Homolytic Reactions of Homocubane and Basketane: Rearrangement of the 9-Basketyl Radical by Multiple β-Scissions

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Abstract: Methods are described for the synthesis of 9-hydroxy- and 9-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (homocubane derivatives) and for the same derivatives of pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (basketane). The 9-homocubyl and 9-basketyl radicals generated from these precursors were observed by EPR spectroscopy. In spite of their very large strain energies, both radicals rearranged extremely slowly, and unrearranged products were obtained from homolytic reactions in solution at temperatures below 150 °C. At higher temperatures the 9-basketyl radical rearranged by a cascade of three β-scissions, the ultimate product being 1-(4-cyclobut-2-enyl)cyclohexa-2,4-diene. The Arrhenius parameters for the rearrangement were found to be $\log(A_r/s^{-1}) = 13.6$, $E_r = 13.5$ kcal mol^{-1}. The 9-homocubyl radical did not rearrange even at 220 °C. An explanation as to why these cage radicals rearrange at least 6 orders of magnitude more slowly than the related cubylcarbinyl radical is presented, and semiempirical SCF-MO calculations are reported.

Introduction

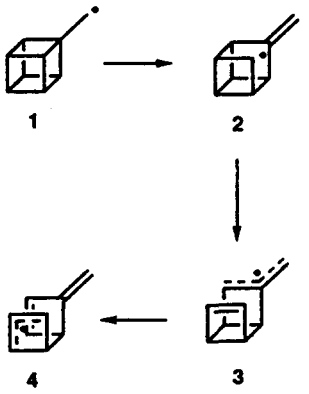
Cubane and the neutral cubyl radical, $C_8H_7^•$, are remarkably stable and do not rearrange in solution, even at high temperatures (150 °C), although the skeleton contains *ca.* 166 kcal mol^{-1} of strain.[1] In conspicuous contrast to this, the cubylcarbinyl radical **1** rearranges by a cascade of three β-scissions (Scheme 1) to give[2,3] the 4-(4-methylenecyclobut-2-enyl)cyclobutenyl radical (**4**). The rate constant of the initial ring-opening was found to be 2.9×10^{10} s^{-1} at 25 °C,[2,4] which ranks it as one of the fastest known radical rearrangements. This contrast in unimolecular reactivity was so novel that it instigated an examination of the homolytic rearrangements of several free radicals with structures incorporating some of the features of both types of radical. We anticipated that the kinetic parameters of their rearrangements and the EPR spectral data of the radicals would disclose essential details of the factors controlling the β-scissions.

The rates of ring-opening reactions generally increase with the amount of strain released in the process.[3] The skeleton of the pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-yl radical (9-homocubyl) (**5**) contains *ca.* 118 kcal mol^{-1} of strain[2] and has four equivalent C_β–C_γ bonds capable of undergoing β-scission to give nonbridgehead alkenes. On this basis, **5** seemed therefore to be a good candidate for rapid unimolecular rearrangement, as did the pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decan-9-yl radical (9-basketyl, bishomocubyl) (**6**), which has *ca.* 113 kcal mol^{-1} of strain.[5] On the

5 **6**

other hand, both the 9-homocubyl and 9-basketyl radicals (**5**, **6**) are highly constrained analogues of the cyclobutylcarbinyl radical. An important property of the latter is that the radical center is freely able to rotate, and this allows the transition state for ring-opening to adopt the conformation which most facilitates the β-scission; the optimal dihedral angle between the SOMO and the C_β–C_γ bond in this arrangement is 0°. The radicals **5** and **6**, however, are much more rigid species in which the dihedral angle between the SOMO and C_β–C_γ is fixed and significantly larger than 0° in each case. Accordingly, it was deemed of interest to examine the effects of such restriction on the capacity of **5** and **6** for rearrangement. This research was also prompted by the need for ultrafast radical "clocks" for use as mechanistic probes, particularly of enzyme-catalyzed transformations,[6] and in this context the extraordinarily rapid rearrangement of another modified cyclobutylcarbinyl system, the 1-bicyclo[1.1.1]-pentylcarbinyl radical, has been the subject of recent reports.[6c,7] It was by no means certain, of course, that the cages of **5** and **6**

Scheme 1



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(4) Choi, S.-Y.; Eaton, P. E.; Newcomb, M.; Yip, Y. C. *J. Am. Chem. Soc.* **1992**, *114*, 6326–6329.
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(6) (a) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1989**, *111*, 1927–1928. (b) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5699–5707. (c) Branchaud, B. P.; Glenn, A. G.; Stiasny, H. C. *J. Org. Chem.* **1991**, *56*, 6656–6659.

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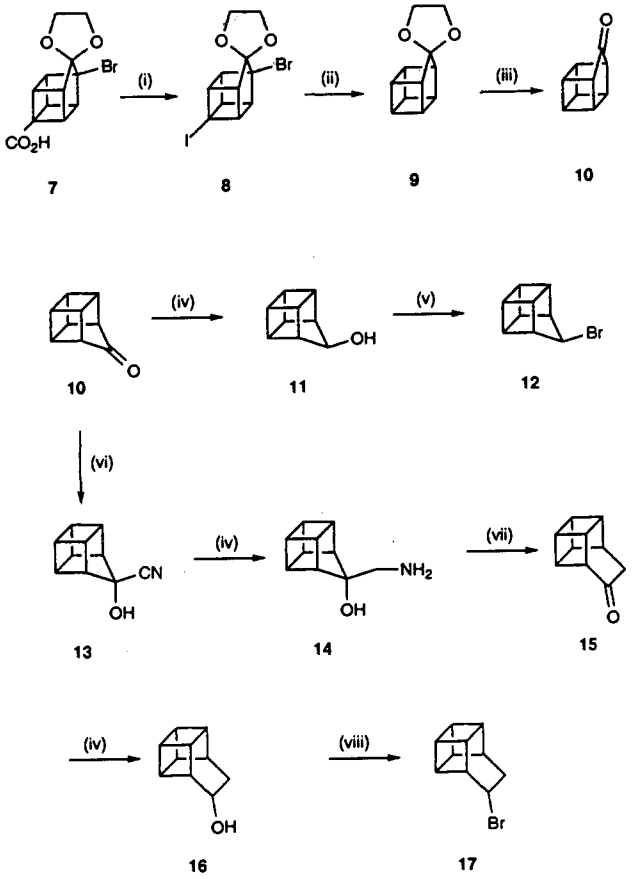
Scheme 2[a]



[a] (i) $Pb(OAc)_4/I_2$,*hν*, (ii) Bu_3SnH, *hν*, (iii) 5% H_2SO_4, (iv) $LiAlH_4$, (v) $SOBr_2$, (vi) HCN, (vii) NO_2^-/H^+, (viii) Ph_3PBr_2, DMF.

would unravel by sequences of β-scissions, because cubane and cubylcarbinyl derivatives can rearrange to a wide variety of products depending on the reagents used and the structural details.[1,2] In fact, we found that the dynamics of the rearrangements of **5** and **6** were dramatically slower than those of **1** by at least 6 orders of magnitude. The mechanistic pathway for **6** involved a cascade of β-scissions analogous to the unraveling of **1**, but, remarkably, **5** remained intact in solution even at temperatures as high as 220 °C.

