A Kinetic and Theoretical Study of Ring-opening of Bicyclo[1.1.1]pentylmethyl and Bicyclo[2.1.1]hexylmethyl Radicals

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The rearrangement of the bicyclo[1.1.1]pentan-1-ylmethyl radical (9) and the bicyclo[2.1.1]hexan-1-yl-methyl radical (10) to the corresponding methylenecycloalkylmethyl radical (11, 12) has been studied kinetically by EPR spectroscopy and, in the case of 10, by tributyltin hydride reduction. Activation energies of 7.1 ± 1.2 kcal mol⁻¹ and 9.3 ± 0.5 kcal mol⁻¹ have been determined for 9 and 10, respectively, while the corresponding pre-exponential factors have been determined to be 12.3 ± 1.5 and 12.0 ± 1.0, respectively. Rearrangement of 9 has an unusually low activation barrier; this has also been investigated by ab initio molecular-orbital calculations. UHF/3-21G level of theory predicts a barrier of 7.8 kcal mol⁻¹, in excellent agreement with that obtained experimentally, while a somewhat higher value (11.2 kcal mol⁻¹) is predicted at the UHF/6-31G* level. All of these data indicate that relief of ring strain is a major contributing factor to the rapid rearrangement of these radicals.

Previous reports,[1–5] have demonstrated that cyclobutylmethyl (and substituted cyclobutylmethyl) radicals (1) are prone to rapid ring-opening to give the isomer 2 by a process which is frequently, though not always,[5] irreversible. The rate constant for ring fission of the parent species 1,[5] for example, is 4.7×10^3 s⁻¹ at 25 °C, and the activation energy of the rearrangement 1 ⟶ 2 is 11.7 kcal mol⁻¹ (1 cal ≡ 4.18 J).

The results of a recent study of the behaviour of the cyclobutylethyl radical 3 by Pigou[6] are consistent with these observations. It was found[6] that 3 cyclises to give, preferentially, the bicyclo[2.1.1]hexylmethyl radical 4 which in turn rearranges rapidly to the isomer 5. An enhanced rate of rearrangement of 4 is expected; the process 4 ⟶ 5 is facilitated because, besides being a cyclobutylmethyl radical, 4 possesses additional skeletal strain.

In order to evaluate the barrier to ring-opening of 4, Pigou[7] recently concluded a kinetic investigation of tributyltin hydride mediated reduction of the corresponding bromide 6. For comparison, a study of the rate of ring-opening of the homologous radicals, 7 and 8, was included. The activation energies of rearrangements of the radicals, 4 and 7,[7] were found to be 10.1 and 11.0 kcal mol⁻¹, respectively; as anticipated, these values are smaller than the barrier for ring-opening of 1. Data for the bicyclo[1.1.1]pentylmethyl radicals 8, however, were unavailable. The radical 8 was found to be so reactive that all
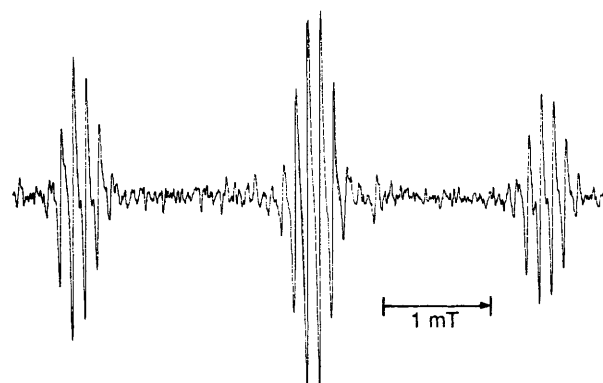

Fig. 1   9.4 GHz EPR spectrum of the bicyclo[1.1.1]pentan-1-methyl radical 9 in n-propane solution at 140 K

attempts to trap it before it succumbed to rearrangement were unsuccessful.[7] We have now determined the absolute rate of ring fission of the parent bicyclo[1.1.1]pentan-1-ylmethyl radical 9 by low-temperature EPR spectroscopy, and have coupled the experimental study with an ab initio determination of the activation energy of ring-opening of 9. The kinetics of the rearrangement of the higher homologue 10 to 12 were also measured, both by EPR spectroscopy and by tributyltin hydride reduction of the bromide, in order to assess the effect of the ester group on the rearrangement of 4.[7]

