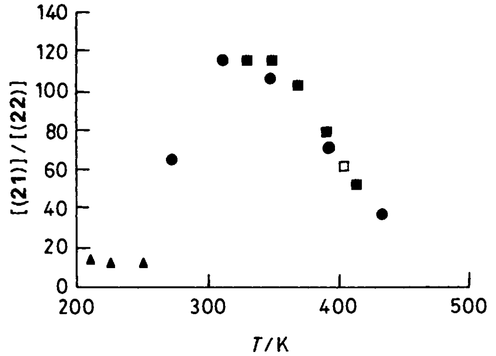
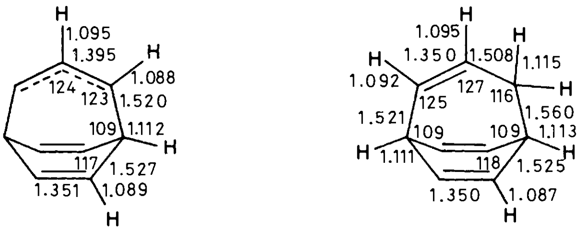


Figure 2. Temperature dependence of the concentration ratio of bicyclotriene (**21**) to barbaralane (**22**): ▲, (**10b**) reduction in ether; ●, (**10b**) reduction, neat; ■, (**9c**) reduction in hexadecane; □, (**9c**) reduction, neat.



(4) **(27)**

Figure 3.

Stabilisation of the (**3**)–(**4**) *Radical Pair; Semiempirical Calculations*.—In the limit of fast fluxionality the unpaired electron is delocalised over the whole surface of the radical and each C atom becomes effectively equivalent. In fact, the nine C atoms can never be *instantaneously* equivalent because a regular polyhedron with nine vertices (Platonic or Kepler–Poinsot type) cannot exist.[23] The nine C atoms take on effective equivalence in a chemical reaction because of the dynamic process which moves the electron from one to another. The delocalisation of the electron which results from fluxionality in the (**3**)–(**4**) pair is therefore different from the delocalisation present in say the allyl radical. No matter how fast the pseudorotational cycles become in (**3**) and (**4**) all sites never become instantaneously equivalent and hence a stationary state with one ninth of the electron density at each C atom cannot be set up. Could the dynamic delocalisation in the (**3**)–(**4**) pair lead to some form of stabilisation, *i.e.* a lowering of the energy? Experimentally the e.s.r. spectra showed the lifetime of radical (**4**) to be similar to that of most carbon-centred radicals, including allyl, in solution. As expected therefore there is no significant kinetic stabilisation of (**4**). To test for thermodynamic stabilisation in (**3**) or (**4**) a measurement of the radical enthalpy of formation or of the bond dissociation energy of a radical precursor is required. Quantitative data of this sort cannot be obtained from the experiments in this paper. Radical (**4**) is certainly formed preferentially on hydrogen abstraction from bicyclo[3.2.2]nona-2,6,8-triene but this indicates no more than the normal allyl stabilisation of (**4**).

The structures of (**4**) and bicyclo[3.2.2]nona-2,6,8-triene (**27**) were computed using the MNDO semiempirical approach[24] (Figure 3). These structures show that (**4**) is a 'normal' allyl-type radical. The C–C and C–H bond lengths and the bond angles of the allyl unit in (**4**) are similar to those computed for allyl itself. Comparison of the rest of the structure of (**4**) with that of (**27**) gives no hint that there is any significant electron delocalisation into this region. The computed structure of (**4**) was used for an INDO[25] calculation of the e.s.r. hfs (Table 1). The calculated hfs are quite close to the experimental, although the INDO results do suggest slightly enhanced spin density at C(6)–C(9). Apart from this minor variation the spin density distribution is virtually the same as that in allyl radicals and no extra stabilisation is indicated.

The stabilisation energy E_S of the radical relative to that of methyl (E_S^{MeH}) is given by equation (2).[26,27] The ΔH_f° values

$$E_S^{MeH}(4) = \Delta H_f^\circ(CH_3^\cdot) - \Delta H_f^\circ(CH_4) - [\Delta H_f^\circ(4) - \Delta H_f^\circ(27)] \quad (2)$$

of (**4**) and (**27**) computed by the MNDO method were 72.7 and 47.0 kcal mol^{-1}, respectively. Thus the computed stabilisation energy of (**4**) was 26.3 kcal mol^{-1}. This is significantly higher than the E_S^{MeH} of allyl computed by the same method[26] *viz.* 21.5 kcal mol^{-1}. However, (**4**) is effectively an alkyl-substituted allyl radical and it seemed likely the extra stabilisation was due simply to inductive/hyperconjugative effects from the substituents. The E_S^{MeH} of *syn*-1,3-dimethylallyl radicals was therefore computed with the CH_3 groups fixed in that conformation with one hydrogen from each eclipsing the *anti*-hydrogens at C(1) and C(3), *i.e.* the conformation most like that of (**4**). The MNDO calculated E_S of *syn*-1,3-dimethyallyl was found to be 26.3 kcal mol^{-1}. The similarity of this result to that for (**4**) shows that the MNDO method does not find any stabilisation in this system beyond that due to the allyl-type delocalisation.

