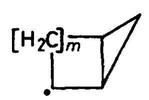
Homolytic Rearrangements of Bicyclo[2.2.0]hexane and Bicyclo[3.2.0]heptane

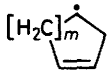
John C. Walton
Department of Chemistry, The University, St. Andrews, Fife KY16 9ST

Free radicals abstract hydrogen from both the bridge and bridgehead sites in bicyclo[2.2.0]hexane (**4**). The bicyclo[2.2.0]hexan-1-yl radical was observed by e.p.r. spectroscopy. The bicyclo[2.2.0]hexan-2-yl radical rearranges by stereoelectronically forbidden β-scission to give cyclohex-3-enyl radicals. Unlike other cyclobutanes, compound (**4**) undergoes an S_H2 reaction with bromine atoms. Free radicals abstract hydrogen only from the methylene groups of the C_5 ring in bicyclo[3.2.0]heptane (**15a**). The bicyclo[3.2.0]heptan-2-yl radicals were observed by e.p.r. spectroscopy, as was their rearrangement, by stereoelectronically allowed β-scission, to 2-(cyclopent-2-enyl)ethyl radicals. Bromine atoms abstract hydrogen from (**15a**) and no S_H2 reaction was detected. The radicals and their rearrangements were studied by semi-empirical MINDO/3 and MNDO methods.

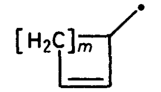
Bicycloalkanes containing cyclopropane and cyclobutane rings undergo a number of unusual reactions with free radicals. The rigid molecular framework, coupled with the large strain energies, leads to unexpected selectivities and, particularly, to novel rearrangement modes.[1] For example, bicyclo[*n*.1.0]-alkan-2-yl radicals (**1**) are preferentially formed by hydrogen abstraction from the corresponding bicycloalkanes; the first two members of the series (**1**; $m = 0$ or 1) rearrange to cycloalkenyl radicals (**2**), but larger rings ($m \geqslant 2$) afford the cycloalkenylmethyl radicals (**3**).[2,3] The e.p.r. spectra of the intermediate radicals are particularly useful for revealing the distribution of spin density and hence the nature of the semi-occupied molecular orbital (SOMO). This information is of major help towards an understanding of the stereoelectronic effects which control the rearrangements, but only a few strained bicycloalkyl radicals have been observed in this way.



(**1**)

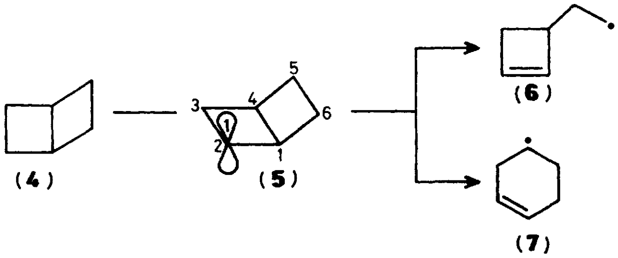


(**2**)



(**3**)

Bicyclo[2.2.0]hexane (**4**) appeared particularly interesting because hydrogen abstraction was expected to give bicyclo-[2.2.0]hexan-2-yl radicals (**5**), which have two potential modes of rearrangement. The radical (**5**) is of the cyclobutylmethyl type; such radicals readily rearrange by β-scission around room temperature.[4,5] According to the stereoelectronic explanation,[6] β-scission occurs readily when the SOMO can overlap with the orbitals of the β,γ-bond. Thus, in structure (**5**), rearrangement to the cyclobutenylethyl radical (**6**) is stereoelectronically allowed, but rearrangement to the cyclohex-3-enyl radical (**7**) is stereoelectronically forbidden because the C(1)–C(4) bond lies in the nodal plane of the SOMO. In the case of bicyclo[*n*.1.0]alkan-2-yl radicals (**1**) there are two analogous rearrangement modes; the type of β-scission was found to depend on the size of the ring containing the SOMO.[2,3] We report in this paper our study of the radical reactions of bicyclo[2.2.0]hexane and bicyclo-[3.2.0]heptane undertaken with the aim of discovering the preferred rearrangement mode of the radical (**5**) and the influence of ring size on the rearrangement of bicyclo[*n*.2.0]-alkan-2-yl radicals in general. A preliminary report of some of the bicyclo[2.2.0]hexane work has already appeared.[7]