Results and Discussion

Kinetic EPR Measurements.—Bicyclo[1.1.1]pentylmethyl radicals (9) were generated by direct photolysis of a solution containing the corresponding bromide and equimolar amounts of triethylsilane and di-*tert*-butyl peroxide in propane at 120–150 K in the cavity of the EPR spectrometer. At temperatures above 170 K ring-opening of 9 was evident and the isomeric radical 11 was detected and identified.[8] Only the ring-opened species 11 was present at temperatures above 250 K; on lowering the temperature the spectrum of the unrearranged radical 9 reappeared. Interestingly, the spectrum of 9 (Fig. 1) consisted of a triplet of octets. Thus the bridgehead (δ) hydrogen gives quite an appreciable hyperfine splitting (hfs)

1   2   3   4

5   6   7

8   10   12
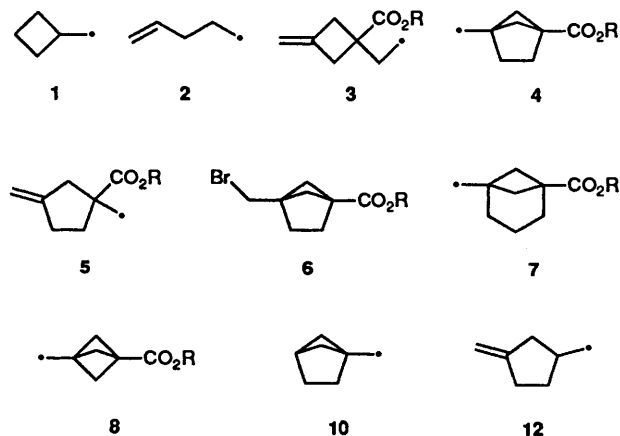
Table 1 EPR parameters of bicycloalkylmethyl and rearranged radicals

| | | hfs/mT | | |
Radical	T/K	a(2 H_α)	a(H_β)	a(other)
Bicyclo[1.1.1]pentan-1-ylmethyl (9)	130	2.17	—	0.118 (6 H_γ), 0.118 (1 H_δ)
Bicyclo[2.1.1]hexan-1-ylmethyl (10)	195	2.15	—	0.154 (2 H_γ), 0.077 (4 H_γ)
3-Methylenecyclobutylmethyl (11)[a]	200	2.18	1.31	0.072 (4 H_γ), 0.072 (2 H_δ)
3-Methylenecyclopentylmethyl (12)	205	2.20	1.92	0.07 (5 H)

[a] For literature values see ref. 8.

**Table 2** Kinetic EPR data for ring-opening of bicyclo[1.1.1]pentan-1-ylmethyl radicals (9)[a]

T/K	[9]/10^{-8} mol dm^{-3}	[11]/10^{-8} mol dm^{-3}	10^8 k_f^9/ 2k_t	k_f^9/10^{-2} s^{-1}
161	13.5	3.96	5.12	4.4
167	8.32	5.55	9.29	8.6
167	9.52	6.01	9.80	9.1
172	7.83	7.77	15.48	15.6
172	7.12	8.83	19.8	20.0
178	4.0	7.32	20.7	22.0
178	5.23	11.8	38.4	40.6
184	2.28	8.86	43.3	52.5
189	1.42	12.5	122.0	154.9

[a] In cyclopropane.

Table 3 Rate constants and Arrhenius parameters for ring-opening of the bicycloalkylmethyl radicals 9 and 10

Radical	k_f/10^3 s^{-1} (300 K)	log(A/ s^{-1})	E/kcal mol^{-1}
Cyclobutylmethyl (1)[a]	6.0	12.3 ± 1.0	11.7 ± 0.3
Bicyclo[1.1.1]pentan-1-ylmethyl (9)	13 400	12.3 ± 1.5	7.1 ± 1.2
Bicyclo[2.2.1]hexan-1-ylmethyl (10)[b]	168	12.0 ± 1.0	9.3 ± 0.5