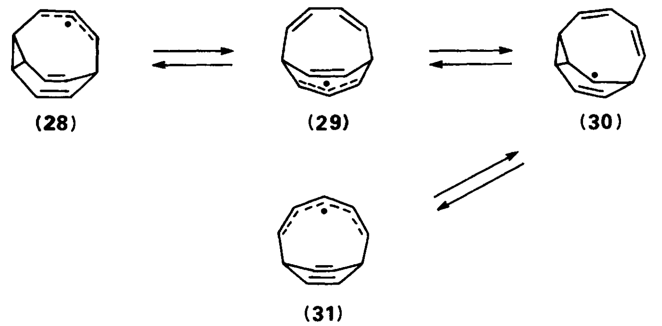
Conclusions

The experimental results demonstrate that the $C_9H_9^\cdot$ pair, (**3**) and (**4**), does rearrange according to the mechanism of Scheme 4. The deuterium scrambling becomes detectable at 200 K under e.s.r. conditions, but full fluxionality is not established until *ca.* 375 K. The bicyclo[3.2.2]nonatrienyl form predominates; the equilibrium constant (k_f/k_c) being *ca.* 100 at 380 K. The preference for structure (**4**) can probably be attributed to the allyl stabilisation in this radical and the results do not indicate any additional thermodynamic stabilisation. The corresponding pair of carbanions behave in a similar fashion *i.e.* the bicyclo-[3.2.2]nonatrienyl structure predominates, and rearrangement probably occurs by a route similar to that of Scheme 4.[11] However, the barbaralanyl carbocation is strongly stabilised in the tricyclic form giving a totally degenerate structure which rapidly rearranges at low temperatures by a divinylcyclopropylmethyl cationic route which does not involve the bicyclo-[3.2.2]nonatrienyl cation.[12,28–30] At higher temperatures the barbaralanyl cation rearranges to the 1,4-bishomotropylium ion.[12,28–30]

Amongst the other structures which might be rendered fluxional by the CPM type rearrangement, that of the tricyclo[4.3.2.0^{2,9}]undeca-3,7,10-trien-5-yl-radical (**28**) appears the most interesting. This radical is potentially capable of fluxionality *via* the four structures (**28**)–(**31**); the sites being exchanged by degenerate rearrangements equivalent to both sevenfold and ninefold pseudo-rotations. Full fluxionality will probably require high temperatures because the delocalised radical (**28**) will undergo β-scission much more slowly than (**3**).

Experimental

E.s.r. spectra were recorded with a Bruker ER 200D spectrometer on degassed solutions in Spectrosil tubes, irradiated with light from a 500 W super-pressure Hg arc. ^1H, ^{13}C, and ^2H n.m.r. spectra were obtained at 300, 75, and 46 MHz, respec-



tively, on a Bruker AM 300 spectrometer utilising $CDCl_3$ solutions at ambient temperature with $SiMe_4$ as an internal standard. G.c.–m.s. analyses were carried out with a Finnegan Incos instrument fitted with a HP1 capillary column. Preparative g.l.c. employed a Pye-Unicam 105 chromatograph with 5 m × 1 cm glass columns packed with 20% FFAP on Chromosorb WAW.

Tricyclo[3.3.1.0^{2,8}]*nona*-3,6-*dien*-9-*one* (*Barbaralone*).—This was made from bicyclo[4.2.1]nona-2,4,7-trien-9-one by the photochemical method of Shechter and co-workers[10] with Michler's ketone as photosensitiser; m.p. 49–51 °C (lit.,[10] 50–51 °C).