Results and Discussion

Syntheses. The radical precursors were prepared from a common intermediate, homocubanone **10**, whose synthesis has been described previously.[8] For this work, **10** was prepared from the bromo acid **7** by a route based on that described by Mehta and associates[8a] but involving the mixed halide **8**. Dehalogenation of **8** with tributyltin hydride gave the ketal **9** which, until now, does not appear to have been fully characterized. Reduction of **10** with lithium aluminum hydride gave the alcohol **11**; however, conversion of this to the corresponding bromide **12** proved to be rather more difficult than anticipated (Scheme 2). Thus, treatment of **11** with concentrated HBr on the one hand, or triphenylphosphine dibromide in CH_2Cl_2 or DMF on the other, gave no reaction or, at best, low yields of 9-bromohomocubane. Both PBr_3 and PBr_5 gave better conversion, but the bromide was contaminated with byproducts which were difficult to remove.

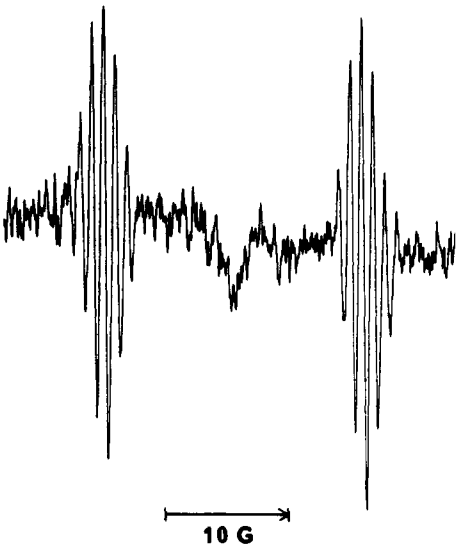


Figure 1. 9.3-GHz EPR spectrum of the homocubyl radical **5** in cyclopropane at 150 K obtained by radical abstraction from precursor **12**.

The most effective route to **12** involved treatment of **11** with thionyl bromide; this gave a product (71%) which could be purified readily.

Conversion of **10** into bishomocubanone (**15**) was achieved as shown in Scheme 2. Although ring expansions of bromohomocubanones have been successfully performed by the use of diazomethane,[9] ketone **10** did not respond favorably to these conditions. Cage homologation in this case was effected *via* a procedure we have previously found to be very reliable.[10] Reduction of the derived cyanohydrin **13** by lithium aluminum hydride produced the amino alcohol **14**, deamination of which proceeded with ring expansion to give the ketone **15** in good yield. The latter was reduced to **16** with lithium aluminum hydride. Unlike its lower homologue **12**, 9-basketanol (**16**) was found to be far more prone to rearrangement during attempts to convert it to the corresponding bromide. Only when the very mild brominating reagent triphenylphosphine dibromide was employed was 9-bromobasketane (**17**) obtained free from contaminants.

EPR Spectra of 9-Homocubyl and 9-Basketyl Radicals. A cyclopropane solution containing **12**, triethylsilane, and di-*tert*-butyl peroxide was photolyzed in the cavity of an EPR spectrometer at low temperatures. The $Et_3Si\cdot$ radical generated in

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2t\text{-BuO}^\cdot \xrightarrow{Et_3SiH} Et_3Si^\cdot + t\text{-BuOH}$$

$$Et_3Si^\cdot + 12 \rightarrow Et_3SiBr + 5$$

this system should abstract bromine from the substrate, leaving the polycyclic radical and/or its rearrangement products as the main EPR-active species. A good spectrum with a large doublet and a much smaller septet hyperfine splitting (hfs) was observed (Figure 1). The doublet hfs can be assigned to H_α of the 9-homocubyl radical **5**. The magnitude of $a(H_\alpha)$ is consistent with **5** being a planar π-radical, unlike the strongly pyramidal σ-cubyl radical.[3] The two β-hydrogens of **5** are at bridgehead sites, essentially in the nodal plane of the p-orbital at C(9) containing the unpaired electron (SOMO). Small $a(H_\beta)$ values are therefore expected for **5**, in agreement with the spectroscopic observations. The radical shows additional long-range splitting from four equivalent γ-hydrogens (Table 1). The spectrum remained visible in the temperature range −120 °C to −70 °C,

(7) Della, E. W.; Schiesser, C. H.; Taylor, D. K.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1329–1333.

(8) (a) Mehta, G.; Sikrishna, A.; Suri, S. C. *J. Org. Chem.* **1980**, *45*, 5375–5377. (b) Dauben, W. G.; Reitman, L. M. *J. Org. Chem.* **1975**, *40*, 835–841. (c) Schleyer, P. v R.; Harper, J. J.; Dunn, G. L.; Dipasquo, V. J.; Hoover, J. R. E. *J. Am. Chem. Soc.* **1967**, *89*, 698–699. (d) Barborak, J. C.; Pettit, R. *J. Am. Chem. Soc.* **1967**, *89*, 3080–3081.

(9) van Seters, A. J. C.; Buza, M.; Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1981**, *37*, 1027–1031.

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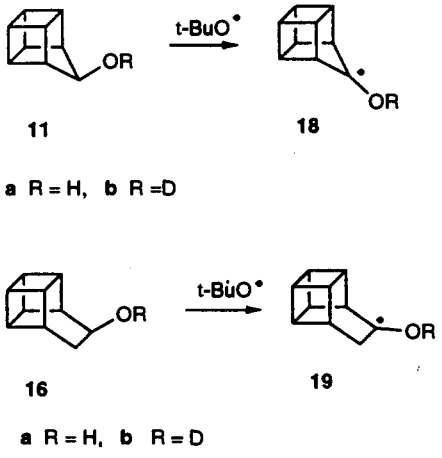
Table 1. EPR Data for 9-Homocubyl and 9-Basketyl Radicals[a]

radical	T (K)	$a(H_\alpha)$	$a(2H_\beta)$	$a(4H_\gamma)$	a(other)
5	160	20.70	0.98	0.98	
18a	170		2.04	0.55	1.60 (OH)
18b	170		2.04	0.55	*b*
radical	T (K)	$a(H_\alpha)$	$a(1H_\beta)$	$a(2H_\beta)$	a(other)
6	170	22.0	1.8	39.8	
19a	170		2.3	31.3	<1.5 (OH)
19b	170		2.2	31.3	*b*

[a] All g-factors 2.003 ± 0.001, hfs in Gauss, all checked by simulation. [b] a(OD) unresolved.

