Comparison of hydrogen abstraction and homolytic substitution in pentacyclo[4.*n*.0.0^{2,5}.0^{3,8}.0^{4,7}]alkanes †

Phillip Lightfoot, Patrizia Pareschi and John C. Walton *

University of St. Andrews, School of Chemistry, St. Andrews, Fife, UK KY16 9ST

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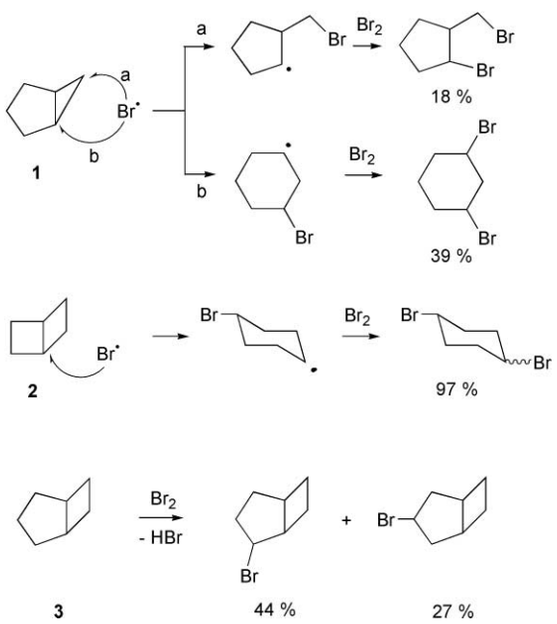
The rate of hydrogen atom abstraction from basketane (pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane) by *tert*-butoxyl radicals to produce 9-basketyl radicals was shown by EPR spectroscopy to be *ca.* 50 mol^{-1} dm^3 s^{-1} at 165 K. A similar study with homocubane (pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane) showed that the rate constant was even smaller (<4 mol^{-1} dm^3 s^{-1} at 165 K). Photobromination of basketane gave a mixture of 9-bromobasketane, bromochlorotricyclodecenes, dibromotricyclodecenes and tetrabromotricyclodecanes. These products were accounted for by a mechanism involving competition between the initial bromine atom abstracting a methylene hydrogen, or homolytically substituting at one or other of the three different cube bridgehead C-atoms. Photobromination of homocubane was also studied but gave only dihalotricycloalkenes and tetrabromotricycloalkanes from homolytic substitution. The two pentacycloalkanes furnish two more examples of the rare homolytic cleavage of carbon–carbon bonds shared by two cyclobutane rings.

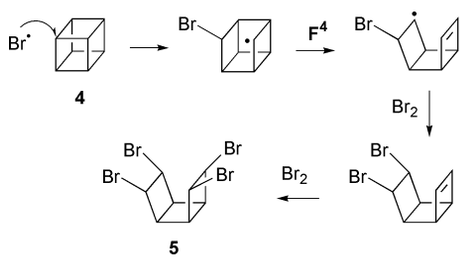
Introduction

Polyatomic free radicals abstract hydrogen atoms (H-abstraction) from strained polycyclic hydrocarbons with greater or lesser facility depending on structural details. Halogen atoms also abstract hydrogen atoms from polycyclic molecules with larger rings (>4-membered) giving monohalides, but they substitute cyclopropane-containing structures with ring cleavage (S_Hi) and formation of dihalides, *e.g.* bicyclo[3.1.0]hexane[1] (**1**, Scheme 1).



Scheme 1

Radical attack on monocyclobutanes occurs exclusively by hydrogen abstraction,[2] but evidence suggests that homolytic substitution, with ring cleavage, supervenes in structures with condensed four-membered rings.[3] Examples of the latter process are rare, but brominations of [*n*.2.2]propellanes[4] and bicyclo[2.2.0]hexane (**2**)[5] occurred with cleavage of the C–C bond shared by the two cyclobutane rings and clean formation of the corresponding dibromides (Scheme 1). The most spectacular example involved photobromination of cubane (pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane, **4**).[6] Substitution by a bromine atom launched a cascade that produced a single stereoisomer of *syn*-tetrabromotricyclo[4.2.0.0^{2,5}]octane (**5**) as the sole product (Scheme 2). Trihalomethyl radicals including $^{\bullet}CCl_3$, $^{\bullet}CBr_3$ and



Scheme 2

$^{\bullet}CI_3$, on the other hand, abstracted a hydrogen atom leading to the formation of monohalocubanes.[7]

