γ -Dissociations of 3-alkylbicyclo[1.1.1]pent-1-yl radicals into [1.1.1]propellane and alkyl radicals: verification of a theoretical prediction

John C. Walton^{*a} and Lewis Whitehead^b

^a School of Chemistry, University of St. Andrews, St. Andrews, Fife, UK KY169ST ^b Department of Chemistry, University of Southampton, Southampton, UK SO171BJ

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The γ -dissociations of 3-substituted bicyclo[1.1.1]pent-1-yl radicals and cyclobutyl radicals were investigated by *ab initio* SCF MO (HF, MP2, MP3 and MP4/6–31G*) and density functional methods (B3LYP/6–31G*). The transition states were found to resemble the product alkyl radical and [1.1.1]propellane or bicyclo[1.1.0]butane. Calculated endothermicities and energy barriers were comparatively low for loss of the *t*-butyl radical from the 3-*t*-butylbicyclo[1.1.1]pent-1-yl radical, which suggested that this dissociation would be significant under laboratory conditions. The dissociation was verified experimentally by means of the reaction of 1-iodo-3-*t*-butylbicyclo[1.1.1]pentane with tributyltin hydride. Arrhenius parameters for this dissociation were determined by end product analysis. The SCF MO and density functional calculations resulted in much higher endothermicities and energy barriers for γ -dissociations of cyclobutyl radicals, hence neither the formation of bicyclo[1.1.0]butane nor alkyl radical addition to this bicyclic compound was predicted to be important.

Small-ring bridgehead radicals have unique geometries and electronic configurations which signal unusual chemistry and enhanced reactivity. Bridgehead radicals are necessarily pyramidal and hence they are expected to be more reactive generally than acyclic *t*-alkyl radicals, such as the essentially planar t-butyl,¹ because pyramidalization reduces steric shielding of the radical centre and reduces radical stabilisation. Pyramidalization also increases the s-character of the SOMO and hence increases nucleophilicity.² The bicyclo[1.1.1]pent-1-yl radical (1a) is the most extreme example of "bridgehead character" known to date.³ Consequently, this radical has attracted a lot of interest in the last few years as experimental methods for studying it have been developed. Recent work has shown that radical 1 is active in atom abstraction⁴ and addition reactions,⁵⁻⁷ and it has even found practical use as a chain carrier in synthetic sequences designed to make strained polycycles. Bicyclo[1.1.1]pent-1-yls 1 have an additional unique feature in that the cross cage distance is very short (ca. 1.80 Å)^{8,9} so that 3-substituents have a powerful influence on chemical properties. Attempts to provide quantitative kinetic, thermodynamic and structural data for strained bridgehead radicals have been meagre owing to the formidable experimental difficulties.^{2,10,11} However, recent kinetic studies established that bicyclo[1.1.1]pent-1-yl radicals add to alkenes and abstract hydrogen considerably more rapidly than do t-butyl radicals.¹² Furthermore, 1 was found to react with three-coordinate phosphorus much more rapidly than primary alkyl radicals.¹³ Because of the increasing technical importance of radicals of type 1, exploration of alternative unimolecular options is imperative.

Bicyclo[1.1.1]pent-1-yl radicals are usually made by addition of some initial radical to [1.1.1]propellane (2). This addition is known to be fast for carbon-centred radicals and for a range of heteroatom-centred radicals.^{14,15} A theoretical study by Feller and Davidson¹⁶ implied that comparatively little expenditure of energy was entailed in the reverse reaction, *i.e.* the γ -dissociation of the C3–H bond of **1a** to produce [1.1.1]propellane 2 and a hydrogen atom (Scheme 1). This diagnosis was endorsed by our *ab initio* MO calculations (6–31G* basis) which gave 27.0 kcal mol⁻¹ as the dissociation energy for this process.¹⁷ These theoretical estimates implied that unimolecular loss of a C-centred radical, more thermodynamically stabilised than the H-atom, *e.g.*, methyl or, better still, *t*-butyl, should occur from 1 at comparatively low temperatures. The viability of this novel γ -scission process has been tested by *ab initio* MO theory for **1a–c**, and experimentally for **1c**, and this paper reports the main findings.

[1.1.]Propellane is a unique molecule with an inverted structure at the two bridgehead carbon atoms.¹⁸ It seemed possible, therefore, that the occurrence of this type of γ -dissociation would be contingent on the co-production of **2** with an alkyl radical and would not be general for related classes of radicals. To assess this prospect, we also examined a closely analogous process, *i.e.*, the γ -dissociation of 3-substituted cyclobutyl radicals **4**, which might be expected to generate an alkyl radical together with bicyclobutane **5**, the next lower homologue of propellane **2** (Scheme 2).