9-*Hydroxybarbaralane* (**9a**).—Sodium borohydride (0.6 g) was added in small portions to barbaralone (2.0 g) in MeOH (120 cm^3) and the solution was stirred for 24 h. The solvent was evaporated and aqueous $NaHCO_3$ (10%; 50 cm^3) was added. The solution was extracted with ether (3 × 100 cm^3), dried (Na_2SO_4), and evaporated and the product was recrystallised from pentane (1.6 g, 79%), m.p. 88–89 °C (lit.,[16] 88–90 °C) δ_H 1.18 (1 H, d, *J* 10 Hz), 2.55 (2 H, q, *J* 4 Hz), 3.62 (1 H, d, *J* 10 Hz), 3.96 (2 H, m), 4.00 (2 H, m), 5.54 (1 H, t, *J* 7 Hz), 5.88 (1 H, t, 7 Hz); δ_C 31.67, 62.36, 72.13, 76.25, 120.79, and 123.13.

9-*Trimethylsilyloxybarbaralane* (**9b**).—To the alcohol (**9a**) (0.5 g, 3.7 mmol) and pyridine (0.3 g, 3.7 mmol) in pentane (30 cm^3) was added trimethylsilyl chloride (0.41 g, 3.7 mmol) drop by drop. The mixture was stirred for 1 h at ambient temperature, filtered and distilled on a vacuum line after removal of the solvent (0.6 g, 79%); δ_H 0.11 (9 H, s), 2.36 (1 H, dt, *J* 4, 8 Hz), 2.52 (1 H, dt, *J* 4, 8 Hz), 3.65 (1 H, dt, *J* 15, 5 Hz), 3.92–3.14 (4 H, m), 5.53 (1 H, t, *J* 7 Hz), and 5.85 (1 H, t, *J* 7 Hz); δ_C 0.28, 31.29, 63.45, 72.51, 75.56, 120.74, and 121.47. A minor amount of unchanged alcohol was present.

9-*Deuterio*-9-*hydroxybarbaralane* (**10a**).—Barbaralone (2.0 g) was reduced with sodium borodeuteride (0.65 g) using the method described for (**9a**); (yield 1.7 g, 83%) m.p. 89–90 °C, δ_H 1.27 (1 H, s), 2.54 (2 H, t, *J* 7 Hz), 3.99 (2 H, m), 4.12 (2 H, m), 5.55 (1 H, t, *J* 8 Hz), and 5.90 (1 H, t, *J* 8 Hz).

9-*Bromobarbaralane* (**9c**).—To the alcohol (**9a**) (1.0 g, 7.5 mmol) and pyridine (0.31 cm^3) in dry ether (20 cm^3) cooled in an ice–salt bath, was added PBr_3 (0.37 cm^3, 3.8 mmol) drop by drop. The mixture was stirred for 2 h whilst it was warmed to room temperature, then water (20 cm^3) was added. The ether layer was washed with 2 mol dm^{-3}, H_2SO_4, saturated aqueous $NaHCO_3$, and dried (Na_2SO_4) and the solvent was distilled off. The residue was extracted with pentane which, on evaporation, gave a clear oil (0.75 g, 51%) which crystallised at *ca.* −10 °C. Attempts to purify the bromide by distillation and column chromatography on silica gel led to significant decomposition. The clear oil was bromide (**9a**) with *ca.* 10% dibromobarbaralane. δ_H 2.73 (2 H, dt, *J* 8, 2 Hz), 4.02 (1 H, t, *J* 2 Hz), 4.10 (4 H, m), 5.61 (1 H, t, *J* 8 Hz), and 5.82 (1 H, t, *J* 8 Hz); δ_C 32.17 (C-1, s), 46.37 (C-9), 73.58 and 75.59 (C-2, -4, -6, -8), and 120.31 and 120.72 (C-3, -7); *m/z* 198, 196 (M^+) and 117 (100%).

9-*Deuterio*-9-*bromobarbaralane* (**10b**).—This was made exactly as described for (**9c**). δ_H 2.73 (2 H, t, *J* 8 Hz), 4.12 (4 H, m), 5.60 (1 H, t, *J* 8 Hz), and 5.82 (1 H, t, *J* 8 Hz); δ_C 32.01 (C-1, -5), 46.06 (satellites) (C-9), 73.52 + 75.53 (C-2, -4, -6, -8), and 120.27 + 120.67 (C-3, -7); δ_D 4.00 (s, 9-D); *m/z* 199 (11%) + 197 (11) (M^+), 118 (100), 117 (73), 92 (12), 58 (14), 51 (13), and 40 (11). The extent of deuterium incorporation was *ca.* 95%.