By way of contrast, bonds shared by cyclobutane and cyclopentane rings are not subject cleavage by S_Hi attack by bromine atoms. For example, photobromination of bicyclo[3.2.0]heptane (**3**) led to a mixture of monobromides from H-abstractions (Scheme 1).[5]

It is evident that there is a direct competition between H-abstraction and homolytic substitution during radical attack on polycycles containing 4-membered rings. To probe the structural factors controlling this competition, we examined the reactions of pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (basketane, **6**) and pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (homocubane, **14**) with *tert*-butoxyl radicals and bromine atoms. These structures contain *both* cubane-like methine sites and *exo*-cubic methylene sites that offer an intriguing internal competition for attacking radicals. High stereoselectivity was observed in the bromination of cubane (Scheme 2) so an additional objective was to discover if similar stereocontrol would prevail for these two related molecules.

† Electronic supplementary information (ESI) available: experimental details (GC-MS) for photobrominations of basketane and homocubane. See http://www.rsc.org/suppdata/p2/b2/b200699e/

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Table 1 Rate constants for H-abstraction from cubane-like and model hydrocarbons by *tert*-butoxyl radicals

Substrate	Type of H abstracted	T/K	k_H/mol^{-1} dm^3 s^{-1}	k_H [a] per H	Ref.
Cyclopropane	CH_2	165	0.27	0.05	9
		183	1.2	0.2	
Cyclopentane	CH_2	165	7.2×10^3	720	10
Cubane	CH	183	$\geqslant$30	$\geqslant$3.8	6 [b]
Me-Cubane	CH_3	183	$\leqslant$30	$\leqslant$10	6 [c]
Homocubane	CH_2	165	$\leqslant$4	$\leqslant$2	tw [d]
Basketane	CH_2	165	50	12	tw [d]

[a] Statistically adjusted for the number of abstractable H-atoms. [b] Calc. from ref. 6 using the k_H(c-C_3H_6) from ref. 9. [c] Calc. assuming k_H of cage Hs = k_H for cubane. [d] 'tw' signifies this work.

Results and discussion

When a solution of basketane (8.75×10^{-5} mol) and di-*tert*-butyl peroxide (DTBP) (0.08 cm^3) in cyclopropane (8.4×10^{-3} mol) was photolysed in the cavity of an EPR spectrometer, signals from both the cyclopropyl and 9-basketyl radical (**7**) were observed. The hyperfine splittings (hfs) from the latter were in good accord with the literature.[8] The signal to noise ratio was rather poor and hence a small contribution from radicals derived by abstraction of methine hydrogen atoms from the cube part of the molecule could not be ruled out, although positive identification was not possible. The measured ratio [basketyl]/[cyclopropyl] was *ca.* 2 at 165 K and hence it follows that k_H(basketyl)/k_H(c-C_3H_6) $\approx$ 190 at 165 K where k_H is the rate constant for H-abstraction from each hydrocarbon (RH) by *tert*-butoxyl radicals:

$$t\text{-BuO}^\bullet + \text{RH} \xrightarrow{k_H} t\text{-BuOH} + \text{R}^\bullet \qquad (1)$$

In a similar spectroscopic experiment with homocubane in cyclopropane only the cyclopropyl radical was detected. From the measured signal to noise ratio we calculated that k_H-(homocubyl)/k_H(c-C_3H_6) $\leqslant$ 15 at 165 K. The Arrhenius parameters for H-abstraction from cyclopropane by *tert*-butoxyl radicals were recently found to be:[9] log(A_H/mol^{-1} dm^3 s^{-1}) = 6.04, E_H/kcal mol^{-1} = 5.0. Using these data the absolute H-abstraction rate constants listed in Table 1 were obtained.

Abstraction of *exo*-cube hydrogens by *tert*-butoxyl radicals from the pentacyclic hydrocarbons was found to be 2 to 3 orders of magnitude slower than from 'normal' methylenes in cyclopentane, but significantly faster than from CH_2 in cyclopropane (except possibly for homocubane). We showed previously that H-abstraction from the CH_3 group of methylcubane was *slower* than H-abstraction of the cube methine hydrogen atoms by *tert*-butoxyl radicals.[6] Table 1 shows that homocubane behaved in a similar way in that the *exo*-cube methylene hydrogens were more difficult to abstract than cube methine hydrogen atoms (of cubane). For basketane, abstraction of the *exo*-cube methylene hydrogens was slightly easier, but was still difficult compared to open chain or monocyclic methylene hydrogens. It is unlikely that these slow rates can be attributed to steric effects because the hydrogens in the cages of **6** and **14** are well 'tied back'.