[a] From ref. 5. [b] From a combination of the EPR and Bu_3SnH reduction data.
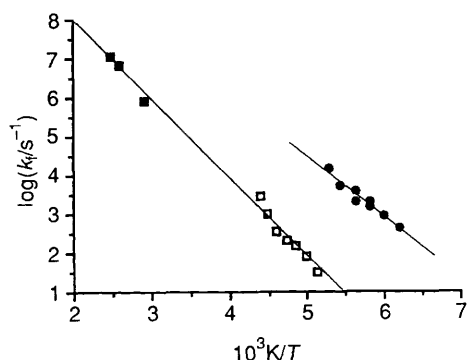
Fig. 2 Arrehenius plot of ring-opening rate constants, k_f: ●, kinetic EPR results for bicyclo[1.1.1]pentan-1-methyl radicals (9), k_f^9; □, kinetic EPR results for bicyclo[2.1.1]hexan-1-methyl radical (10), k_f^{10}; ■, tin hydride reduction derived k_f^{10} values

(0.12 mT) which was not resolved from that of the γ-methylene hydrogens. This value is in good agreement with our calculated value of 0.14 mT (see later). The EPR parameters of 9 and 11 are displayed in Table 1.

The measured concentrations of unrearranged and re-arranged radicals, 9 and 11, within the temperature range 160–190 K in cyclopropane solution are recorded in Table 2,

together with the values of k_f^9/2k_t derived by the usual treatment;[9,10] 2k_t being the rate constant for bimolecular termination reactions of 9.

Termination rates of small transient radicals in solution are mainly controlled by the viscosity. As is usual, therefore, we have employed Fischer's accurate values for the self-termination of tert-butyl radicals in heptane,[11] correcting for the difference in viscosity between heptane and cyclopropane as described previously.[3] The rate constants for ring-opening of 9 are plotted in Arrhenius form in Fig. 2.

Table 3 contains the rate constants and Arrhenius parameters associated with ring-opening of the radical 9. The low activation energy of 7.1 kcal mol^{-1} demonstrates clearly that relief of ring strain has a major influence on the rate of rearrangement which is considerably enhanced over that of the cyclobutylmethyl radical (1). Indeed, 9 ring-opens only eight times more slowly than the cyclopropylmethyl radical (13)[9a,12–15] Ring fission of 13 occurs with extraordinary rapidity and the reaction has special significance in mechanistic studies as a 'radical clock'. The most recent rate constant[15] for rearrangement of 13 is 1.0 × 10^8 s^{-1}. The low activation barrier observed for rearrangement of the bicyclo[1.1.1]pentylmethyl system (9) is presumably also responsible for the rapid rearrangement of the diradical species 14 produced by photochemically induced addition of diphenylcarbene to [1.1.1]propellane.[16] Radical 11 itself undergoes ring-opening at higher temperatures (210–250 K) to give the 2-allylallyl radical 15. The kinetics of this rearrangement have also been studied by the EPR method, radical 11 being generated from 3-bromomethylmethylenecyclo-butane.[8] Because the activation energy for ring-opening of 11 (i.e. 11.5 kcal mol^{-1}) is much greater than that for ring opening of 9 we find a remarkable situation in which these two rearrangements are completely 'temperature resolved' thus permitting them to be studied individually by the same technique.

9   11   15

13   14
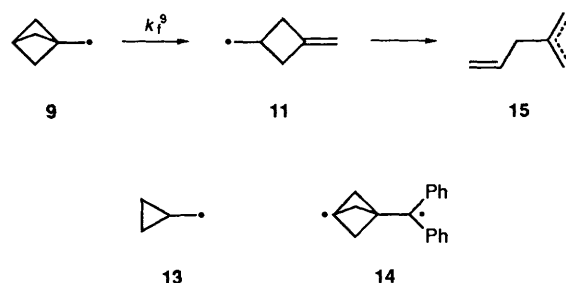
The behaviour of the bicyclo[2.1.1]hexylmethyl radical 10 was also studied kinetically by the EPR spectroscopic technique. Radicals 10 were generated from the parent bromide by abstraction of bromine with photochemically generated Me_3Sn· radicals in tert-butylbenzene solution. The spectrum of the unrearranged radical 10 was observed below 200 K as a triplet, each component being further split by long-range interactions. The best simulation was obtained with two sets of non-equivalent γ-hydrogens (Table 1). Above ca. 210 K the