Bicyclo[3.2.2]*nona*-2,6,8-*triene* (**27**).—The bromide (**9c**) (75 mg, 0.38 mmol) and tributyltin hydride (110 mg, 0.38 mmol) were purged with nitrogen and then irradiated in a thin-walled Pyrex tube with light from a 250 W medium pressure Hg arc at 105 °C for 2.5 h. The product mixture was diluted with CH_2Cl_2 and the triene was isolated by preparative g.l.c. to give a white solid (20 mg, 45%), δ_H 2.18 (2 H, q, *J* 4 Hz), 3.01 (1 H, m), 3.15 (1 H, q, *J* 8 Hz), 5.02 (1 H, dt, *J* 15, 4 Hz), 6.04 (1 H, tt, *J* 15, 4 Hz), 6.23 (2 H, t, *J* 8 Hz), and 6.60 (2 H, t, *J* 8 Hz); δ_C 27.08 (C-4), 34.95 (C-1), 35.88 (C-5), 126.08 (C-3), 129.77 (C-6, -9), 131.93 (C-2), and 138.01 (C-7, -8); *m/z* 118 (42%, M^+), 117 (100), 115 (43), 103 (10), 91 (49), 78 (12), 77 (15), and 65 (23).

Reduction of 9-*Bromo*-9-*deuteriobarbaralane* (**10b**) *with Tributyltin Hydride*.—Bromide (**10b**) (50 mm^3, 0.31 mmol) and Bu_3SnH (81 mm^3, 0.31 mmol) were purged with nitrogen and irradiated in a thin-walled Pyrex tube with light from a 125 W medium pressure Hg arc for 2.5 h at 120°C. G.c.–m.s. analysis showed one major and two minor products, together with traces of the reactants and Bu_3SnBr. The products were separated by preparative g.l.c. The first peak eluted was a minor impurity tentatively identified as bicyclo[3.2.2]nona-6,8-diene; probably the reduction product from the minor amount of dibromobarbaralane present in the reactant (see above). The major peak was shown to be deuteriated bicyclo[3.2.2]nona-2,6,8-triene (**21**) from the following spectroscopic data: δ_H 2.17 (2 H, m), 3.00 (1 H, m), 3.11 (1 H, m), 4.98 (1 H, m), 6.00 (1 H, m), 6.19 (2 H, t, *J* 7 Hz), and 6.57 (2 H, t, *J* 7 Hz). The ^{31}C n.m.r. resonance lines were each accompanied by one or more satellite lines as follows, all satellites were not resolved; δ_C [26.96, 27.07] (C-4), [34.74, 34.82, 34.86] (C-5), [36.75, 35.83, 35.86] (C-1), [125.91, 126.06] (C-3), [128.62, 129.76] (C-6, -9), [131.80, 131.87, 131.93, 131.99] (C-2), and [137.88, 137.94, 138.01] (C-7, -8). Each group of satellites is caused by the small chemical shift of the ^{13}C nucleus when a deuterium atom is absent, directly bonded or bonded to adjacent C atoms. The 46 MHz ^{2}H n.m.r. spectrum showed seven singlets, one for each possible isomer at δ_D 2.09, 2.98, 3.04, 4.95, 5.98, 6.17, and 6.57. The relative intensities are in Table 2. The second minor component was identified as deuteriated barbaralane (**22**) from its ^{1}H n.m.r. spectrum: δ_H 1.07 (1 H, t, *J* 4 Hz) 2.49 (2 H, m), [3.88 (m), 4.02 (m), 4.14 (m)] (4 H), and 5.18 (2 H, m). This is similar to the literature spectrum,[16] except for the three multiplets in the region δ 3.88–4.14. These resonances are the average of H(2, 4, 6, 8) during the divinylcyclopropane-type rearrangement. In the deuteriated molecule (**22**) three different averages are possible depending on the position of deuterium substitution. There was insufficient material for ^{13}C and ^{2}H n.m.r. spectra. A series of reactions was carried out in which the reaction temperature was varied. In each case the relative yields of products were determined by g.l.c. analysis (Figure 2), product (**21**) was then separated by preparative g.l.c. and the ^{2}H n.m.r. spectrum obtained (Table 2). A second series of reactions of (**10b**) and (**9c**) was carried out with 15 mm^3

bromide, Bu_3SnH (27 mm^3) and hexadecane or ether (150 mm^3) as solvent. Temperature was varied and photolysis times were adjusted to obtain a high conversion, although this proved impossible, in reasonable times, with reactions at 0 °C and below. Solubility problems were also encountered, even with ether solvent, for these low-temperature runs. The results are in Figure 2.