Experimental

EI mass spectra were obtained with 70 eV electron impact ionisation on a VG (Winsford, Cheshire, UK) Autospec spectrometer. GC-MS analyses were run on a Finnigan (Sunnyvale, CA, USA) Incos 50 quadrupole instrument





coupled to a Hewlett-Packard (Avondale, PA, USA) HP 5890 chromatograph fitted with a 25 m HP 17 capillary column (50% phenyl methyl silicone). For analytical GC a Philips (Eindhoven, The Netherlands) PU 4500 chromatograph, fitted with a 5 m column packed with 10% OV-101 on Chromosorb WAW operated at 80 °C, was used. 1,1-Dibromo-2,2-bis(chloromethyl)cyclopropane was prepared by the method of Della and Taylor¹⁹ and [1.1.1]propellane was synthesised as described in the literature.^{5,6}

1-Iodo-3-t-butylbicyclo[1.1.1]pentane 7c

[1.1.1]Propellane (1.06 g, 0.016 mol) and 2-iodo-2-methylpropane (3.0 g, 0.016 mol) in diethyl ether (100 cm³) were irradiated for 6 h in a water-cooled, quartz photochemical reactor at ambient temperature with light from a 150 W Hg lamp. The solvent was evaporated and the product was distilled to yield iodide **7c** as pale yellow crystals (1.04 g, 26%), mp 105 °C; $\delta_{\rm H}$ (300 MHz, CDCl₃) 0.81 (9H, s, 3 × CH₃), 2.09 (6H, s, 3 × CH₂); $\delta_{\rm C}$ (75 MHz) 26.2, 32.11, 46.7, 49.72, 56.48; *m/z* 250 (M⁺, 2%), 194 (8), 193 (14), 192 (9), 128 (18), 127 (5), 123 (18), 115 (19), 108 (22), 93 (53), 83 (93), 67 (38), 57 (100), 56 (61).

Reaction of 7c with tributyltin hydride

1-Iodo-3-*t*-butylbicyclo[1.1.1]pentane (20 mg, 0.8 mmol) and tributyltin hydride (30 µl, 1.6 mmol) in C_6D_6 (0.5 cm³) in an NMR tube were photolysed at 80 °C for 4 h with light from a 150 W Hg arc. The ¹H NMR spectrum of the product mixture showed the presence of [1.1.1]propellane (2) (δ_H 2.02) together with 3-*t*-butylbicyclo[1.1.1]pentane (8), the spectrum of the latter [δ_H 0.82 (9H, s), 1.59 (6H, s), 2.48 (1H, s)] being in good agreement with the literature.²⁰ GC-MS analysis verified the presence of isobutane (confirmed by retention time comparisons with authentic material) and 8 [*m*/*z* 109 (11%), 91 (7) 84 (73) 83 (100), 82 (22), 67 (65), 56 (32), 55 (95), 42 (23), 41 (72), 40 (43)].

Kinetics of dissociation of radical 1c

Photolytic reactions were carried out as described above with **7c** and excess tributyltin hydride (0.216 mol dm⁻³) in C₆D₆ or *t*-butylbenzene as solvent. The following product ratios, [8]/[*t*-BuOH], were determined by GC analysis: 323 K, 781; 338 K, 725; 353 K, 249; 368 K, 42.7; 392 K, 105; and 423 K, 25.7.

Results and discussion

Ab initio SCF and density functional calculations

Ab initio SCF computations were carried out using the Gaussian 94 suite of programs²¹ (revisions D.4 and E.1) employing a $6-31G^*$ basis set and electron correlation up to MP4. Structures were fully optimised at the HF and MP2-fc levels, starting in each case from a C_{3v} point group geometry and using the spin-restricted (RHF) and spin-unrestricted (UHF) methods for closed shell and open shell species, respectively; then single point calculations were performed at MP3 and MP4 levels. Selected species were also examined using density functional theory with no geometry constraints (B3LYP/6-31G*).²² The dissociations and reverse radical addition reactions were explored by means of reaction coordinate scans performed at the Hartree–Fock 6–31G* level of theory. These scans involved incrementing the bond distance between the substituent species and C3 of the cage, then allowing the rest of the geometry to optimise. The location of the transition states at the Hartree-Fock energy maxima was confirmed by performing frequency calculations to establish one imaginary frequency. Normal harmonic vibrational frequencies and zero point vibrational energies (ZPVEs) were evaluated for each species at the HF, MP2 and B3LYP levels of calculation. The MP2-ZPVEs and thermal vibrational corrections were used in deriving energy changes for the MP3 and MP4 data. The transition state (TS) geometries were subsequently optimised at the MP2 level, followed by single point MP3 and MP4 calculations. In the B3LYP calculations, TS geometries were partly optimised starting from the MP2 data. Initial computed $\langle S^2 \rangle$ values were >0.75 and <0.76 for all radicals from HF and MP2 calculations, showing that contamination from higher spin states was minimal. However, the initial $\langle S^2 \rangle$ values of the transition states were significantly in excess of this, partitcularly for the HF and MP2 methods, for which values as high as 0.9 were found for TS 3c. This indicated significant contamination of the wavefunctions with quartet and higher spin states. However, spin projection was employed to remove this and spin projected energies were utilised for all the open shell systems. Overall energy changes ΔH_{298} and activation energy differences ΔE_{d} and ΔE_{a} for the forward dissociation and reverse addition reactions, respectively, were derived from the calculated optimum energies, zero point vibrational energies and thermal vibrational corrections $(H_{298} - H_0)$ of the individual species.