Table 4 Kinetic EPR data for ring-opening of bicyclo[2.1.1]hexan-1-ylmethyl radical (10)[a]

| T/K	$[10]/10^{-7}$ mol dm^{-3}	$[12]/10^{-7}$ mol dm^{-3}	$10^7 k_f{}^{10}/$ $2k_t$	$k_f{}^{10}/$ 10^{-2} s^{-1}
195	5.66	1.94	2.61	0.32
200	5.44	3.20	5.08	0.82
206	4.79	4.03	7.42	1.60
211	4.42	4.02	7.68	2.09
217	4.27	4.80	10.20	3.64
223	2.99	6.57	21.01	9.63
228	1.97	9.24	52.58	29.4

[a] In *tert*-butylbenzene.

Table 5 Products of the reduction of 1-bromomethylbicyclo[2.1.1]-hexane with tri-*n*-butyltin hydride[a]

T/K	$[15]/$ mol dm^{-3}	$[16]/$ mol dm^{-3}	$k_f{}^{10}/k_H$	$k_f{}^{10}/$ 10^{-6} s^{-1}
343	0.091	0.135	0.16	0.84
386	0.063	0.0389	0.67	6.41
405[b]	0.015	0.0132	0.97	11.62

[a] [Bu$_2$SnH] = 1.13 mol dm^{-3}, [bromide] = 0.226 mol dm^{-3}. [b] [bromide] = 0.090 mol dm^{-3}.

9   **11**   **18**
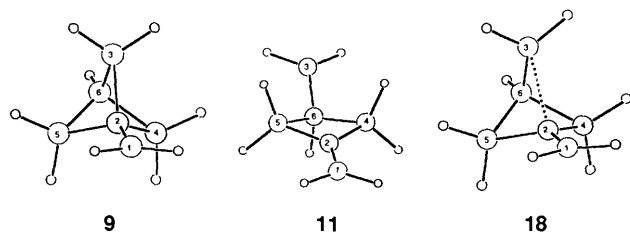
Fig. 3 *ab initio* (UHF/6-31G*) optimised structures for the bicyclo-[1.1.1]pentan-1-ylmethyl radical **9**, the 3-methylenecyclobutylmethyl radical **11** and the transition state **18** to rearrangement

spectrum of **10** weakened and that of the rearranged radical **12** appeared (see Table 1 for EPR hfs); on lowering the temperature **12** disappeared and **10** reappeared. The concentrations of **10** and **12** were measured in the range 195–230 K and the rate constant for ring opening, k_f,[10] was obtained by the method described above (Table 4). The Arrhenius plot is included in Fig. 2.

The ring-opening of radical **10** was also studied by reduction of the parent bromide with tri-n-butyltin hydride. Only two products were obtained, 1-methylbicyclo[2.1.1]hexane (**16**) and 3-methyl-1-methylenecyclopentane (**17**), and the amounts formed at each temperature are given in Table 5.

16   **17**
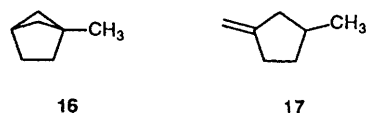
The rate constant ratio $k_f{}^{10}/k_H$, where k_H is the rate constant for hydrogen abstraction by **10** and **12** from Bu$_3$SnH, was evaluated in the same way as described previously.[5,8] The derived $k_f{}^{10}$ values are plotted in Fig. 2 which shows very satisfactory agreement with the data obtained at lower temperatures by EPR spectroscopy. The Arrhenius parameters obtained by combining both sets of results are given in Table 3. The Arrhenius parameters are consistent with those deduced by Pigou and Taylor[7] for the substituted radical **4** [log A = (12.16 ± 0.48) s^{-1} and E_{act} = (10.1 ± 0.7) kcal mol^{-1}],

suggesting that the process is affected only marginally by the presence of the ester function.

Theoretical Study.—The bicyclo[1.1.1]pentylmethyl radical **9**, the 3-methylenecyclobutylmethyl radical **11** and the transition state **18** for the rearrangement of **9** to **11** were located as stationary points on the C$_6$H$_9$ potential-energy surface at both UHF/3-21G and UHF/6-31G* (*ab initio*) levels of theory.