Scheme 3

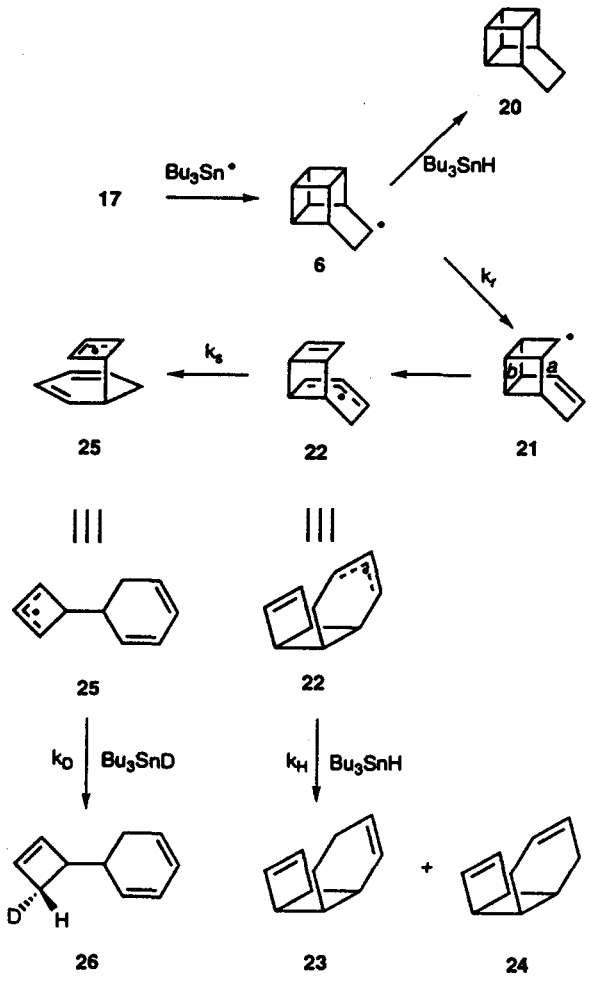


which indicated that **5** rearranged much more slowly than **1**. The α-hydroxy- (**18a**) and α-deuterioxy-9-homocubyl radicals (**18b**) were also spectroscopically observed on hydrogen abstraction from **11** with photochemically generated *t*-BuO· radicals (Scheme 3). The unrearranged radicals could be observed at temperatures up to −30 °C; above this no signals were detectable. The hydroxy substituent caused minor changes in the spin density distribution, but the hyperfine splittings (Table 1) were entirely consistent with the detected species being substituted homocubyl radicals.

The EPR spectrum of the 9-basketyl radical (**6**) was obtained in a similar way using **17** as the substrate. The hfs from H_α was normal for a planar radical center (Table 1); in addition, the spectrum showed large hfs from two equivalent H_β and a small doublet splitting from a single β-hydrogen. This latter hfs can be assigned to the bridgehead hydrogen which is essentially in the nodal plane of the SOMO. No long-range hyperfine splittings were resolved, but the line width (1.5 G) was considerably larger than that of **5** and probably masked γ-hydrogen hfs. The analogous 9-hydroxy (**19a**) and 9-deuterioxy radicals (**19b**) were generated by hydrogen abstraction from the corresponding alcohols **16** (Scheme 3), and their EPR parameters are in Table 1. The parent radical **6** was spectroscopically observable up to −70 °C, and **19a,b** were detectable at −30 °C; above these temperatures no signals appeared, *i.e.*, rearranged radicals were not detected. For both **12** and **17**, EPR samples with hexamethylditin in place of triethylsilane were examined, but no well-defined spectra were obtained. The spectra of **5** and **6** correspond to some of the most highly strained cage radicals ever observed spectroscopically and demonstrate the remarkable stability of the homocubyl and basketyl cage structures, even after the removal of one hydrogen atom.

Rearrangement of 9-Basketyl and 9-Homocubyl Radicals. The EPR experiments showed that radicals **5** and **6** rearranged too slowly for the dynamics to be accessible to kinetic EPR measurements. An alternative approach was therefore adopted in which each bromide was reacted with tributyltin hydride. In this process the cage radicals are generated by bromine abstraction

Scheme 4



with photochemically produced tributyltin radicals. The cage radical and/or its rearrangement counterpart then abstract hydrogen from the tributyltin hydride to give hydrocarbon products by the well-known chain reaction.

The tributyltin hydride reduction of **17** at 70 °C gave a single product which proved to be unrearranged basketane (**20**). However, when the reduction was carried out at 212 °C, a mixture containing **20** together with two rearranged hydrocarbons was obtained. This mixture was not separable by chromatography, but the NMR spectra (300 and 500 MHz) were sufficiently well resolved for the the products to be identified as tricyclo[4.4.0.$0^{2,5}$]-deca-3,7-diene (**23**) and tricyclo[4.4.0.$0^{2,5}$]deca-3,8-diene (**24**), and the assignments for **23** were confirmed by a 2D COSY spectrum. A plausible explanation for the formation of these products is presented in Scheme 4.

Radical **6** undergoes β-scission to give **21**, which has several different possibilities for further β-scissions. The rearrangement of **21** will be under stereoelectronic control, like other cyclobutylcarbinyl-type rearrangements.[11] The p-orbital containing the unpaired electron is parallel to the β-C–C bonds marked *a* and *b*, but scission of *b* leads to formation of the resonance-stabilized allyl-type radical **22**. Thus *b* scission is favored, and this rearrangement is expected to be extremely rapid because of the large amount of strain relief and the comparative thermodynamic stability of **22**. Radical **22** can then abstract hydrogen at either end of the allyl system to give the observed products **23** and **24**. Statistically a 1:1 mixture of **23** and **24** would be expected. However, the experimental ratio **23**:**24** was 4:1 at 212 °C, and

(11) Castaing, M.; Pereyre, M.; Ratier, M.; Blum, P.; Davies, A. G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 287–292. Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1083–1092. Ingold, K. U.; Maillard, B.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 970–974.

Table 2. Kinetics of the Reduction of 9-Bromobasketane (**17**) with Bu_3SnH[a]

T (°C)	[**20**] (M)	[**23** + **24**] (M)	k_r/k_H[b] (M^{-1})	10^7k_r[c] (s^{-1})
140	1.71	0.25	0.27	0.35
155	1.74	0.22	0.23	0.35
180	1.55	0.41	0.48	0.94
204	1.16	0.71	1.20	2.84
220	1.11	0.85	1.42	3.85

[a] [Bu_3SnH] = 2.98 M, [**17**] = 1.96 M, except at 204 °C, when it was 1.87 M. [b] Obtained by an iterative procedure. [c] Derived by use of $\log(k_H) = 9.07 - 3.69/\theta$ (ref 17).

Table 3. Kinetic Data for the Rearrangements of 9-Basketyl (**6**) and Related Radicals

radical	k_r (25 °C) (s^{-1})	$\log[A_r/s^{-1}]$	E_r (kcal mol^{-1})	ref
cyclobutylcarbinyl (**38**)	4.7×10^3	12.6	12.2	19
cubylcarbinyl (**1**)	2.9×10^{10}	13.2	3.7	4
9-basketyl (**6**)	4.5×10^3	13.6	13.5	*c*
9-homocubyl (**5**)	$<1 \times 10^2$	[13.0][a]	>14.9[b]	*c*
tricyclo[4.4.0.$0^{2,5}$]deca-3,7-dienyl (**22**)	2.2×10^2	[13.0][a]	14.5[b]	*c*

[a] Assumed value. [b] Estimated values; see text. [c] This work.

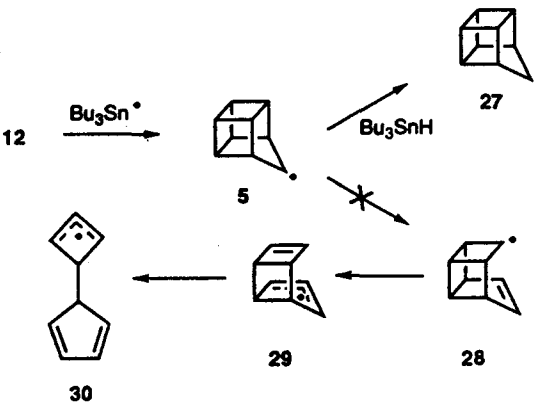
it is likely therefore that the hydrogen abstraction step is controlled by subtle steric effects.