9-Basketyl and 9-homocubyl radicals are formed on H-abstraction, but the EPR hfs of both species indicated they are essentially planar π-radicals without abnormal features to their spin distributions.[8] It is likely therefore that the slow rates of abstraction of *exo*-cube hydrogens must be due to an adverse polar effect in the transition state. A study of cubane by electron momentum spectroscopy (EMS) indicated considerable negative charge on the C-atoms and a balancing positive charge on the H-atoms in the ground state.[11,12] If this charge distribution carries over into methylcubane, homocubane and basketane the consequence will be significant positive charge on the *exo*-cube C-atoms and this might explain why an electrophilic radical like *t*-BuO$^\bullet$ abstracts reluctantly. Hrovat and Borden carried out an *ab initio* study of methylcubane and also found evidence for an adverse polar effect on abstraction of the methyl H-atoms by methoxyl radicals.[13] Using a 6-31G* basis set, and computing energies at the UMP2 and PUMP2 levels, they found that the transition state for abstraction of methyl hydrogen was higher in energy than that for abstraction of cube methine hydrogen. They attributed this effect to the ability of the cubyl carbons to accommodate positive charge in the transition state. Our experimental results with **6** and **14** indicate that similar effects operate for the methylene groups of these related pentacycles.

Halogenations of **6** and **4** set up competitions between hydrogen abstraction from the *exo*-cube methylenes and homolytic substitutions at the cube bridgeheads. Photobrominations of **6** were carried out in CCl_4 solution with both 1 and 2 mol equivalents of bromine. GC-MS analyses showed the formation of 9-bromobasketane (**8**), three chlorobromotricycloalkenes, eight dibromotricycloalkenes and six tetrabromotricycloalkanes in the yields shown in Table 2. Several minor components (<10% total) were also present. As Table 2 shows, the amount of bromine made only a small difference to the product distribution.

Separation and isolation of the products were attempted by a combination of fractional crystallisation and chromatography. Owing to the small amounts of material available, and the similarities in their solubilities and chromatographic behaviours, characterisation was only achieved for four components. The MS of component number 1095 showed it to have the constitution $C_{10}H_{12}Br_2$ and it is safe to assume this must be one of the dibromotricycloalkenes listed in Scheme 4. The ^{1}H NMR spectrum of pure 1095 showed it to be an unsymmetrical isomer and the best fit was with D5, *i.e.* 1,2-dibromotricyclo-[4.4.0.0^{2,5}]dec-7-ene (5.9% by GC and 9.6% by NMR). Samples of two fairly pure tetrabromides were also obtained. A crystal of component number 1715 (5% by GC) was analysed by X-ray diffraction which showed this to be tetrabromide **12** (T2) *i.e.* 3,4,7,8-tetrabromotricyclo[4.2.2.0^{2,5}]decane. The crystal structure confirmed this molecular structure, and revealed that both pairs of bromine atoms were *cis* (see Fig. 1). All bond lengths

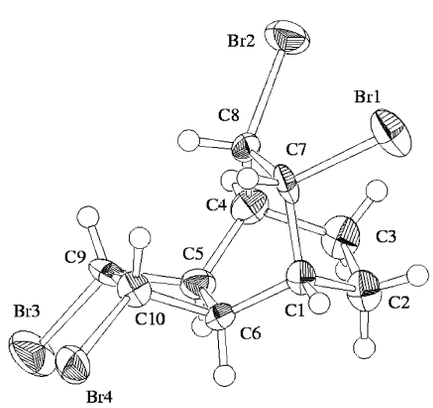


Fig. 1 ORTEP representation of the X-ray diffraction structure of component number 1715, *i.e.* 3,4,7,8-tetrabromotricyclo[4.2.2.0^{2,5}]-decane (**12**, T2).

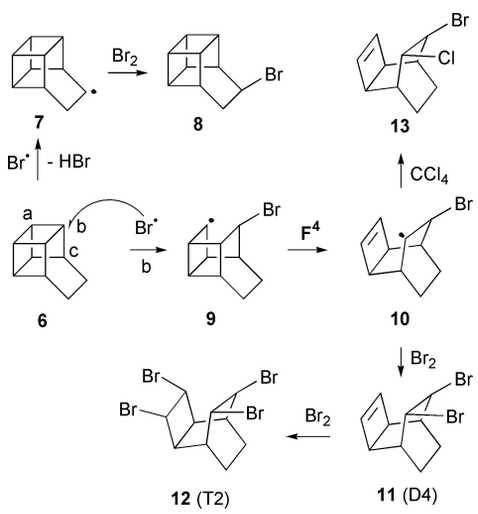
Table 2 Products from photobrominations of basketane and homocubane in CCl_4 at 25 °C[a]