All calculations were performed with the GAUSSIAN 90 system of programs.[17] All geometries were optimized to the appropriate stationary point by the application of gradient-optimisation techniques[18] and were proven as corresponding to minima or saddle points by evaluation of the complete set of harmonic frequencies at both levels of theory. The calculated structural data and energies are listed in Table 6 and are displayed pictorially in Fig. 3.

Qualitatively, all of the structures in Fig. 3 are as expected. Closer inspection of the data in Table 6, however, reveals that the transition-state separation {[r[C(2)C(3)] in **18**]} is calculated to be significantly shorter than that normally associated with inter- and intra-molecular radical addition reactions of alkyl radicals,[19,20] namely 2.2–2.4 Å. This 'early' transition state is clearly a consequence of the strain inherent in **9** and is consistent with the theoretical data available for the rearrangements of other strained radicals,[21,22] in which the relief of ring strain is a major contributing factor in determining transition-state geometry and activation barrier.

The barrier† for the rearrangement of **9** to **11** is calculated to be 7.8 and 11.2 kcal mol^{-1} at UHF/3-21G and UHF/6-31G* levels of theory, respectively. Interestingly, the lower level of theory predicts a barrier which is in excellent agreement with the experimentally determined value of 7.1 ± 1.2 kcal mol^{-1}, while the higher level appears to overestimate the energy barrier somewhat.

Our calculations also indicate the unlikelihood of the reversibility of this rearrangement. Both levels of theory indicate the substantially exothermic nature of the reaction. The rearranged radical **11** is found to be 22.1 and 21.5 kcal mol^{-1} at UHF/3-21G and UHF/6-31G* levels of theory, respectively, lower in energy than the starting radical **9**.

When INDO hyperfine-coupling calculations[23] were carried out on the UHF/3-21G optimised structure of **9**, hyperfine splittings of a(H$_\alpha$) = 1.95 mT, a(H$_\gamma$) = 0.10 mT and a(H$_\delta$) = 0.14 mT were obtained. Considering that these calculations make no allowance for the rotation of the methylene group in **9**, they are in good agreement with the EPR data (see Table 1) and provide extra evidence for the appreciable hyperfine splitting to the bridgehead (δ) hydrogen in **9**.

Experimental

^{1}H NMR spectra were recorded on a Hitachi R-1200 spectrometer and ^{13}C NMR on a JEOL FX900 instrument in CDCl$_3$ solutions at ambient temperature with Me$_4$Si as an internal standard. Mass spectra were obtained on Kratos MS25RF and Finnegan Incos spectrometers. EPR spectra were recorded with a Bruker ER 200D spectrometer operating with 100 kHz modulation. Samples were prepared in Spectrosil tubes, degassed and photolysed in the cavity by light from a 500 W super pressure Hg lamp. *ab initio* and INDO calculations were carried out on a SUN SparcStation 1+.

1-Tosyloxymethylbicyclo[1.1.1]*pentane.*—A solution of bi-cyclo[1.1.1]pentane-1-carboxylic acid[24] (2.09 g) in anhydrous

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† The activation energies include the zero-point vibrational energy correction.

Table 6 *ab initio* calculated geometries[a] and energies [b] for structures **9, 11** and **18**