Overall, the rearrangement of **6** comprises a cascade of two β-scissions. It is evident that the possibility exists of a further β-scission of radical **22** to give **25** (Scheme 4). In the analogous rearrangement of the cubylcarbinyl radical, the intermediate corresponding to **22** is **3**, which was shown to rearrange rapidly and completely to give **4** (Scheme 1). Two factors will contribute to the abatement of this β-scission in **22**. First, **22** contains less strain than **3** (two four-membered rings and one six-membered ring in comparison with three four-membered rings). Second, β-scission of **22** is in competition with hydrogen abstraction from Bu_3SnH. At the very high temperatures of the basketyl experiments (212 °C), hydrogen abstraction will be much faster than in the cubylcarbinyl experiments (78 °C),[2] and hence β-scission of **22** will compete less effectively. To test this hypothesis and help confirm the product structures, the reduction of **17** with tributyltin deuteride was examined. In this case, the deuterium abstraction step will be slower in accord with the kinetic isotope effect (k_D/k_H). At 212 °C, the reduction products were 9-deuteriobasketane (49.4%) and 9-deuteriotricyclo[4.4.0.$0^{2,5}$]-deca-3,7-diene (*i.e.*, **23-*D***) (46.8%), together with a minor amount (3.9%) of 1-(4-deuteriocyclobut-2-enyl)cyclohexa-2,4-diene (**26**). The isomer **24-*D*** was formed in only trace amounts (<1%). Thus, the complete cascade of three β-scissions was observable with a slower hydrogen donor, showing that the rearrangement pathway of **6** is entirely analogous to that of **1**, even though the rate is vastly slower.

A series of Bu_3SnH reductions of **17** was carried out in the range 140–220 °C, and the final concentrations of **20** and **23** + **24** were determined by GC. The rate constants for the rearrangement of **6** to **22** (k_r) were determined using an integrated rate equation,[11,12] and the data are given in Table 2. Tin hydride reductions are normally carried out at much lower temperatures, and therefore two control experiments were performed to check the stability of the reactants and products. At $T > 150$ °C, the reductions will be complete in a few minutes. A sample of **17** was irradiated at 190 °C for 10 min in the absence of Bu_3SnH. The bromide darkened considerably, but GC/MS and NMR analysis showed that none of the reduction products **20**, **23**, or **24** had formed and that **17** was still the main component. Second, **20** formed in a reduction at 85 °C and showed no decomposition on

(12) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Chem. Commun.* **1974**, 472–473.

Scheme 5



raising the temperature to 200 °C and maintaining it there for 2 h under illumination.

The rate of hydrogen abstraction from Bu_3SnH by carbon-centered radicals is not sensitive to the radical structure, and therefore k_H values were taken from the literature.[13] Arrhenius parameters derived from the resulting k_r values are in Table 3. For the tributyltin deuteride reduction it can easily be shown that

$$d[\mathbf{26}]/d[\mathbf{23}\text{-}D] = k_s/k_D[Bu_3SnD] \quad (1)$$

and that

$$d[\mathbf{20}\text{-}D]/d[\mathbf{23}\text{-}D] = (k_D[Bu_3SnD] + k_s)/k_r \quad (2)$$

The reactions corresponding to each rate constant are shown in Scheme 4. Neglecting corrections to (1) due to integration and substituting the experimental [**26**]/[**23-*D***] ratio and the literature value[13] of k_D at 212 °C, gives k_s(212 °C) = 2.8×10^6 s^{-1}. The Arrhenius preexponential factors of rearrangements of this general type are normally *ca.* 10^{13} s^{-1}. Assuming this to hold for the rearrangement of **22** leads to an estimate of 14.5 kcal mol^{-1} for the activation energy and hence k_s(25 °C) = 2.2×10^2 s^{-1}. Thus, rearrangement of **22** is slower than rearrangement of the archetypal cyclobutylcarbinyl radical (Table 3). This is probably because **22** is thermodynamically stabilized by the resonance delocalization of the unpaired electron.

Equation 2 can be applied to derive the kinetic isotope effect on hydrogen abstraction from Bu_3SnD by carbon-centred radicals. Thus, insertion of the derived k_s and k_r values leads to k_H/k_D(212 °C) = 2.5, which, in view of the temperature difference, is in very satisfactory agreement with previously reported values of 2.7 and 2.8 at 25 °C for cyclohexyl and *tert*-butyl radicals, respectively.[14] Alternatively, substitution of the k_s value from eq 1 together with the literature k_D value[13] into eq 2 gives k_r (212 °C) = 3.5×10^7 s^{-1}, which is in excellent agreement with the k_r data from the Bu_3SnH reductions (Table 2) and gives confidence in the internal consistency of the kinetic results.

The reduction of 9-bromohomocubane (**12**) with Bu_3SnH was examined at several temperatures. Even at the highest practicable temperature (218 °C), the reaction produced a single product, homocubane (**27**). Consequently, the intermediate radical **5** failed to rearrange even at this elevated temperature (Scheme 5). From the amount of **27** and the detection limit for rearranged hydrocarbons in the product chromatogram, we estimate that k_r(**5**, 218 °C) < 2.4×10^6 s^{-1}. By assuming that $\log[A_r/s^{-1}]$ = 13.0, we estimated the lower limit of the activation energy and the upper limit of the rate constant at 25 °C (Table 3).

The data in Table 3 show that the 9-basketyl radical rearranges nearly 7 orders of magnitude more slowly than the cubylcarbinyl

(13) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742.

(14) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 1055–1056; 7047–7055.

radical at 25 °C and that for the homocubyl radical the difference is even greater. Most of this reduction in rate is due to the much greater Arrhenius activation energies for **6** and probably for **5**. Kinetically, both **6** and **5** resemble the cubyl radical **31** which also rearranges extremely slowly, if at all. For **31** the absence of rearrangement is easily understood because β-scission would produce the highly strained bridgehead alkenyl radical **32**. In contrast to this, the first step in the rearrangement of **6** gives **21** and proceeds ultimately to **25** (Scheme 4). Similarly, β-scission of **5** would initially produce **28**, and ultimately **30**, with release of most of the original cage strain, *i.e.*, a plausible, downhill pathway exists which is analogous to the rearrangement of **1**. Possibly, the slow rearrangement of **5** and **6** in comparison with **1** could partly be accounted for by the fact that there will be less relief of strain. For example, strain relief for **6** → **25** is *ca.* 78 and for **5** → **30** is *ca.* 82 in comparison with 106 kcal mol^{-1} for **1** → **4**. However, the overall relief of strain is so large for both **5** and **6** that it is difficult to accept that this could be responsible for such enormous reductions in the rearrangement rates. This caveat is supported by the fact that there is only *ca.* 26 kcal mol^{-1} relief of ring strain in the β-scission of the cyclobutylcarbinyl radical, and yet it rearranges more rapidly[15] than either **5** or **6** (Table 3).