The main calculated geometric parameters of the bridgehead radicals, the TSs for their dissociation and the product species are listed in Table 1.

The MP2 bond lengths and angles of the bridgehead molecules 2 and 5 are essentially identical with those reported previously^{9,26} and in close agreement with the B3LYP data; congruence with the experimental structures (Table 1) is also impressive. The MP2 calculated geometries of radicals 1a-c and 4a,b are generally close to the B3LYP calculated structures, the main difference being that the latter method predicts slightly longer C-C and C-H bonds. As is normally found, the radical structures displayed a shortening of their C2-C1. bonds and a lengthening of their C3-C2 bonds in comparison with the hydrocarbons from which they were derived. The cross-cage distances between the bridgeheads [R(C1-C3)] in radicals 1a-c were calculated to be short, as expected, and all three methods indicated a slight lengthening of this bond as Me and t-Bu replaced H as the 3-substituent. Noteworthy features of TS geometries for dissociation of radicals 1a-c were first, the comparatively long (>2 Å) distances between the 3substituent and the cage. Second, in all three cases, the geometry of the cage part of the molecule had closed up dramatically and was approaching that of [1.1.1]propellane. Simultaneously, the geometries of the Me and t-Bu substituents closely resembled those of the free Me' and t-Bu' radicals. We can conclude that the TSs for the dissociations are "late" on the reaction coordinate and that the TSs of the matching reverse addition reactions are "early". Analogous structural behaviour was calculated for the dissociations of the cyclobutyl radicals 4a,b (see Table 1).

The calculated energies (H_0) of the radicals, TSs and dissociation products are listed in Table 2. The HF, MP2 and B3LYP data are for fully optimised geometries but the MP3 and MP4 data refer to single point calculations obtained with the MP2 geometry. Quantitative calculations of thermochemical parameters are difficult to achieve and require large basis sets. However, with MP4/6–31G* and similar basis sets, good agreement with experiment has been achieved, provided ZPVEs and thermal vibrational enthalpies are taken into account.^{27,28} We calculated ZPVEs and thermal vibrational enthalpies at the HF, MP2 and B3LYP levels. Our energies have not been scaled, first, because this introduces an empiri-