	9		**18**		**11**	
	3-21G	6-31G*	3-21G	6-31G*	3-21G	6-31G*
$r[C(1)C(2)]$	1.466	1.476	1.397	1.405	1.309	1.314
$r[C(2)C(3)]$	1.587	1.558	1.944	1.953	3.408	3.433
$r[C(2)C(4)]$	1.580	1.553	1.558	1.532	1.532	1.517
$r[C(2)C(6)]$	1.924	1.881	1.984	1.950	2.168	2.134
$r[C(3)C(6)]$	1.573	1.545	1.536	1.516	1.492	1.492
$r[C(4)C(6)]$	1.566	1.540	1.564	1.541	1.577	1.555
$r[C(1)H]$	1.073	1.075	1.073	1.075	1.074	1.076
$r[C(3)H]$	1.080	1.084	1.077	10.79	1.074	1.076
$r[C(4)H]$	1.081	1.085	1.080	1.084	1.083	1.086
$r[C(4)H']$	1.081	1.084	1.083	1.087	1.080	1.084
$r[C(6)H]$	1.073	1.081	1.075	1.084	1.085	1.089
$\theta[C(1)C(2)C(3)]$	127.8	127.7	125.4	125.7	—	—
$\theta[C(1)C(2)C(4)]$	128.3	127.8	132.6	132.5	133.8	134.1
$\theta[C(1)C(2)C(6)]$	180.0	180.0	171.5	171.4	169.4	165.3
$\theta[C(2)C(3)C(6)]$	75.3	74.6	68.4	67.4	—	—
$\theta[C(2)C(6)C(3)]$	52.8	53.0	65.6	67.3	136.4	141.8
$\theta[C(2)C(1)H]$	120.5	120.5	120.8	120.7	121.6	121.6
$\theta[C(2)C(3)H]$	115.8	116.5	113.2	114.1	—	—
$\theta[C(2)C(4)H]$	116.4	116.7	117.8	118.5	112.2	112.2
$\theta[C(2)C(4)H']$	115.7	116.4	113.3	113.5	116.3	117.3
$\theta[C(2)C(6)H]$	180.0	180.0	171.2	170.2	111.5	107.7
$\theta[C(6)C(3)H]$	—	—	—	—	120.3	120.2
$\omega[C(1)C(2)C(3)H]$	67.4	67.3	67.1	67.2	—	—
$\omega[C(1)C(2)C(4)H]$	67.4	67.3	55.3	54.5	81.8	87.4
$\omega[C(1)C(2)C(4)H']$	−67.4	−66.9	−77.5	−77.3	−46.5	−39.6
$\omega[C(1)C(2)C(6)H]$	—	—	—	—	0.0	0.0
$\omega[C(2)C(6)C(3)H]$	—	—	—	—	97.1	98.7
$\omega[C(3)C(2)C(1)H]$	85.8	83.8	85.6	84.1	90.0	90.0
$E(UHF)$[b]	−231.022 193 4	−232.315 919 2	−231.008 224 7	−232.296 107 7	−231.055 362 1	−232.347 836 6
E_{ZP}[c]	0.138 807 1	0.139 628 4	0.137 230 7	0.137 627 5	0.136 696 7	0.137 222 9
R_{rel}[d]	0.0	0.0	7.8	11.2	−22.1	−21.5

[a] Distances in Å, angles in degrees. [b] Energies in Hartree (1 H = 627.5 kcal mol⁻¹). [c] Zero-point energy. [d] Relative energy in kcal mol⁻¹ (including zero-point energy correction).

ether (8 cm³) was added dropwise to a solution of lithium aluminium hydride (1.4 g) in ether (10 cm³) at 50 °C under an atmosphere of nitrogen. The mixture was heated under reflux for 2 h and then cooled to 0 °C. Excess reagent was destroyed by dropwise addition of saturated sodium sulphate solution, and the mixture filtered. The precipitate was washed with ether and the combined ether layers were dried (MgSO₄) and evaporated to give 1-hydroxymethylbicyclo[1.1.1]pentane (98%) which was used without further purification; δ_H [25] 1.73 (6 H, s), 2.47 (1 H, exch. D₂O), 2.53 (1 H, s) and 3.51 (2 H, s); δ_C 27.9, 45.5, 48.8 and 63.4 ppm. The alcohol (1.7 g) was dissolved in dichloromethane (20 cm³) to which tosyl chloride (3.8 g) and pyridine (2 cm³) were added. The mixture was stirred at ambient temperature for 2 days and then washed with 5% HCl (2 × 15 cm³) and water (2 × 15 cm³) before being dried (MgSO₄) and evaporated. Recrystallisation of the residue from ether–pentane gave 1-tosyloxybicyclo[1.1.1]pentane (75%), m.p. 39–41 °C; δ_H 1.72 (6 H, s), 2.44 (3 H, s), 2.49 (1 H, s), 3.94 (2 H, s) and 7.3–7.9 (4 H, m); δ_C 21.6, 28.5, 41.8, 49.5, 70.2, 127.8, 129.75, 133.2 and 144.65 ppm (Found: C, 62.1; H, 6.3. C₁₃H₁₆O₃S requires C, 61.9; H, 6.4%).