Reduction of (**10b**) *with Tributyltin Deuteride.*—The reduction was carried out at 104 °C exactly as described for the Bu_3SnH reductions, except that the irradiation time was quadrupled. The two products were separated as before and, due to the greater proportion of barbaralane formed, ^{2}H n.m.r. spectra were obtained for both. The ^{2}H spectrum of the doubly labelled bicyclo[3.2.2]nona-2,6,8-triene was similar to that given above, except for the peak intensities which are in Table 2. The barbaralane showed δ_D 1.04 (9-D) 2.36 (1-, 5-D) 3.87 (2-, 4-, 6-, 8-D) and 5.66 (3-, 7-D), *i.e.* this confirms the deuterium scrambling to every site: the relative intensities are in Table 2.

Bicyclo[3.2.2]*nona*-3,6,8-*trien*-2-*one* (**12**).[31]—Cycloheptatrienylacetyl chloride[32] (2 g) in dry hexane (25 cm^3) was added slowly over 3 days to a gently refluxing solution of triethylamine (4.3 cm^3) in dry hexane (110 cm^3). The solution was filtered, concentrated and separated by chromatography on silica gel (60–120 mesh) using 10% ether in light petroleum (b.p. 40–60 °C) as the eluant. Ketone (**12**) was eluted immediately before the indan-1-one and was obtained in *ca.* 20% yield, δ_H 3.90 (1 H, m), 4.27 (1 H, m), 5.15 (1 H, dd, *J* 13, 2 Hz), 6.43 (2 H, dt, *J* 2, 8 Hz), 6.78 (2 H, dt *J* 2, 8 Hz), and 7.12 (1 H, dd, *J* 13, 8 Hz).

Deuteriobicyclo[3.2.2]*nona*-3,6,8-*trien*-2-*ol* (**13**).—Ketone (**12**) was reduced with $NaBD_4$ using the method described for (**9a**) to give (**13**) in 48% yield, δ_H 1.62 (1 H, s), 3.25 (1 H, q, *J* 8 Hz), 3.53 (1 H, m), 5.00 (1 H, dd, *J* 13, 2 Hz), 6.13 (1 H, m), 6.2–6.4 (2 H, m), 6.70 (1 H, m), and 6.82 (1 H, m); δ_C 37.01, 44.15, [64.88, 65.01, 65.14 weak] C(4), 127.7, 128.66, 128.95, 136.74, 140.81, and 142.29.

Reaction of Alcohol (**13**) *with Phosphorus Tribromide.*—The monodeuterio alcohol (**13**) (0.2 g) and pyridine (0.06 ml) in dry ether (10 cm^3) were cooled in an ice–salt bath and PBr_3 (0.1 cm^3) in dry ether (0.5 cm^3) was added dropwise. The solution was stirred for 30 min, and worked up as above for (**9c**). The product (63%) was 9-bromo-2-deuteriotricyclo[3.3.1.0^{2,8}]nona-3,6-triene (**4**), δ_H 2.74 (2 H, m), 3.95–4.35 (3 H, m), 5.61 (1 H, m), and 5.83 (1 H, m). δ_C 31.65 (C-1), 32.66 (C-5), 46.35 (C-9), 70–80 (broad signals for C-2, -4, -6, -8) 120.34, 120.74 (C-3, -7), [each line was accompanied by satellites]; δ_D 3.98 [minor impurity at 2.70]; *m/z*, 199 197 (M^+, 1%), 118 (100), 117 (41), 116 (63), 115 (17), 92 (22), 63 (11), 52 (7), and 39 (7). In a similar reaction at −78 °C product (**14**) was accompanied by 4-bromo-4-deuteriobicyclo[3.2.2]nona-2,6,8-triene (**11**) in 13% yield relative to (**14**); δ_H 3.27 (1 H, m), 3.63 (1 H, m), 4.85 (1 H, m), 5.14 (1 H, m), 6.23 (2 H, t, *J* 8 Hz), 6.72 (1 H, t, *J* 7 Hz), and 6.82 (1 H, t, *J* 7 Hz). The averaged signals for H(2, 4, 6, 8) and C(2, 4, 6, 8) show that (**14**) exists as the mixture (**14a**) + (**14b**) at ambient temperature.

Reduction of the Bromide (**14**) *with Tributyltin Hydride.*—The reduction was carried out as described above with (**14**) (0.2 g) in hexadecane (0.5 cm^3) at 130 °C. The g.c.–m.s. showed the same two products (**21**) and (**22**) and the former was isolated by preparative g.l.c. The ^{1}H and ^{13}C n.m.r. spectra were essentially identical with those given above. The ^{2}H spectrum showed the expected seven signals; their relative intensities are in Table 2.

Acknowledgements

I thank Dr. C. Glidewell for valuable discussions and Miss S. Stewart for some of the experimental work.

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Received 23rd *May* 1989; *Paper* 9/02161B