Reactant	Br_2/mol equiv.	**8** or **15** (%)	TCAClBr (%)	$TCABr_2$ (%)	$TCABr_4$ (%)	k_H/k_S
Basketane (**7**)	1.0	1.9 (1.6)[b]	5.8	60.3	23.0	0.02
Basketane (**7**)	2.0	1.0	1.6	66.1	29.3	0.01
Homocubane (**14**)	2.04	<0.15	1.4	62.8	34.8	<0.002
Homocubane (**14**)	1.5	<0.11	1.9	71.5	26.1	<0.001

[a] TCA signifies tricycloalkene or tricycloalkane. [b] Yield from ^{1}H NMR analysis.

were within the expected ranges (Table 3) and there were no significant intermolecular contacts (closest Br–H = 2.95 Å). An ORTEP representation of the structure is given in Fig. 1. The MS, ^{1}H and ^{13}C NMR spectra of component number 1687 showed this to be an unsymmetrical tetrabromo compound and the best fit was with component T4, *i.e.* 3,4,7,8-tetrabromotricyclo[4.4.0.0^{2,5}]decane (11.4% by GC and 12.3% by NMR).

A partial mechanism for the bromination of **6** is shown in Scheme 3.[14] The 9-bromobasketane **8** will be formed by initial



Scheme 3

abstraction of one of the four methylene hydrogen atoms followed by bromine transfer to the intermediate 9-basketyl radical (**7**) by molecular bromine. Previous research[8] showed that **7** does not rearrange by β-scission at ambient temperature even though its cage contains *ca.* 113 kcal mol^{-1} of strain.[15] Homolytic substitution of **6** can occur at three different bridgehead sites (*a*–*c*). Attack at *a* or *b* can lead to scission of three C–C bonds, although because of symmetry, two of these cleavage processes at *a* lead to the same products. Substitutions at *c* can lead to scission of two bonds but each will give the same products. A representative example mechanism for substitution at site *b* is depicted in Scheme 3.

Bromine atom attack generates intermediate radical **9** that immediately rearranges by β-scission (**F**^{4})[14] to afford tricyclic radical **10**. The latter abstracts from molecular bromine to produce the dibromotricycloalkene **11** (D4) or abstracts chlorine from CCl_4 to produce the analogous chlorobromide **13**. Addition of a second molecule of bromine then leads to tetrabromide **12** (T2). By analogy with cubane (see Scheme 1), the final bromine addition will be *cis* because one side of the double bond is screened by the cage structure.

All the possible di- and tetra-bromides obtainable by homolytic substitution of **6** are shown in Scheme 4. In deriving these structures no distinction has been made for enantiomers, or other stereoisomers, because they would not be separable by the chromatographic method used here. The final bromine addition step is constrained to be *cis* in most cases by steric shielding from the cage structures. The *cis* addition was confirmed for **12** (T2) by the X-ray diffraction structure. In the case of T4 and T5

Table 3 Final bond lengths (Å) and angles (deg) for the crystal structure of **12**