1-*Bromomethylbicyclo*[1.1.1]*pentane*.—The sulphonate above (1.1 g) was dissolved in dry tetrahydrofuran (THF) (20 cm³) to which anhydrous lithium bromide (4 equiv.) was added. The solution was stirred at ambient temperature for 20 h, after which it was diluted with pentane (50 cm³) and washed with water (6 × 30 cm³) before being dried (MgSO₄). The solution

* 1 Torr = 101 32/760 Pa.

was concentrated *in vacuo* (0 °C/50 Torr*) and the residue distilled (Kugelrohr: 90 °C/75 Torr) to give the bromide (75%); δ_H 1.77 (6 H, s), 2.47 (1 H, s) and 3.37 (2 H, s); δ_C 26.8, 34.3, 44.1 and 49.7 ppm (Found: C, 44.4; H, 5.8. C₆H₉Br requires C, 44.7; H, 5.6%).

1-*Tosyloxymethylbicyclo*[2.1.1]*hexane*.—Bicyclo[2.1.1]-hexane-1-carboxylic acid [26] (1.6 g) was treated with LiAlH₄ (2 g) in ether (80 cm³) as described [27] to give 1-hydroxymethylbicyclo[2.1.1]hexane (93%) which was converted into the corresponding tosylate (81%) as outlined above. 1-Tosyloxymethylbicyclo[2.1.1]hexane as purified by recrystallisation from ether–pentane had m.p. 43–45 °C,[27] δ_H 0.88–1.70 (8 H, m), 2.40–2.52 (m) and 2.45 (total 4 H, s), 4.12 (2 H, s) and 7.28–7.88 (4 H, m).

1-*Bromomethylbicyclo*[2.1.1]*hexane*.—1-Tosyloxymethyl-bicyclo[2.1.1]hexane (1.0 g) was treated with lithium bromide in THF as described above for the lower homologue. Distillation (Kugelrohr: 105 °C/50 Torr) yielded the pure bromide [27] (72%); δ_H 0.98–1.75 (8 H, m), 2.42–2.50 (1 H, m) and 3.59 (2 H, s); δ_C 28.8, 29.7, 36.0, 37.7, 41.7 and 51.6 ppm (Found: C, 48.3; H, 6.1. C₇H₁₁Br requires C, 48.0; H, 6.3%).

Reduction of 1-*Bromomethylbicyclo*[2.1.1]*hexane with Tri-n-butyltin Hydride*.—To a degassed solution of the bromide (0.01 cm³, 0.081 mmol) in *tert*-butylbenzene (0.25 cm³) at 70 °C in a quartz tube was added Bu₃SnH (0.101 cm³, 0.41 mmol) and the mixture was photolysed for 1 h with light from a 250 W medium pressure Hg lamp. GC–MS analysis on an HP 17 capillary column showed only two products. The first eluted was 1-

methylbicyclo[2.1.1]hexane (16) with a mass spectrum identical with that of authentic material; m/z (%) 96 (M$^+$, 2), 81 (100), 79 (16), 68 (22), 67 (33), 55 (62), 54 (22), 53 (16), 41 (27), 40 (10) and 39 (47). The second eluted was identified as 1-methyl-3-methylenecyclopentane (17); m/z (%) 96 (M$^+$, 22), 81 (100), 79 (22), 68 (12), 67 (22), 55 (20), 54 (18), 41 (25), 40 (13) and 39 (48).

Kinetics of 1-*Bromomethylbicyclo*[2.1.1]*hexane Reduction.*—Reactions were carried out as described above, using the same quantities, except for the highest-temperature experiment (see Table 5), and by adding the Bu$_3$SnH to preheated solutions of the bromide. n-Hexane (0.005 cm^3) was added to each solution as an internal standard. The k_r^{10}/k_H values were obtained at each temperature from the final product concentrations and the initial Bu$_3$SnH concentration by means of an integrated rate equation.[8] Best values of the rate constant ratio were located with an iterative computer program based on the NAG routine CO5 AXF.

Acknowledgements

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