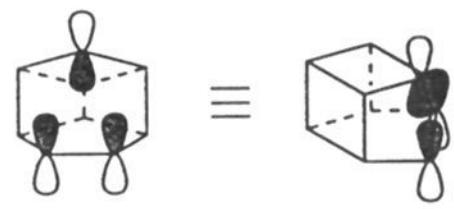
Another factor which significantly affects the rates of β-scission reactions is the degree of overlap between the SOMO and the σ*-orbital of the bond undergoing scission.[16] Optimum overlap is attained when the dihedral angle between the SOMO and the C_β–$C\gamma$ bond is 0°, and this arrangement can readily be achieved in the transition state for ring-opening of radical **1** because of unrestricted rotation of the SOMO. Models indicate that in the ground states of **5** and **6** the analogous dihedral angles are fixed by the cage structures at about 40° and 30°, respectively, thus precluding optimum overlap. It follows that the extent of overlap of the SOMO with the C_β–$C\gamma$ bond increases in the order **5** to **6** to **1**, which correlates with the rate constants for β-scission. However, optimum overlap is not mandatory for β-scission to occur. For example, the spiro[2.3]hex-4-yl radical (**33**) and homologous radicals rearrange rapidly even though the SOMO and the C_β–C_γ bond are staggered.[17] Similarly, the bicyclo-

33

34

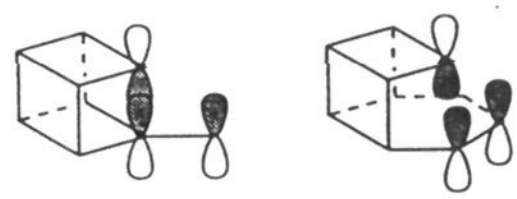
[2.1.0]pent-2-yl radical (**34**) undergoes rapid β-scission in spite of the fact that the C_β–C_γ bond is in the nodal plane of the SOMO (*i.e.*, $\phi = 90°$).[18,19] It follows that the nonoptimum overlap in **6** and **5** also seems inadequate to account for their slow-to-imperceptible β-scissions.

It is worthwhile drawing attention to the unique structure of the product of the first β-scission of **5**, *i.e.*, radical **28**. The frontier orbital arrangement is shown in **28a**. In this structure the SOMO



28a 28a

is held by the symmetrical cage structure directly above the center of the π-orbital of the newly formed double bond. In fact, the rigid structure ensures that the distance separating the SOMO and either of the carbon atoms of this double bond will not be much greater than a "normal" C–C bond length. Thus all three p-orbitals will still significantly overlap in a triangular array in the ground state of **28**. Simple frontier orbital treatments of this situation indicate that this type of interaction produces one bonding and two degenerate antibonding MOs, so one of the three electrons must occupy a high-energy antibonding orbital.[20] This will greatly increase the energy of radical **28** and may explain why the activation energy for β-scission of **5** is so high.[21] In the radical **2**, formed by the first β-scission of **1**, the SOMO is also held close to the newly formed π-bond, but in this case overlap is at one end of the double bond, **2a**. The frontier MOs in this situation consist



2a 21a

of one bonding, one nonbonding, and one antibonding orbital. The three electrons can occupy the bonding and nonbonding MOs, so the energy of **2** is comparatively low. Radical **21** formed in the first β-scission of **6** will be an unsymmetrical homologue, *i.e.*, **21a**, where the distance of the SOMO from the double bond is greater and its placement is not so central as in **28a**. Thus, the energy of **21** will not be so high, and this may explain why the rearrangement of **6**, though sluggish, is faster than that of **5**.

Theoretical Study of Strained Cyclobutylcarbinyl Radical Ring-Opening. We decided to examine the potential energy surfaces for the rearrangement of the intermediate radicals **5** and **6** in an

Table 4. Experimental and Calculated Energy Barriers to Ring-Opening of Some Cyclobutylcarbinyl Radicals

radical rearrangement	Δ*H*(calcd)[a] (kcal mol^{-1})	E_r (kcal mol^{-1}) exptl	E_r (kcal mol^{-1}) calcd[b]
cubyl (**31**) → **32**	+19.2	na[c]	28.2
cubylcarbinyl (**1**) → **2**	−17.4	3.7[d]	6.1
9-homocubyl (**5**) → **28**	−10.3	>14.9[e]	16.1
9-basketyl (**6**) → **21**	−12.4	13.5[e]	16.7
6-norcubylcarbinyl (**35**) → **40**	−23.0	<4.5[f]	5.9
1-bicyclo[1.1.1]pentylcarbinyl (**36**) → **39**	−39.0	7.1[g]	9.1[h]
1-bicyclo[2.1.1]hexylcarbinyl (**37**) → **41**	−43.5	9.3[g]	11.8
cyclobutylcarbinyl (**38**) → **42**	+5.2	12.2[i]	23.4
3-methylenecyclobutylcarbinyl (**39**) → **43**	+1.2	11.5[i]	23.9

[a] MINDO/3-estimated enthalpy of reaction. [b] MINDO/3-estimated. [c] Not available; rate too slow to be determined. [d] Reference 4. [e] This work. [f] Upper limit (unpublished data, Della and Walton). [g] Reference 7. [h] *Ab initio* estimates (ref 7) are 7.8 (3-21G) and 11.2 kcal mol^{-1} (6-31G*). [i] Reference 19.

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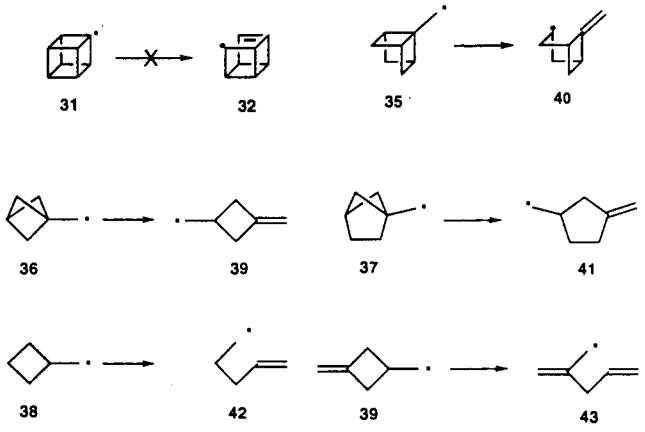
(21) Note that structure **28a** is similar to the hypothetical transition state of a 1,2-migration of an alkyl group in an alkyl radical. 1,2-Alkyl migrations fail to occur for the same reason, *i.e.*, the high energy of this transition state.

attempt to provide an explanation for their reluctance to ring-open. We felt that MINDO/3 would yield the most reliable data for the ring-openings **5** → **28** and **6** → **21** because our experience[22] has been that this method consistently outperforms both AM1 and MNDO when applied to highly strained systems of this kind, and we have observed both that MINDO/3 data on strained molecules are generally in very good agreement with those obtained by *ab initio* calculations at the 6–31G* level and that they correlate well with experimental results.

Calculated activation energies and heats of reaction for ring-opening of radicals **5** and **6** and, for comparison, the related strained cyclobutylcarbinyl radicals **1**, **31**, and **35-39** are displayed in Table 4, which reveals that for the strained substrates, **1**, **5**, **6**, **31**, and **35–37**, the calculated and experimental values of E_r are in very good agreement with each other. While the 9-homocubyl and 9-basketyl radicals (**5** and **6**) are predicted to rearrange with considerably lower exothermicities than the remaining strained radicals, an examination of the calculated structures of **21** and **28** did not provide corroboration for the explanation presented above for the slow rate of ring-opening of **5** compared to **6** as embodied in the forms **2a**, **21a**, and **28a**. Since the semiempirical results do not support the expectation based on frontier orbital theory, an *ab initio* study including full allowance for electron correlation is obviously desirable.