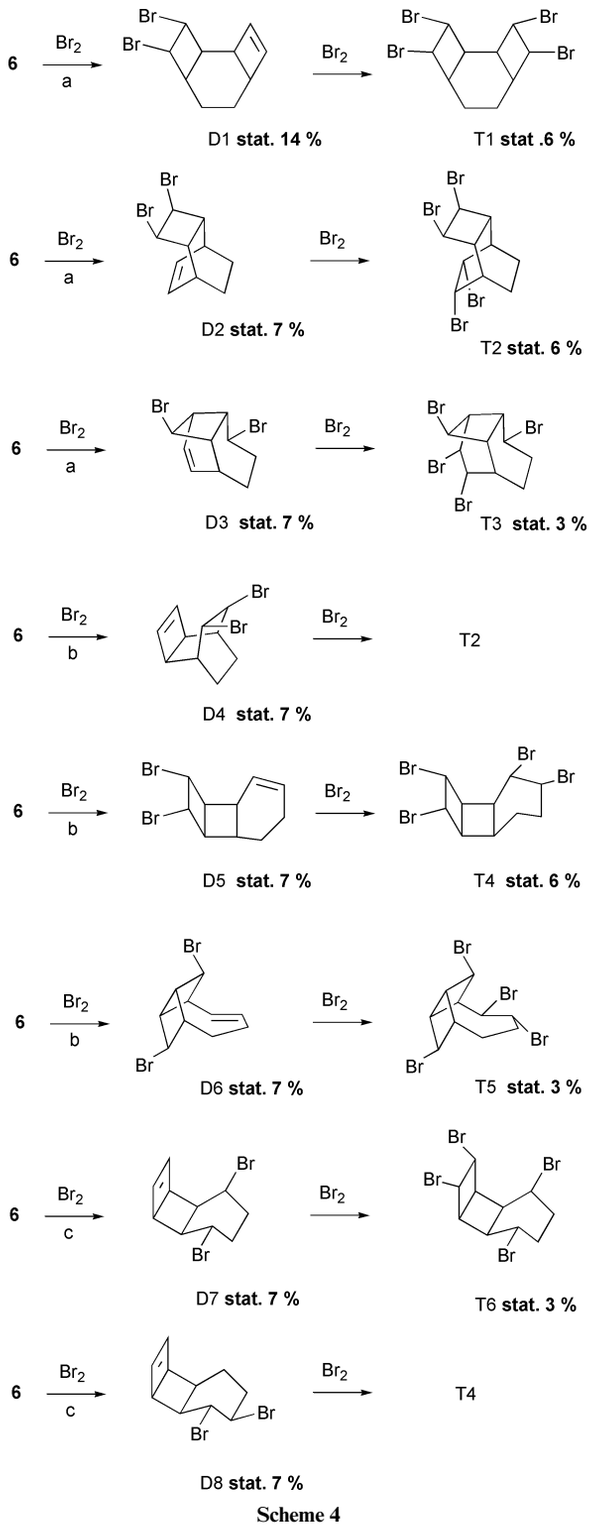
Br(1)–C(7)	1.96(1)	C(3)–C(4)	1.55(2)
Br(2)–C(8)	1.97(1)	C(4)–C(5)	1.54(2)
Br(3)–C(9)	1.94(1)	C(4)–C(8)	1.53(1)
Br(4)–C(10)	1.93(1)	C(5)–C(6)	1.55(2)
C(1)–C(2)	1.53(1)	C(5)–C(9)	1.55(2)
C(1)–C(6)	1.53(1)	C(6)–C(10)	1.53(1)
C(1)–C(7)	1.54(1)	C(7)–C(8)	1.54(1)
C(2)–C(3)	1.54(2)	C(9)–C(10)	1.51(2)
C(2)–C(1)–C(6)	105.7(9)	C(5)–C(6)–C(10)	88.8(8)
C(2)–C(1)–C(7)	110(1)	Br(1)–C(7)–C(1)	108.9(7)
C(6)–C(1)–C(7)	109.0(9)	Br(1)–C(7)–C(8)	117.3(8)
C(1)–C(2)–C(3)	110(1)	C(1)–C(7)–C(8)	108.4(9)
C(2)–C(3)–C(4)	111(1)	Br(2)–C(8)–C(4)	108.9(8)
C(3)–C(4)–C(5)	105.6(9)	Br(2)–C(8)–C(7)	115.5(8)
C(3)–C(4)–C(8)	107.1(9)	C(4)–C(8)–C(7)	112.9(9)
C(5)–C(4)–C(8)	108(1)	Br(3)–C(9)–C(5)	112.1(8)
C(4)–C(5)–C(6)	110.3(9)	Br(3)–C(9)–C(10)	116.0(8)
C(4)–C(5)–C(9)	118.8(9)	C(5)–C(9)–C(10)	89.7(9)
C(6)–C(5)–C(9)	88.8(9)	Br(4)–C(10)–C(6)	118.0(8)
C(1)–C(6)–C(5)	110.5(9)	Br(4)–C(10)–C(9)	121.1(8)
C(1)–C(6)–C(10)	123(1)	C(6)–C(10)–C(9)	91.0(9)

however, the normal *trans* addition mode may prevail, or a mixture might result. On the assumption that only one mode prevails in each case, eight dibromides and six tetrabromides are expected, in good agreement with the observed chromatograms. As indicated above, some minor unidentified product peaks were also visible on the chromatograms and it is probable these were additional isomers resulting from non-stereospecific addition of bromine. The characterisation of one dibromide and two tetrabromides (see above) lends good support to the proposed reaction pathways.