Table 1 Calculated structures of radicals and	transition	states
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Species	Unit ^a	HF/6-31G*	MP2/6-31G*	B3LYP/6-31G*	Obs. ^b
Bicyclo[1.1.1]pentyl	<i>R</i> (C1–C2)	1.535	1.541	1.549	
1a	R(C1-C3)	1.814	1.800	1.806	
	R(C2-C3)	1.546	1.548	1.555	
	R(C2-H)	1.080	1.101	1.102	
	/ (C2C1C4)	89.3	89.7	89.8	
	\angle (C1C2C3)	72.1	71.3	71.1	
	∠(C2C3H)	126.4	125.8	125.7	
TS 3a	R(C1-C2)	1.508	1.508	1.521	
	R(C1–C3)	1.587	1.540	1.598	
	R(C2-C3)	1.508	1.508	1.521	
	R(C3-H)	2.090	2.090	2.090	
	K(C2-H)	94.9	96.3	94.9	
	(C1C2C3)	63.5	61.4	63.4	
	\angle (C2C3H)	121.8	120.7	121.7	
3-Methylbicyclo[1.1.1]pentyl	$\overline{R}(C1-C2)$	1.532	1.538	1.544	
1b	R(C1-C3)	1.823	1.809	1.818	
	R(C2-C3)	1.553	1.554	1.563	
	R(C3–C6)	1.515	1.516	1.524	
	R(C2-H)	1.083	1.093	1.094	
	R(C6–H)	1.086	1.094	1.096	
	\angle (C2C1C4)	89.4	89.8	89.9	
	$\angle (C1C2C3)$	/1.0 1267	/1.0 126.2	/1.0 126.3	
	/ (HC6H)	108.2	108 5	108 3	
TS 3b	R(C1-C2)	1.515	1.509	1.525	
	R(C1-C3)	1.640	1.556	1.636	
	R(C2-C3)	1.515	1.509	1.525	
	R(C3-C6)	2.342	2.342	2.342	
	R(C2-H)	1.078	1.087	1.089	
	R(C6–H)	1.075	1.081	1.085	
	\angle (C2C1C4)	93.5	95.8	93.9	
	\angle (C1C2C3)	65.6	62.1	64.8	
	$\angle (U2C3C0)$	122.8	121.0	122.4	
3-t-Butylbicyclo[1 1 1]pentyl	R(C1-C2)	1 530	110.5	117.2	
1c	R(C1-C2) R(C1-C3)	1.824	1.806	1.816	
	R(C2-C3)	1.557	1.558	1.566	
	R(C3-C6)	1.535	1.532	1.550	
	R(C2-H)	1.083	1.093	1.093	
	R(C6–C7)	1.535	1.529	1.539	
	∠(C2C1C4)	89.7	90.1	90.2	
	\angle (C1C2C3)	72.4	71.4	71.5	
	\angle (C2C3C6)	126.9	126.3	126.3	
TS 2a	$P(C_1, C_0C_1)$	109.4	109.8	109.7	
15 50	R(C1-C2) R(C1-C3)	1.517	1.511	1.528	
	R(C2-C3)	1.000	1.500	1.047	
	R(C3-C6)	2.302	2.302	2.302	
	R(C2-H)	1.078	1.087	1.089	
	R(C6-C7)	1.508	1.495	1.504	
	∠(C2C1C4)	93.3	95.6	93.7	
	∠(C1C2C3)	65.9	62.4	65.2	
	\angle (C2C3C6)	123.0	121.2	122.6	
[1 1 1] Propellance ?	\angle (C7C6C7) P(C1-C2)	115.7	117.1	116.4	1 505
LI.I.I Propenane 2	R(C1 - C2)	1.503	1.310	1.318	1.525
	$R(C^2-H)$	1.544	1.590	1.300	1.390
	/(C2C1C4)	90.6	94.8	95.4	95.1
	\angle (C1C2C3)	61.8	63.5	62.7	63.1
	∠(C1C3H)	117.6	117.2	117.5	116.9
Bicyclo[1.1.0]butane 5	R(C1–C2)	1.488	1.494	1.499	1.489
	R(C1–C3)	1.467	1.500	1.494	1.497
	R(C1-H)	1.070	1.080	1.081	1.071
	R(C2-H)	1.078	1.089	1090	1.093
	\angle (C2C3C4)	98.4	98.7	98.8	100 4
Cyclobutyl 49	E(C1-C2)	130.4	129.5	129.8	128.4
Cyclobulyi 4a	$\frac{R(C2-C2)}{R(C2-C3)}$	1.510	1.505	1.505	
	R(C1-C3)	2.127	2.114	2.127	
	R(C1-H)	1.076	1.086	1.086	
	R(C2-H)	1.088	1.097	1.101	
	R(C3-H)	1.083	1.093	1.094	
	∠(C2C1C4)	93.6	93.5	94.6	
	\angle (C1C2C3)	87.9	87.4	87.8	
	∠(C2C3C4)	90.1	89.5	89.8	
	\angle (C2C1H)	131.4	131.5	132.7	
	∠(C1C3H)	113.4	116.4	114.5	

 Table 1—Continued

Species	Unit ^a	HF/6-31G*	MP2/6-31G*	B3LYP/6-31G*	Obs. ^b
TS 6a	R(C1–C2)	1.522	1.495	1.503	
	R(C2-C3)	1.522	1.495	1.503	
	R(C1-C3)	1.887	1.555	1.595	
	R(C1-H)	1.080	1.096	1.092	
	R(C2-H)	1.080	1.091	1.092	
	R(C3-H)	1.645	1.645	1.645	
	\angle (C2C1C4)	85.6	95.4	94.4	
	\angle (C1C2C3)	76.6	62.7	64.1	
	\angle (C2C3C4)	85.6	95.4	94.4	
	\angle (C2C1H)	156.5	154.6	154.9	
	∠(C1C3H)	127.7	127.2	127.5	
3-Methylcyclobutyl	R(C1-C2)	1.508	1.502		
4b	R(C2-C3)	1.559	1.559		
	R(C1–C3)	2.133	2.120		
	R(C1–H)	1.075	1.085		
	R(C2-H)	1.088	1.099		
	R(C3–C5)	1.521	1.519		
	∠(C2C1C4)	93.8	93.8		
	∠(C1C2C3)	88.1	87.7		
	∠(C2C3C4)	89.9	89.3		
	∠(C2C1H)	131.5	131.8		
	∠(C2C3C5)	115.3	113.9		
a Ameleo in deserve hand lengthe	:	· Coheren 1 and 2	f., 1 (a <i>b</i> F 1 1 13 D a a a 11a a a a	6 22 1 24

"Angles in degrees; bond lengths in angstroms; see Schemes 1 and 2 for key to numbering. "[1.1.1]Propellane: rets. 23 and 24. Bicyclo[1.1.0]butane: ref. 25.

