Cyclization of Deca-5,9-dienyl and 2-(But-3-enyl)cyclohexyl Radicals

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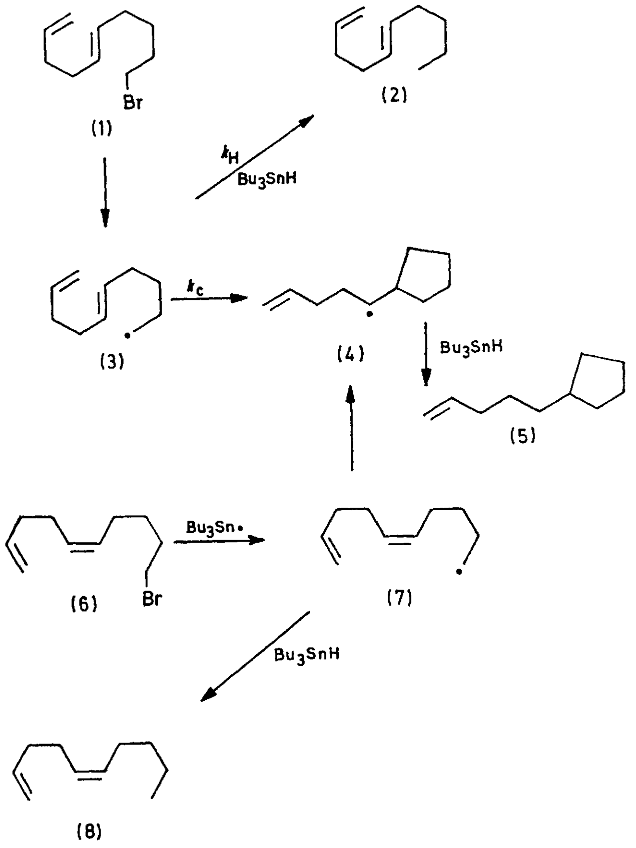
Summary The radicals *cis*- and *trans*-deca-5,9-dienyl and 2-(but-3-enyl)cyclohexyl all undergo cyclization by 1,5-addition; no evidence was found for concerted addition across both double bonds in the dienyl radicals.

The stereospecific formation of *trans*-decalin derivatives by intramolecular free-radical reactions of suitable dienes has recently been reported.[1,2] We now describe reactions of some simple radicals, the results of which are pertinent to the proposed mechanisms.

Treatment of *trans*-1-bromodeca-5,9-diene† (**1**) with Bu_3SnH in benzene[3] at 65° gave only *trans*-deca-1,5-diene (**2**) and pent-4-enylcyclopentane (**5**). Although the yields of total products were uniformly high ($\geqslant 77\%$), even under conditions of very low reactant concentration, the yield of cyclized product (**5**) varied with stannane concentration as expected on the basis of the proposed mechanism (Scheme).

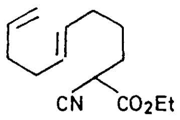


Scheme

Values of the ratio of the rate constants for cyclization (k_C) and hydrogen-atom transfer (k_H) were calculated by computer methods, using an iterative procedure, from the integrated rate expression (1) in which $[S]_0$ and $[S]_F$ are initial and final stannane concentrations and [C] is the final concentration of cyclized products.

$$[C] = k_C/k_H\{\ln([S]_0 + k_C/k_H) - \ln([S]_F + k_C/k_H)\} \quad (1)$$

The values of k_C/k_H so obtained (0·45—0·56) are slightly greater than that (*ca.* 0·2)[4,5] determined for cyclization of the hex-5-enyl radical at the same temperature. Experiments at different temperatures (35°, 75°, 101°) gave values of k_C/k_H (0·29, 0·54, 0·66) which showed an approximately linear dependence on $e^{1/T}$. The value of $\Delta H^{\ddagger}_{C} - \Delta H^{\ddagger}_{H}$ obtained (2·9 kcal mol^{-1}) is similar to that determined for cyclization of hex-5-enyl radical.[5]



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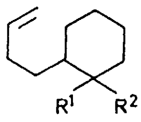

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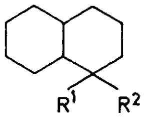

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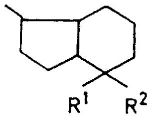

(12)

a; R^1 = CN, R^2 = CO_2Et
b; R^1 = R^2 = H

The reaction of *cis*-1-bromodeca-5,9-diene (**6**) with Bu_3SnH gave similar results. The only products were pent-4-enylcyclopentane (**5**) and the *cis*-diene (**8**), and k_C/k_H at 65° (0·38) was only slightly less than that for the *trans*-isomer; possibly there is greater steric hindrance in the transition state for cyclization of the *cis*-radical (**7**).

It is clear from these results that the dienyl radicals (**3**) and (**7**) behave as expected in the light of the reactions of simple alkenyl radicals.[4–7] Cyclization occurs exclusively in the 1,5-direction, and the product radical (**4**), like its acyclic analogue (pent-4-enyl radical),[8] does not undergo intramolecular addition.

A model for the proposed second step [(**10a**) → (**11a**)][1] in the cyclization of the substituted dienyl radical (**9**)[1] was provided by treatment of 1-(but-3-enyl)-2-chlorocyclohexane with Bu_3SnH. When $[Bu_3SnH]_0 = 0{\cdot}106$M the major products (80%) were the various stereoisomers of 1-methylhydrindane, and *trans*-decalin was obtained in very small yield (*ca.* 1·5%). It thus appears that cyclization of the butenylcyclohexyl radical (**10b**) proceeds almost exclusively in the 1,5-direction to afford (**12b**).

On the basis of these results we conclude that the stereospecific formation of *trans*-decalin derivatives by cyclization of the dienyl radical (**9**)[1] or by radical addition to germacrene[2] occurs because of special substituent effects in the particular substrates used and does not represent examples of processes of wide generality.

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† All compounds had spectroscopic properties (n.m.r., i.r., and mass spectra) consistent with the proposed structures and gave satisfactory microanalytical data.

[1] M. Julia, F. Le Goffic, and L. Katz, *Bull. Soc. chim. France*, **1964**, 1122.
[2] T. W. Sam and J. K. Sutherland, *Chem. Comm.*, 1971, 970.
[3] H. G. Kuivila, *Accounts Chem. Res.*, 1968, **1**, 299; D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, 1968, **90**, 7047.
[4] C. Walling and A. Cioffari, *J. Amer. Chem. Soc.*, 1972, **94**, 6059.
[5] A. L. J. Beckwith and R. B. Holloway, unpublished observations.
[6] A. L. J. Beckwith in 'Essays on Free-radical Chemistry,' *Chem. Soc. Special Publ.*, 1970, No. 24, p. 239.
[7] M. Julia, *Accounts Chem. Res.*, 1971, **4**, 386.
[8] C. Walling and M. S. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 2262.