If the homolytic substitution steps by bromine atoms took place on a purely statistical basis then the relative yields shown on Scheme 4 would be expected. These yields have been scaled to the total dibromide (66%) and tetrabromide (29%) found (Table 2). The observed yields of D4 (**11**) (5.9–9.6%) spanned the statistical prediction of 7%. The observed yield of T2 (**12**) (5%) was also close to the statistical value of 6%. However, agreement was poor for T4 (obs. 11.4–12.3%, *vs.* stat. 6%). Furthermore, although specific structures cannot be assigned to the remaining products, the observed yields of many must deviate significantly from the statistical predictions (see Experimental section), which can therefore at best only be regarded as ball park estimates.

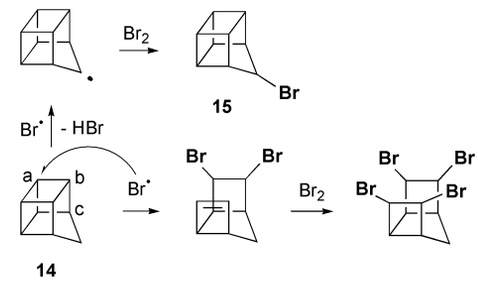
The experimental yields for D4 and T4 exceed the statistical yields and this gives a hint that bromine attack at bridgeheads *b* may be favoured. This is in reasonable accord with expectation because *b* bridgeheads are sterically more exposed than *a* bridgeheads; and the *c* bridgeheads are probably less strained than the others.

Photobrominations of homocubane **14** were carried out in CCl_4 with 1.5 and 2 mol equivalents of bromine. GC-MS analyses showed no trace of 9-bromohomocubane **15**, but revealed a single chlorobromotricycloalkene, five dibromotricycloalkenes and seven tetrabromotricycloalkanes. The yields of each class of product are recorded in Table 2. Attempts to isolate pure individual components by chromatography were unsuccessful.



Scheme 4

The mechanism of homocubane photobromination (Scheme 5) is expected to be analogous to that of basketane. Three bridgehead sites are available for homolytic substitution and, with the proviso that stereoisomers are ignored and that molecular bromine adds to the alkenes in only one of *cis* or *trans* fashion (*i.e.* does not give both for a given tricycloalkene), then eight dibromotricycloalkenes and six tetrabromotricycloalkanes should be formed. Representative examples are shown in Scheme 5. Only five dibromo isomers were detected, probably because of overlaps on the chromatogram and/or because individual isomers were formed in quantities too small for positive identification. One more tetrabromotricycloalkane than expected was observed and this can probably be explained because of non-stereospecific Br_2 addition. The greater range in



Scheme 5

the yields of individual components (see Experimental section), as compared with basketane, is an indication that the homolytic substitution was less statistical with homocubane.

From the ratio of the yield of **8** or **15** to the combined yield of the corresponding substitution products (including chlorobromo, dibromo, and tetrabromo compounds) the ratios of the rate constants for hydrogen abstraction (k_H) to homolytic substitution (k_S) were calculated for each pentacycle (Table 2); where k_S is a composite rate constant for all three bridgehead sites. The results show that for basketane, Br-atom substitution was about 2 orders of magnitude faster than H-abstraction. For homocubane the factor was at least 3 orders of magnitude. As shown above, *t*-BuO$^{\bullet}$ radicals abstract hydrogen less readily from homocubane. The smaller k_H/k_S ratio measured for homocubane probably indicates that Br atoms also abstract methylene hydrogen more slowly from this molecule.

Conclusions

Abstraction of *exo*-cube hydrogen atoms by *tert*-butoxyl radicals from pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]alkanes was shown to be very slow at 165 K for basketane, and undetectable for homocubane (and methylcubane[6]). This unexpected phenomenon was attributed to a polar effect in the transition state of the reaction. A minor amount of abstraction of the methylene hydrogens of basketane by bromine atoms was observed. The main process, however, was homolytic substitution that occurred at all three bridgeheads to give a mixture of dihalotricycloalkenes and tetrabromotricycloalkanes. Photobromination of homocubane was also studied but hydrogen abstraction was undetectable and only the products of homolytic substitution were observed. The homolytic substitution processes were analogous to that observed in the photobromination of cubane, except that they halted more easily after consumption of one equivalent of bromine and were less stereoselective. The basketane and homocubane brominations represent two more examples of the rare preferred homolytic cleavage of carbon–carbon bonds shared by two cyclobutane rings.