cal element into the results, and second, because a recent study has shown that the scale factors for MP2 and B3LYP data are very close to unity.²⁹ Only the HF vibrational modes are significantly overestimated, but the errors that this introduces into the final energy differences are very small. Individual energies were therefore estimated using the following expression:

 $H_{298} = H_0(\text{level}/6-31\text{G*}) + \text{ZPVE}(\text{level}/6-31\text{G*})$

 $+ (H_{298} - H_0)_{vib}(level/6-31G^*)$

except for the H_{298} values at MP3 and MP4 where the ZPVEs and $(H_{298} - H_0)_{\rm vib}$ values calculated at MP2 were used. Using these data, the reaction enthalpies (ΔH_{298}) and the energy difference between the TS and the initial bridge-head radical (ΔE_d) and the energy difference between the TS and the product species (ΔE_a) were calculated (Table 3).

Not surprisingly, large swings between the various methods of calculation were observed in the ΔH_{298} and ΔE values. Usually the HF and B3LYP methods were in good agreement except that the B3LYP calculations indicated lower activation energies for the reverse radical addition reactions. All methods agreed that the γ -dissociations of the bicyclo[1.1.1]pent-1-yl radicals would be endothermic and that the additions of H⁻ and alkyl radicals to [1.1.1]propellane would be exothermic. The B3LYP reaction coordinate indicated essentially no energy maximum for radical 1a. Reaction coordinate scans were not successful for radical 4b because of sudden discontinuities, possibly because algorithms were unable to cope with the symmetry change. The γ -dissociation of each cyclobutyl radical 4 was calculated by all the methods to be 14-20 kcal mol⁻¹ more endothermic than the dissociation of the homologous radical 1. Because the dissociation of each radical 1 produces [1.1.1] propellane the enthalpy change ΔH_{298} , and to a large extent ΔE_{d} , should be controlled by the thermodynamic stabilisation of the released alkyl radical. The experimentally determined stabilisation energy of t-Bu is ca. 9 kcal mol⁻¹ greater than that of Me^{.30} Similarly, Me[.] is 10-15 kcal mol⁻¹ more stable than the H-atom (depending on how this is assessed).³¹ Hence the calculated ΔH_{298} values are expected to decrease by 10-15 kcal mol⁻¹ on introducing the 3-Me substituent and by about a further 9 kcal mol⁻¹ on changing this to t-Bu. Provided that the Hammond postulate holds for this series of dissociations, corresponding decreases in the ΔE_d values are expected. Reference to Table 3 shows that only the HF and B3LYP data roughly follow this trend but that the MP2 and MP4 methods predict decreases in ΔE_d only from 1b to 1c, while the MP3 data show only small variations.

Table 2 Calculated energies H_0 (hartree) for radicals 1 and 4, TSs and products^a

Species	HF/6-31G* Geometry optimised	MP2/6-31G* Geometry optimised	MP3/6-31G* Single point ^b	MP4/6–31G* Single point ^b	B3LYP/6-31G* Geometry optimised
1a	-193.26378	-193.89417	- 193.92895	- 193.96181	- 194.58419
1b	-232.30489	-233.06774	-233.11061	-233.14416	-233.90380
1c	-349.40676	-350.57519	-350.64221	-350.69623	-351.84512
TS 3a	-193.18522	-193.84244	-193.864223	-193.89986	- 194.51299
TS 3b	-232.23756	-233.01298	-233.04823	-233.07887	-233.84488
TS 3c	-349.35211	-350.52916	-350.58198	-350.64939	-351.80234
2	-192.69107	-193.35028	-193.37039	-193.40612	-194.00898
5	-154.87177	-155.38997	-155.41770	-155.44389	-155.94805
4a	-155.46726	-155.96192	-155.99835	-156.02168	-156.54532
4b	-194.50398	-195.13148	-195.17813	-195.20665	-195.86192
TS 6a	-155.28210	-155.81956	-155.84614	-195.87341	-156.39284
CH ₃ .	- 39.55899	-39.67074	-39.68585	- 39.68936	- 39.83829
t-Bu	-156.67501	-157.17911	-157.22232	-157.24550	-157.79833

^{*a*} H_0 for the H-atom = -0.49823 (HF, MP2, etc.) and -0.50027 (B3LYP). ^{*b*} With MP2 geometry.