Conclusions

9-Homocubyl and 9-basketyl radicals are highly strained, but they rearrange extremely slowly by β-scission reactions. Consequently, the EPR spectra of both unrearranged radicals could be observed, and unrearranged products were obtained in homolytic reactions in solution at $T < 150$ °C. Above this temperature, **6** rearranged by a cascade of three β-scissions which was analogous to the rearrangement of the cubylcarbinyl radical.

Experimental Section

Routine ^{1}H NMR spectra (200 MHz) were obtained on Varian Gemini 200 and Hitachi RS-1200 spectrometers. ^{13}C and some ^{1}H NMR (300 MHz) data were collected on Bruker AM300 and Varian Gemini-300 instruments. NMR measurements were made in $CDCl_3$ solution unless otherwise stated, and chemical shifts relative to TMS are reported in ppm (δ). Mass spectra and high-resolution mass spectra (HRMS) were recorded on a Kratos M25RF spectrometer. EPR spectra were recorded with a Bruker ER 200D spectrometer operating at 9.3 GHz with 100 kHz modulation. Samples were prepared in Spectrosil tubes, degassed, and photolyzed in the cavity by light from a 500-W super-pressure Hg lamp. GC/MS analyses were run on a Finnigan Incos 50 quadrupole mass spectrometer using a Hewlett-Packard HP5890 gas chromatograph. Elemental analyses were carried out by the Australian Microanalytical Service. Standard MINDO/3 calculations were performed using the MOPAC (version 6) package.[23] Geometries of the various structures were determined at the unrestricted Hartree–Fock (UHF) level by applying Davidon–Fletcher–Powell optimization[24] without symmetry restraints. Evaluation of the force constant matrices showed the structures of the unrearranged and rearranged radicals to exist as local minima on the potential energy surface. Transition states for rearrangement were located using the reaction coordinate approach[25] and proved by the existence of one (only) negative eigenvalue in the pertinent force constant matrix.[26] 1-Bromo-4-carboxypentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one ethylene acetal (**7**) was prepared as described.[27]

1-Bromo-4-iodopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one Ethylene Acetal (8). Treatment of the bromo acid **7** (12.0g, 40 mmol) with lead tetraacetate and iodine as described[28] followed by sublimation (Kugelrohr, 110 °C/0.05 mmHg) of the product afforded the iodide **8** (14.9 g, 97%), mp 136 °C (lit.[29] mp 138–139 °C).

Pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one Ethylene Acetal (9). Tributyltin hydride (28 mL, 0.1 mol) was added to a solution of the iodide **8** (14.8 g, 39 mmol) and AIBN (200 mg) in ether (350 mL). The mixture was irradiated (300-W tungsten lamp) for 5 h and then quenched with excess iodomethane. The solvent was evaporated and the residue chromatographed (silica gel). Tin-containing compounds were eluted with hexane, and the acetal was obtained in the fraction eluted with 1:4 ether/hexane. Distillation (Kugelrohr, 85 °C/2mmHg) gave the pure acetal **9** (6.7 g, 99%): ^{1}H NMR δ 2.80–3.10 (m, 2H), 3.10–3.40 (m, 2H) 3.40–3.70 (m, 4H), 3.90 (s, 1H); ^{13}C NMR δ 42.09, 46.08, 64.92; mass spectrum *m/z* (relative intensity) 176 (38), 175 (88), 149 (39), 131 (93), 117 (53), 105 (100); HRMS calcd for $C_{11}H_{12}O_2$ [M·$^+$] 176.0837, found 176.0818. Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.0; H, 6.9. Found C, 74.8; H, 6.6.

Pentacyclo[4.3.0.0.^{2,5}0.^{3,8}0.^{4,7}]nonan-9-one (10). Pentacyclo-[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one ethylene acetal (**9**) (4.5 g, 26 mmol) was deketalyzed with 5% H_2SO_4 as described.[30] The precipitated ketone was extracted with methylene chloride, and the organic extracts were dried ($MgSO_4$) and concentrated to dryness. Distillation (Kugelrohr, 105 °C/9mm) of the residue afforded the ketone **10** (3.2 g, 95%) mp 67–69 °C (lit.[30] mp 66–68 °C).

9-Homocubanol (11). To a solution of lithium aluminum hydride (1.0 g, 26 mmol) in ether (90 mL) at reflux was added a solution of the ketone **10** (1.7 g, 13 mmol) in ether (40 mL). The resulting mixture was refluxed for 1.5 h, cooled to room temperature, and quenched with a saturated solution of sodium sulfate. The mixture was filtered and the solids triturated with ether. Evaporation of the ether and recrystallization of the residue from pentane afforded the alcohol **11** (1.6 g, 93%), mp 160 °C (lit.[31] mp 157 °C).

9-Bromohomocubane (12). Thionyl bromide (2 mL) was added to a solution of the alcohol **11** (520 mg, 3.9 mmol) in $CDCl_3$ (10 mL), and the ensuing mixture was stirred at room temperature for 1 h and then at reflux for 5 h with protection from moisture. The mixture was then cooled and washed with sodium metabisulfite solution (3 × 20 mL), and the organic layer was dried ($MgSO_4$) and evaporated at room temperature. Distillation (Kugelrohr, 100–110 °C/6mm) afforded 9-bromohomocubane (**12**) (514 mg, 71%) as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 3.05–3.72 (m, 8H), 4.32 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 40.38, 42.71, 43.58, 50.50, 63.26; MS(EI) *m/z* (relative intensity) 117 (100), 115 (94), 105 (21), 91 (63); HRMS(EI) [M – Br]·$^+$ calcd for C_9H_9 117.0704, found 117.0706. Anal. Calcd for C_9H_9Br: C, 54.9; H, 4.6. Found: C, 55.2; H, 4.6.

9-Hydroxyhomocubane-9-carbonitrile (13). The ketone **10** (4.4 g, 33 mmol) was converted into the cyanohydrin **13** with ethereal HCN according to the reported method.[32] Sublimation (110 °C/2.5 mmHg) of the crude product furnished **13** (5.3 g, 100%), mp 72–74 °C: ^{1}H NMR ($CDCl_3$) δ 3.12–3.83 (m, 8H), 2.23 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 39.07,

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42.10 (C9), 44.0, 45.6; MS(EI) *m/z* (relative intensity) 133 (5), 131 (59), 103 (100), 91 (18), 78 (95); HRMS(EI) calcd for C_9H_9O [M − CN]·+ 133.0653, found 133.0651. Anal. Calcd for $C_{10}H_9NO$: C, 75.5; H, 5.7. Found: C, 75.7; H, 5.8.

9-(Aminomethyl)homocuban-9-ol (14). The cyanohydrin **10** (5.5 g, 35 mmol) was reduced with lithium aluminum hydride as described above for the preparation of **11**. The solids were triturated with methylene chloride and the organic phase was separated and dried (Na_2SO_4). Evaporation of the solvent afforded the amino alcohol **14** (5.1 g, 90%), mp 128–131 °C: ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 3H, NH_2 and OH), 2.64 (s, 2H, CH_2), 2.88–3.98 (m, 2H), 3.06–3.41 (m, 4H), 3.49–3.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 40.85, 41.08 (CH_2), 42.06, 43.00, 49.25, 95.95 (C9); MS(EI) *m/z* (relative intensity) 163 (1), 156 (10), 145 (100), 131 (83), 117 (85), 105 (95); HRMS(EI) calcd for $C_{10}H_{13}NO$ 163.0997, found 163.1007. This product was used without further purification.

Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decan-9-one (15). A solution of the amino alcohol **14** (5.1 g, 31 mmol) in 10% aqueous acetic acid (100 mL) at 0 °C was treated with a solution of sodium nitrite (3.1 g, 45 mmol) in H_2O (40 mL). The cooling bath was removed after 30 min and the mixture stirred overnight. The mixture was then extracted with ether (2 × 300 mL), and the ether fractions were back-washed with aqueous ammonium chloride (200 mL), and then dried ($MgSO_4$) and evaporated to afford the ketone **15** (3.9 g, 85%), mp 86 °C (lit.[33] mp 82–83 °C).

Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decan-9-ol (16). The ketone **15** (2.8 g, 19 mmol) was reduced to the corresponding alcohol **13**, (2.68 g, 94%), mp 134 °C (lit.[34] mp 136–137 °C), with lithium aluminum hydride as described above for the preparation of **11**.

9-Bromopentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (17). A solution of the alcohol **16** (2.0 g, 13.5 mmol) and triphenylphosphine (3.86 g, 14.8 mmol) in DMF (13 mL) was treated dropwise at −10 °C with a solution of bromine (2.23 g, 14.2 mmol) in DMF (6 mL) in a manner similar to that described by Hrubiec and Smith.[35] The ensuing mixture was stirred at 0 °C for 3 h and then overnight at room temperature. The mixture was extracted with pentane (4 × 100 mL) and the combined pentane extracts were washed with water (200 mL), and then filtered, dried ($MgSO_4$) and evaporated at room temperature. The residue was triturated with pentane and the pentane evaporated. Distillation of the residue (Kugelrohr, 130 °C/4.5mm) furnished the desired bromide **17** (2.15 g, 75%): ^{1}H NMR ($CDCl_3$) δ 1.98–2.41 (m, 2H, CH_2), 2.50–3.60 (m, 8H), 4.25–4.67 (m, 1H, CHBr); ^{13}C NMR ($CDCl_3$) δ 30.64, 32.78, 36.87, 38.10, 38.48, 35.53, 40.15, 41.25, 43.85, 47.06; MS(EI) *m/z* (relative intensity) 131 (100), 129 (72), 115 (32), 104 (24), 91 (84); HRMS(EI) [M − Br]·+ calcd for $C_{10}H_{11}$ 131.0861, found 131.0872.

EPR Spectra. The bromide (*ca.* 5 mg) was dissolved in di-*tert*-butyl peroxide (*ca.* 30 μL) and triethylsilane (*ca.* 20 μL). This solution was placed into a quartz EPR tube and degassed on a vacuum line by a series of freeze–pump–thaw cycles. The solvent, cyclopropane, was distilled in, and the tube was sealed. Experiments were also carried out with hexamethylditin in place of triethylsilane, but no well-defined spectra were observed. In the hydrogen abstraction experiments, samples were prepared in a similar way but without Et_3SiH or $Me_3SnSnMe_3$.

Reduction of 9-Homocubyl Bromide with Bu_3SnH. A 5-mm NMR tube containing **12** (29.0 mg, 0.15 mmol) was submerged in an oil bath at 70 °C for 10 s. Bu_3SnH (54.1 mg, 0.21 mmol) was injected into the NMR tube, which was then sealed and left under a 400-W UV light in the oil bath for 1 h. GC/MS analysis of the resultant mixture showed that the reaction had yielded a single product. The mixture contained residual tin compounds which could not be satisfactorily separated by TLC. The following NMR spectra were therefore of both homocubane and unwanted tin products; the peaks of the latter have been ignored: ^{1}H NMR δ 3.27 (m, 2H), 3.22 (m, 4H), 3.11 (qn, *J* = 8.50 Hz, 2H) (this spectrum was essentially identical to that reported[2] for homocubane except for a peak at 1.65 ppm (s, 2H) which was obscured by organotin residues); ^{13}C NMR δ 45.40 (CH_2), 44.21 (CH), 44.02 (CH), 41.71 (CH); EIMS *m/z* (relative intensity) 118 (9), 117 (100), 115 (48), 103 (12), 91 (60), 77 (20), 65 (29), 52 (43), 39 (96), 27 (14). The spectroscopic data are fully consistent with the reported values[36] for homocubane. The experiment was repeated at 220 °C with identical results.

Reduction of 9-Bromobasketane. A 10-mm NMR tube containing **17** (0.50 g, 2.4 mmol), was submerged in an oil bath at 212 °C for 10 s. Immediately, Bu_3SnH (0.97 g, 3.9 mmol) was injected into the heated NMR tube. The tube was then sealed and left under a 400-W UV light in the oil bath at 212 °C for 35 min. The product was decanted into a small-scale distillation apparatus, leaving a gray metallic tin residue. Distillation on a vacuum line at ca. 0.01 Torr was carried out in two stages to give an overall yield of 181 mg (57%). In the first stage, two fractions were obtained: a sublimed, sugary white, crystalline solid (74.8 mg, 23.6%), which was shown by NMR to be the unrearranged product, *i.e.*, **20**, mp 102–104 °C (see small-scale reduction for spectroscopic data), and a colorless liquid (74.3 mg, 23.4%). GC analysis showed this liquid to be a mixture of **20** and the two rearranged compounds, tricyclo[4.4.0.0^{2,5}]-deca-3,8-diene (**23**) and tricyclo[4.4.0.0^{2,5}]deca-3,7-diene (**24**). The assignment of the peaks in the following NMR spectra was made possible with the aid of data obtained from a 2D COSY spectrum. The minor product **24** (20 rel %): ^{1}H NMR δ 5.96 (dd, *J* = 3.25, 4.84 Hz, $H^{8,9}$), 5.86 (s, $H^{3,4}$), 2.65 (m, $H^{2,5}$), 2.50 (m, $H^{1,6}$), 2.06 (t, *J* = 4.57 Hz, $H^{7',10'}$), 1.37 (m, $H^{7,10}$); ^{13}C NMR δ 138.28 ($C^{3,4}$), 129.97 ($C^{8,9}$), 46.20 ($C^{2,5}$), 34.36 ($C^{1,6}$), 23.99 ($C^{7,10}$); EIMS *m/z* (relative intensity) 131 (10), 117 (81), 103 (11), 91 (100), 79 (32), 78 (100), 77 (71), 65 (30), 54 (56), 51 (47), 39 (84), 27 (51). The major product **23** (80 rel %): ^{1}H NMR δ 6.00 (d, *J* = 2.76 Hz, $H^{3 \text{ or } 4}$), 5.90 (d, *J* = 2.76 Hz, $H^{4 \text{ or } 3}$), 5.85 (m, H^7), 5.33 (dddd, *J* = 1.30, 2.69, 3.96, 9.56 Hz, H^8), 3.19 (m, $H^{5 \text{ or } 2}$) [this peak was only resolved from basketane resonances on a 500-MHz spectrum], 2.98 (d, *J* = 3.13 Hz, $H^{2 \text{ or } 5}$), 2.32 (ddt, *J* = 17.82, 4.94, 2.54 Hz, $H^{9 \text{ or } 9'}$), 2.11 (dd, *J* = 6.45, 3.98 Hz, H^1), 2.03 (t, *J* = 4.88 Hz, $H^{10 \text{ or } 10'}$), 1.98 (t, *J* = 4.88 Hz, $H^{10' \text{ or } 10}$), 1.77 (dm, *J* = 17.81 Hz, $H^{9' \text{ or } 9}$), 1.57 (d, *J* = 10.74 Hz, H^6); ^{13}C NMR δ 139.09 ($C^{3 \text{ or } 4}$), 137.96 ($C^{4 \text{ or } 3}$), 133.54 ($C^{8 \text{ or } 7}$), 124.45 ($C^{7 \text{ or } 8}$), 57.89 ($C^{2 \text{ or } 5}$), 54.94 ($C^{5 \text{ or } 2}$), 33.98 (C^9), 33.49 (C^1), 31.84 (C^6), 29.12 (C^{10}); EIMS *m/z* (relative intensity) 131 (12), 117 (64), 104 (22), 91 (83), 79 (44), 78 (78), 77 (52), 65 (32), 54 (43), 51 (49), 39 (100), 27 (68). A second stage of distillation gave an additional 31.6 mg (10.0%).