Experimental

^{1}H NMR spectra were recorded at 200 or 300 MHz and ^{13}C NMR spectra at 75 MHz, in $CDCl_3$ solution with tetramethylsilane ($\delta_H = \delta_C = 0$) as reference. Coupling constants are expressed in Hz. Ether refers to diethyl ether. Light petroleum refers to the fraction boiling in the range 40–60 °C. EI mass spectra were obtained with 70 eV electron impact ionisation and CI spectra with isobutane as the target gas on a VG Autospec spectrometer. GC-MS analyses were run on a Finnigan Incos 50 quadrupole instrument coupled to a Hewlett Packard HP 5890 chromatograph fitted with a 25 m HP 17 capillary column (50% phenyl methyl silicone). Chromatographic purifications were carried out using either Sorbsil C60 40/60A or BDH 40–63 μm silica gel eluting with the given solvent mixture. EPR spectra were obtained with a Bruker ER 200D spectrometer operating at 9 GHz with 100 kHz

modulation. The basketane and homocubane were gifts from Professor E. W. Della, Flinders University.

EPR study of H-abstraction from 6 and 14

Samples of each hydrocarbon were weighed into 4 mm od quartz tubes, dissolved in DTBP and degassed on a vacuum line. Measured amounts of cyclopropane were distilled in before the tubes were flame sealed. Basketane (0.0116 g, 0.088 mmol) and DTBP (0.08 cm^3) in cyclopropane (0.49 cm^3, 8.4 mmol) were photolysed in the EPR cavity by unfiltered light from a 500 W super pressure Hg lamp. The EPR spectrum at 165 K showed signals for the 9-basketyl [a(1H) = 2.20, a(2H) = 3.98, a(1H) = 0.18 mT)] and cyclopropyl radicals in a ratio of *ca.* 2 as determined by simulations. Homocubane (0.0083 g, 0.070 mmol) DTBP (0.08 cm^3) in cyclopropane (0.44 cm^3, 7.54 mmol) were photolysed in a similar way. The resulting spectrum at 165 K showed the cyclopropyl radical, but no trace of the 9-homocubyl radical. The signal to noise ratio for cyclopropyl was 7 : 1 indicating that [9-basketyl]/[cyclopropyl] ⩽ 0.14.

Photobromination of basketane (6)

To basketane (0.184 g, 1.39 mmol) in deaerated CCl_4 (5.0 cm^3) bromine (0.445 g, 2.78 mmol) was added drop by drop. The tube was exposed to daylight at 25 °C for 12 h and then analysed by GC-MS; peak no. 616, 9-bromobasketane **8** (1%, 1.9%) (lit. MS[7]); no. 984 $C_{10}H_{12}ClBr$ (<1%, 2.1%); no. 1008, $C_{10}H_{12}ClBr$ (1.6%, 1.3%); no. 1013, $C_{10}H_{12}ClBr$ (<1%, 2.4%); no. 1082, $C_{10}H_{12}Br_2$ (<1%, 4.8%); no. 1095, $C_{10}H_{12}Br_2$ (5.9%, 7.4%); no. 1100, $C_{10}H_{12}Br_2$ (9.4%, 5.1%); no. 1109, $C_{10}H_{12}Br_2$ (13.7%, 9.9%); no. 1115, $C_{10}H_{12}Br_2$ (18.7%, 8.8%); no. 1134, $C_{10}H_{12}Br_2$ (10.0%, 7.2%); %); no. 1147, $C_{10}H_{12}Br_2$ (6.6%, 5.9%); no. 1179, $C_{10}H_{12}Br_2$ (1.8%, 11.2%); no. 1562, $C_{10}H_{12}Br_4$ (1.6%, 0.8%); no. 1589, $C_{10}H_{12}Br_4$ (1.7%, 1.9%); no. 1687, $C_{10}H_{12}Br_4$ (11.4%, 7.5%); no. 1715, $C_{10}H_{12}Br_4$ (5.0%, 6.1%); no. 1725, $C_{10}H_{12}Br_4$ (7.3%, <1%); no. 1789, $C_{10}H_{12}Br_4$ (2.3%, 6.7%). Unidentified components amounted to 1.3% (8.9%, 2nd reaction). A second experiment was carried out with **6** (6.8 mg, 0.052 mmol) and Br_2 (8.2 mg, 0.052 mmol) in CCl_4 (0.18 cm^3). The GC chromatograms were similar except that significant unreacted basketane remained after 24 h; the yields for each component are noted above (second yield figures). The product mixture from the first reaction was separated into several fractions by crystallisation from pentane–CCl_4 mixtures. Promising fractions were chromatographed on silica gel (light petroleum–ether). Each fraction was checked by GC-MS to correlate separated components (and mixtures) with the original chromatogram. Eventually three almost pure components were obtained. No. 1095, δ_H 1.35–1.65 (2 H, m), 2.15–2.45 (4 H, m), 2.87–3.08 (2 H, m), 4.55 (1 H, t, J = 7.1), 4.84 (1 H, dd, J = 7.1, 9.2), 5.35 (1 H, d, J = 9.1), the quantity was insufficient for a ^{13}C NMR spectrum, 1,2-dibromotricyclo[4.4.0.0^{2,5}]dec-7-ene (D5). No. 1687, δ_H 1.36–1.43 (1 H, m), 1.81 (2 H, dt, J = 14.9, 5.4), 2.02–2.16 (1 H, m), 2.38 (1 H, m), 2.42 (1 H, m), 3.01–3.17 (2 H, m), 4.35 (1 H, d, J = 6.6), 4.80 (1 H, dt, J = 6.7, 1.3), 4.95 (1 H, dd, J = 6.6, 3.6), 5.79 (1 H, dt, J = 7.9, 1.2); δ_C 18.31 (CH_2), 26.40 (CH_2), 35.79 (CH), 37.99 (CH), 45.79 (2 × CH), 48.85 (CH), 49.11 (CH), 55.58 (CH), 57.18 (CH), 3,4,7,8-tetrabromotricyclo[4.4.0.0^{2,5}]decane (T4). The structure of a crystal of no. 1715 was solved by X-ray diffraction (see below and electronic supplementary information), *i.e.* 3,4,7,8-tetrabromotricyclo-[4.2.2.0^{2,5}]decane, **12** (T2). The ^1H NMR of the total reaction mixture from the first bromination showed the following yields: no. 616, 9-bromobasketane (**8**) 1.6%; no. 1095, 9.6%; no. 1687, 12.3%. MS data for individual components are given in the ESI.