Table 3 Calculated dissociation enthalpies (ΔH_{298}) and activation energies for γ -dissociations and additions to 2 and 5^a

Reaction	Parameter	HF	MP2	MP3	MP4	B3LYP
$1a \rightarrow 2 + H^{\cdot}$	ΔH_{298}	31.8	14.9	24.1	22.3	33.8
	ΔE_{d}	35.7	20.8	28.9	27.2	33.5
	$\Delta E_{\mathrm{a}}^{-}$	3.9	5.9	4.8	4.9	-0.3
$1b \rightarrow 2 + Me^{\cdot}$	ΔH_{298}	22.4	17.0	21.8	18.2	23.5
	ΔE_{d}	33.6	27.0	31.8	33.7	30.3
	$\Delta E_{\mathrm{a}}^{\circ}$	11.2	10.0	10.0	15.5	6.7
$1c \rightarrow 2 + t$ -Bu'	ΔH_{298}	15.5	20.3	22.6	19.6	15.0
	ΔE_{d}	27.7	23.7	32.6	24.2	21.4
	$\Delta E_{\mathrm{a}}^{-}$	12.2	3.4	10.0	4.6	6.4
$4a \rightarrow 5 + H^{\cdot}$	ΔH_{298}	48.4	33.1	38.6	36.8	49.1
	ΔE_{d}	102.1	78.1	84.3	81.8	85.0
	$\Delta E_{\mathrm{a}}^{\circ}$	53.7	45.0	45.7	45.0	35.9
$4b \rightarrow 5 + Me^{-1}$	ΔH_{298}	36.1	32.9	35.3	34.7	36.9
Including ZPVEs and thermal vibrational corrections (see text); energies in kcal mol ^{-1} (1 cal = 4.184 J).						

Hence the trends and absolute values of the HF and B3LYP reaction enthalpies and activation energies are more credible. Of particular note are the low ΔH_{298} and ΔE_d predicted for loss of *t*-Bu[·] from 1c (Table 3). These calculated energy differences imply that loss of the *t*-Bu[·] radical, and hence other radicals with appreciable stabilisation energies such as benzyl and allyl, should occur comparatively rapidly and should be detectable within the normal temperature range of organic laboratory experiments (25–150 °C). On the other hand, all five computational methods yielded much greater ΔH_{298} and ΔE_d values for the cyclobutyl radical dissociations, which suggested that this process would be unimportant in the normal temperature range.

The calculated ΔE_a values are fairly small (<6 for addition of H' and $< \sim 10$ kcal mol⁻¹ for addition of alkyl radicals) and this agrees well with the known easy addition of a variety of radicals to 2. Quantitative experimental data for comparison with the calculated ΔE_{as} are sparse. Scaiano and coworkers^{15,32} reported that the rate constant for addition of Et₃Si[•] to 2 was 6×10^8 dm³ mol⁻¹ s⁻¹ at 21 °C. With a "normal" Arrhenius pre-exponential factor of ca. 1010 dm³ $mol^{-1} s^{-1}$, this corresponds to an activation energy of *ca*. 2 kcal mol⁻¹, which compares very well with the calculated ΔE_a values. In contrast, the large calculated ΔE_a values for addition of Me' and H' to bicyclo[1.1.1]butane suggest that this reaction will be considerably more difficult. Quantitative kinetic data are not available for radical addition to 5, but the theoretical prediction is in good agreement with the few qualitative observations which indicate that 5 is much inferior to 2 in this aspect of reactivity.33 For instance, radical addition of CCl₄ to 5 was reported⁵ to be about seven times slower than that to 2.

Experimental study of the γ -dissociation of the 3-*t*-butylbicyclo[1.1.1]pent-1-yl radical 1c

We generated radical 1c and examined its behaviour by end product analysis over a range of temperatures to test our theoretical prediction. 1-Iodo-3-t-butylbicyclo[1.1.1]pentane 7c was chosen as the radical precursor and prepared from 1,1bis(chloromethyl)-2,2-dibromocyclopropane, via 2,^{34,35} as shown in Scheme 3. Radical 1c was generated from 7c by treatment with tributyltin hydride in hydrocarbon solution at various temperatures using photochemical initiation. Products from the reaction in benzene at 80 °C were shown by a combination of GC, NMR and MS to be 1-t-butylbicyclo[1.1.1]pentane (8) and isobutane (ratio 1:0.004). The main process is transfer of hydrogen from the organotin hydride to the 3-tbutylbicyclo[1.1.1]pent-1-yl radical 1c, formed by abstraction of iodine from 3. However, the formation of isobutane established that radical 1c does dissociate with loss of a t-Bu radical, which picks up hydrogen, even at 80 °C (see Scheme

3). The ¹H NMR spectrum of the product mixture showed evidence of the formation of [1.1.1]propellane ($\delta_{\rm H}$ 2.02, s) but, not surprisingly, the amount was extremely small, because **2** will rapidly polymerise under the reaction conditions.