Kinetics of the Reduction of 9-Bromobasketane. The reaction was carried out as for homocubyl bromide but with **17** (29 mg, 0.14 mmol). At 70 °C, one product was observed by GC/MS: ^{1}H NMR δ 3.19 (q, *J* = 3.01 Hz, 2H), 3.04 (m, 4H), 2.67 (m, 2H), 1.44 (t, *J* = 1.59 Hz, 2H); ^{13}C NMR δ 44.00 (CH), 40.16 (CH), 32.96 (CH),17.16 (CH_2); EIMS *m/z* (relative intensity) 131 (11), 117 (37), 104 (31), 91 (83), 78 (96), 65 (30), 51 (51), 39 (100), 27 (63). The spectroscopic data were consistent with literature values for basketane.[32] When the experiment was repeated at 220 °C, two product peaks were observed by GC/MS. One was the unrearranged basketane peak, while the other was found to be two overlapping peaks of two rearranged products (see large-scale reduction for spectroscopic data). The reaction was carried out at a range of temperatures (140, 150, 180, 204, and 220 °C) on the same scale to determine the kinetic parameters of the rearrangement. The k_r/k_H values were obtained at each temperature from the final product concentrations and the initial Bu_3SnH concentration by means of an integrated rate equation.[11,12] Best values of the rate constant ratios were located with an iterative computer program based on NAG routine CO5 AXF.

The following control experiments were carried out (a) a 5-mm NMR tube containing **17** (29 mg, 0.14 mmol) was submerged in an oil bath at 85 °C for 10 s. Bu_3SnH (54.1 mg, 0.21 mmol) was injected into the NMR tube, which was then sealed and left in the oil bath under irradiation with a 400-W UV light for 40 min. GC/MS and NMR data obtained on the resultant mixture showed that the reaction had yielded a single product **20**. The oil bath was then heated to 200 °C and the mixture returned to the oil bath for a further 2 h of irradiation. GC/MS analysis of the mixture showed no further reaction of the basketane. (b) A 5-mm NMR tube containing **17** (29 mg, 0.14 mmol) was submerged in an oil bath at 190 °C and irradiated with a 400-W UV light for 10 min. No Bu_3SnH was added. The GC/MS analysis of the product mixture showed none of the reduction products, **20**, **23**, or **24**, observed with the presence of Bu_3SnH. The ^{1}H NMR showed the starting material to be the main component along with other undeterminable side products.

Reduction of 17 with Bu_3SnD. A 5-mm NMR tube containing **17** (29.0 mg, 0.15 mmol) was submerged in an oil bath at 210 °C for 10 s. Bu_3SnD (54.1 mg, 0.36 mmol) was injected into the NMR tube, which was then sealed and left in the oil bath under irradiation with a 400-W UV light for 45 min. The GC/MS obtained from the resultant mixture showed that the reaction had yielded two main products, 9-deuterobasketane and 9-deuteriotricyclo[4.4.0.0^{2,5}]deca-3,7-diene. The resultant mixture contained residual tin products which could not be separated.

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The following NMR spectrum was therefore of both 9-deuteriobasketane and 9-deuteriotricyclo[4.4.0.0^{2,5}]deca-3,7-diene and of the unwanted tin residues. The peaks of the organotin components have been ignored. 9-Deuteriobasketane (49.4%): ^{1}H NMR δ 3.19 (qn, J = 3.01 Hz, 2H), 3.04 (m, 4H), 2.67 (m, 2H), 1.44 (obscured by butyl group from organotin); ^{2}H NMR δ 1.44 (s, D^9); ^{13}C NMR δ 43.54 (CH) 39.70 (CH), 32.43 (CH), 16.56 (CHD,CH$_2$); EIMS m/z (relative intensity) 132 (27), 118 (58), 104 (39), 91 (65), 78 (100), 65 (24), 52 (48), 39 (58), 27 (27). 9-Deuteriotricyclo[4.4.0.0^{2,5}]deca-3,7-diene (46.8%): ^{1}H NMR δ 6.00 (d, J = 2.80 Hz, H$^{3\text{ or }4}$), 5.90 (d, J = 2.80 Hz, H$^{4\text{ or }3}$), 5.85 (m, H^7), 5.33 (ddd, J = 1.30, 3.96, 9.56 Hz, H^8), 3.19 (unresolved), 2.98 (d, J = 3.13 Hz, H$^{2\text{ or }5}$), 2.11 (dd, J = 6.45, 4.00 Hz, H^1), 2.03 (t, J = 4.88 Hz, H$^{10\text{ or }10'}$), 1.98 (d, J = 4.88 Hz, H$^{10'\text{ or }10}$), 1.77 (dm, J = 17.81 Hz, H$^{9'\text{ or }9}$), 1.57 (obscured by butyl group from organotin); ^{2}H NMR δ 2.32 (s, D^9); ^{13}C NMR δ 139.07 (C$^{3\text{ or }4}$), 137.95 (C$^{4\text{ or }3}$), 133.61 (C$^{8\text{ or }7}$), 124.39 (C$^{7\text{ or }8}$), 57.83 (C$^{2\text{ or }5}$), 54.87 (C$^{5\text{ or }2}$), 33.82 (C^9), 33.44 (C^1), 31.69 (C^6), 29.10 (C^{10}); EIMS m/z (relative intensity) 132 (25), 118 (100), 105 (28), 91 (77), 78 (81), 65 (28), 51 (35), 39 (53), 27 (27). In the product mixture, little 7-deuteriotricyclo[4.4.0.0^{2,5}]deca-3,8-diene was observed. Instead, the ^{1}H NMR spectrum showed additional peaks in the alkene region, which we assign to 1-(4-deuteriocyclobut-2-enyl)-cyclohexa-2,4-diene (**26**) (3.9%): ^{1}H NMR δ 6.41 (dd, J = 4.32, 2.98 Hz), 6.10 (s, 2H), 6.04 (dd, J = 3.32, 4.44 Hz), 5.29 (s), 3.66 (m), 3.54 (m), 3.43 (m), 3.08 (m), 2.84 (m); ^{2}H NMR δ 1.8 (s); ^{13}C NMR δ 139.80 (CH), 134.44 (CH), 130.37 (CH), 44.84 (CH), 42.09 (CH), 41.10 (CH), (other ^{13}C data obscured by organotin residues); EIMS m/z (relative intensity) 133 (11), 129 (50), 115 (17), 102 (12), 74 (12), 62 (12), 52 (100), 39 (21), 26 (11).

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