Crystal structure determination

A crystal of compound no. 1715 from the basketane bromination was mounted in air on a glass fibre, and data were collected at room temperature on a Rigaku AFC7S automated 4-circle diffractometer.

Crystal data: $C_{10}H_{12}Br_4$, M = 451.82, monoclinic, a = 11.072(4), b = 9.078(4), c = 12.442(4) Å, β = 101.65(3)°, T = 298 K, space group $P2_1/n$, Z = 4, μ(Mo-Kα) = 13.1 mm^{-1}, 2431 reflections measured, 2307 unique (R_{int} = 0.06). Final $R(F^2)$, $R_w(F^2)$ = 0.089, 0.084 for 2154 unique data. CCDC reference number 178165. See http://www.rsc.org/suppdata/p2/b2/b200699e/ for crystallographic files in .cif or other electronic format. See Table 3 and Fig. 1.

Photobromination of homocubane (14)

To **14** (4.6 mg, 0.039 mmol) in deaerated CCl_4 (0.14 cm^3) bromine (9.4 mg, 0.058 mmol) was added drop by drop. The solution was exposed to daylight for 12 h at 25 °C and then analysed by GC-MS. No. 759, $C_9H_{10}ClBr$; (1.4%, 1.9%); no. 847, $C_9H_{10}Br_2$ (17.8%, 23.2%); no. 864, $C_9H_{10}Br_2$ (3.8%, 15.7%); no. 903, $C_9H_{10}Br_2$ (5.3%, 7.2%); no. 917, $C_9H_{10}Br_2$ (3.2%, 8.0%); no. 936, $C_9H_{10}Br_2$ (33.0%, 17.4%); no. 1284, $C_9H_{10}Br_4$ (7.6%, 5.3%); no. 1296, $C_9H_{10}Br_4$ (9.1%, 8.9%); no. 1303, $C_9H_{10}Br_4$ (4.6%, 3.2%); no. 1322, $C_9H_{10}Br_4$ (2.1%, 0.3%); no. 1379, $C_9H_{10}Br_4$ (3.7%, 0.6%); no. 1386, $C_9H_{10}Br_4$ (5.4%, 6.2%); no. 1420, $C_9H_{10}Br_4$ (2.3%, 1.6%). 9-Bromohomocubane (**15**) was estimated to be <0.15% (<0.11%) from the chromatogram. A second experiment was carried out with **14** (208 mg, 1.76 mmol) and Br_2 (423 mg, 2.64 mmol) in CCl_4 (6.0 cm^3). The GC chromatograms were similar and the yields for each component are noted above (second yield figures). The product mixture from this second reaction was separated into several fractions by crystallisation from pentane–CCl_4 mixtures and promising fractions were chromatographed on silica gel (light petroleum–ether). Each fraction was checked by GC-MS to correlate components with the original chromatogram. Unfortunately, all attempts led to mixtures containing a range of components. MS data are given in the ESI.

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