Radical clock methodology was employed to determine rate data for the γ -scission reaction (k_d). Photochemical reductions were carried out in C₆D₆ or t-butylbenzene with excess tributyltin hydride (0.22 M) and the product ratio was measured by GC at a series of temperatures (50-150 °C). It can easily be shown that $k_d = k_H [Me_3 CH] [Bu_3 SnH] / [8]$, where k_H is the rate constant for hydrogen abstraction from tributyltin hydride by the intermediate radicals. This rate constant is well established for the t-Bu radical $\lceil \log(k_{\rm H}/{\rm dm^3 mol^{-1}}) \rceil$ $s^{-1} = 8.43 - 2.95/2.3RT$ ³⁶ but is unknown for 1c. Recent research has shown that bicyclo[1.1.1]pentyl radicals abstract hydrogen from dienes significantly faster (ca. 50-fold) than do t-Bu' radicals.¹² Rate constants for hydrogen transfer from Bu₃SnH are nearly the same for primary and tertiary alkyl radicals 34 but do increase significantly for $\sigma\mbox{-radicals}.$ Hence the $k_{\rm H}$ data measured for the cyclopropyl radical $[\log(k_{\rm H}/\rm s^{-1}) = 9.3 - 1.9/2.3RT]$ ³⁷ which has a σ -structure more similar to that of radical 1c than a tertiary alkyl radical, will be the most appropriate. A plot of the derived k_d values vs. 1/T gave a satisfactory straight line (r = 0.93) from which the following Arrhenius parameters were derived:

 $\log(k_{\rm d}/{\rm s}^{-1}) = 12.1 \pm 2.0/{\rm s}^{-1} - (11.4 \pm 3.0 \text{ kcal mol}^{-1}/2.3RT)$

The measured pre-exponential factor is close (within the error limits) to the "normal" value of 10^{13} s⁻¹ for a unimolecular decomposition, which lends credence to the results. These



Scheme 3

experimental data confirmed our theoretical prediction that γ -dissociation would be a significant process for loss of t-Bu from radical 1c. The rate of dissociation of 1c is not large at room temperature $[k_d(25 \degree C) = 6 \times 10^3 \text{ s}^{-1}]$, but the reaction gains in importance at higher temperatures. The experimental Arrhenius activation energy refers to the dissociation in solution for T > 273 K and is therefore not directly comparable with the computed ΔE_d values (Table 3) which refer to isolated molecules. Normally, however, experimental activation energies for neutral free radical reactions in hydrocarbon solutions are very similar to the corresponding gas phase values. There is a significant discrepancy of about a factor of two between the calculated ΔE_{a} s and the experimental activation energy. Highly strained open shell species such as 1 and 2 are a severe test of theory and this is shown by the considerable swings from level to level in the calculated energy differences; perhaps a more sophisticated basis set is needed. The experimental pre-exponential factor is on the low side. An increase in this would lead to a correspondingly higher activation energy, perhaps as high as 15 kcal mol⁻¹. Taking the potential error limits on both calculated and experimental data into account, the difference between theory and experiment is not inordinate.

Conclusions

Ab initio computations predict that radical additions to [1.1.1]propellane are exothermic and should occur with low activation energies. This is in good agreement with qualitative experimental evidence. Calculated enthalpies and activation energies indicated that the reverse γ -dissociations of 3alkylbicyclo[1.1.1]pent-1-yl radicals could be important for extrusion of stabilised radicals. Experimentally, loss of t-Bu from 1c was confirmed and the kinetic study indicated a remarkably low activation energy for a C-C bond fission. This result implies that similar loss of other thermodynamically stabilised radicals such as benzyl and allyl should become competitive at temperatures above ambient. 3-Benzylbicyclo[1.1.1]pentane derivatives have been prepared via 3-benzylbicyclo[1.1.1]pent-1-yl radicals.13,38 However, the addition of benzyl bromide to 2 did not proceed smoothly³⁸ and a possible cause of this is obviously competition from the γ -dissociation. The formation of [1.1.1]propellane substantially promotes C-C bond fission, which occurs much more readily in 1 than in analogous γ -dissociations of the next lower homologue *i.e.* 3-substituted-cyclobutyl radicals 4. γ -Dissociation of 1 is also more facile than analogous β scissions of alkyl radicals to yield alkenes.

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References

- 1 D. Griller, K. U. Ingold, P. J. Krusic and H. Fischer, J. Am. Chem. Soc., 1978, 100, 6750.
- 2 J. C. Walton, Chem. Soc. Rev., 1992, 21, 105.
- 3 The tetrahedryl radical is even more "tied back" but will be unstable and has not been reported.
- 4 E. W. Della and I. J. Lochert, Org. Prep. Proced. Int., 1996, 28, 411.
- 5 K. B. Wiberg and S. T. Waddell, J. Am. Chem. Soc., 1990, 112, 2194.

- 6 P. Kaszynski, N. D. McMurdie and J. Michl, J. Org. Chem., 1991, 56, 307; P. Kaszynski, A. C. Friedli and J. Michl, J. Am. Chem. Soc., 1992, 114, 601.
- 7 E. W. Della, P. E. Pigou, C. H. Schiesser and D. K. Taylor, J. Org. Chem., 1991, 56, 4659.
- 8 A. Almenningen, B. Andersen and B. A. Nyhus, Acta Chem. Scand., 1971, 25, 1217.
- 9 K. B. Wiberg, C. M. Hadad, S. Sieber and P. v. R. Schleyer, J. Am. Chem. Soc., 1992, 114, 5820.
- 10 See, for example, R. C. Fort and P. v. R. Schleyer, J. Am. Chem. Soc., 1971, 93, 3189; C. Rüchardt, Angew. Chem., Int. Ed. Engl., 1970, 9, 830; P. S. Engel, Chem. Rev., 1980, 80, 99.
- C. Rüchardt, K. Herwig and S. Eichler, *Tetrahedron Lett.*, 1969, 421; B. Giese, *Tetrahedron Lett.*, 1979, 857; B. Giese and J. Stellmach, *Chem. Ber.*, 1980, **113**, 3294.
- 12 J. T. Banks, K. U. Ingold, E. W. Della and J. C. Walton, *Tetra*hedron Lett., 1996, 37, 8059.
- 13 K. P. Dockery and W. G. Bentrude, J. Am. Chem. Soc., 1997, 119, 1388.
- 14 U. Bunz, K. Polborn, H.-U. Wagner and G. Szeimies, *Chem. Ber.*, 1988, **121**, 1785.
- 15 P. F. McGarry, L. J. Johnston and J. C. Scaiano, J. Org. Chem., 1989, 54, 6133.
- 16 D. Feller and E. R. Davidson, J. Am. Chem. Soc., 1987, 109, 4133.
- 17 W. Adcock, G. T. Binmore, A. R Krstic, J. C. Walton and J. Wilkie, J. Am. Chem. Soc., 1995, 117, 2758.
- 18 K. B. Wiberg and F. H. Walker, J. Am. Chem. Soc., 1982, 104, 5239; K. B. Wiberg, Tetrahedron Lett., 1985, 26, 599.
- 19 E. W. Della and D. K. Taylor, J. Org. Chem., 1994, 59, 2986.
- 20 E. W. Della, D. K. Taylor and J. Tsanaktsidis, *Tetrahedron Lett.*, 1990, 36, 5219.
- 21 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Allaham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Anders, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzales and J. A. Pople, *Gaussian 94, Revisions D.4 and E.1*, Gaussian, Pittsburg, PA, 1995.
- 22 A. D. Becke, J. Chem. Phys., 1993, 98, 5648.
- 23 L. Hedberg and K. Hedberg, J. Am. Chem. Soc., 1985, 107, 7257.
- 24 K. B. Wiberg, W. P. Dailey, F. H. Walker, S. T. Waddell, L. S. Crocker and M. Newton, J. Am. Chem. Soc., 1985, 107, 7247.
- 25 K. W. Cox, M. D. Harmony, G. Nelson and K. B. Wiberg, J. Chem. Phys., 1968, 50, 1976; J. Am. Chem. Soc., 1968, 90, 3395.
- 26 J. Pacansky and M. Yoshimine, J. Phys. Chem., 1985, 89, 1880.
- 27 L. A. Curtis and J. A. Pople, J. Chem. Phys., 1988, 88, 7405.
- 28 L. A. Curtis and J. A. Pople, J. Chem. Phys., 1989, 91, 2420.
- 29 A. P. Scott and L. Radom, J. Phys. Chem., 1996, 100, 16502; W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986, ch. 6, p. 133.
- 30 J. Berkowitz, C. B. Ellison and D. Gutman, J. Phys. Chem., 1994, 98, 2744.
- 31 D. F. McMillen and D. M. Golden, Annu. Rev. Phys. Chem., 1982, 33, 493.
- 32 J. C. Scaiano and P. F. McGarry, *Tetrahedron Lett.*, 1993, 34, 1243.
- 33 K. U. Ingold and J. C. Walton, *Acc. Chem. Res.*, 1986, **19**, 72, and references cited therein.
- 34 K. Semmler, G. Szeimies and G. Belzner, J. Am. Chem. Soc., 1985, 107, 6410; J. Belzner, U. Bunz, K. Semmler, G. Szeimies, K. Opitz and A. Schlüter, Chem. Ber., 1989, 112, 397.
- 35 P. Kaszynski and J. Michl, J. Org. Chem., 1988, 53, 4593.
- 36 C. Chatgilialoglu, K. U. Ingold and J. C. Scaiano, J. Am. Chem. Soc., 1981, 103, 7739.
- 37 L. J. Johnston, J. Lusztyk, D. D. M. Wayner, A. N. Abeywickreyma, A. L. J. Beckwith, J. C. Scaiano and K. U. Ingold, J. Am. Chem. Soc., 1985, 107, 4594.
- 38 P. Kaszynski and J. Michl, J. Am. Chem. Soc., 1988, 110, 5225.

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