Results and Discussion

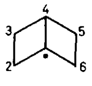
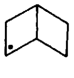
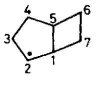
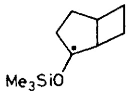
cis-*Bicyclo*[2.2.0]*hexane* (**4**).—The substrate (**4**) was made in low yield by the mercury-photosensitised photolysis of hexa-1,5-diene,[8] and isolated from the mixture of hydrocarbons by fractional distillation followed by preparative g.l.c. Attempts were also made to prepare (**4**) by pyrolysis of the nitrosobenzene adduct of cyclohexa-1,3-diene.[9] However, no (**4**) was obtained by either conventional pyrolysis or flash vacuum pyrolysis of this adduct.

Degassed solutions of (**4**) in di-t-butyl peroxide were irradiated in the cavity of the e.p.r. spectrometer but the spectrum consisted of a very broad featureless signal under these conditions. When cyclopropane was added as solvent the main radical detected was cyclopropyl, but the cyclopropyl spectrum was accompanied by a set of weak, fairly broad lines. Comparison with the spectrum of the cyclohex-3-enyl radical (**7**), specially generated for this purpose from 4-bromocyclohexene (**11**) [$a(H_\alpha) = 22.0$ G;* $a(2H_\beta) = 25.6$ G; $a(2H_\beta) = 30.5$ G at 220 K], showed no correspondence. Thus (**7**) is not the main radical generated by hydrogen abstraction from (**4**). Analysis of the spectrum agreed fairly well with two sets of triplets and a doublet hyperfine splitting (h.f.s.), but this analysis remains uncertain because of the weakness of the spectrum and its overlap with that of cyclopropyl radical. Attempts to obtain spectra free from cyclopropyl radical interference, by using dichlorodifluoromethane as solvent, led to such weak signals that no further information could be obtained. The tentative e.p.r. parameters deduced from the spectra in cyclopropane are given in Table 1. Obviously, these hyperfine splittings cannot correspond to the radical expected from hydrogen abstraction by t-butoxyl radicals, *i.e.* (**5**) (see Table 1), nor do they correspond to either of the rearranged radicals (**6**) and (**7**). It is most likely therefore that the species detected is the bridgehead, bicyclo[2.2.0]hexan-1-yl radical (**8**), which gives a small (6.2 G) h.f.s. from H-4 and two sets of triplet splittings from the non-equivalent *exo-* and *endo*-hydrogen atoms at C(2) and C(6).

---

* 1 G = 0.1 mT; 1 cal = 4.18 J.

Table 1. E.p.r. parameters of radicals derived from bicyclo[2.2.0]hexane and bicyclo[3.2.0]heptane

Radical		*T*/K	Exptl. h.f.s/G	INDO h.f.s./G	
	(**8**)	140	22.0[a]	H(2,6-*exo*)	28.7[b]
			10.7	H(2,6-*endo*)	9.3
			6.2	H(4)	9.1
			< 1.5	H(3,5-*exo*)	4.2
			< 1.5	H(3,5-*endo*)	4.8
	(**5**)			H(2)	−18.0[b]
				H(1)	29.6
				H(3-*exo*)	51.5
				H(3-*endo*)	38.0
	(**16a**)	206	21.5[d]	H(2)	−18.1[c]
			24.8	H(3-*exo*)	44.9
			24.8	H(3-*endo*)	48.5
			46.7	H(1)	41.0
	(**16b**)	228	23.5		
			23.5		
			37.5		

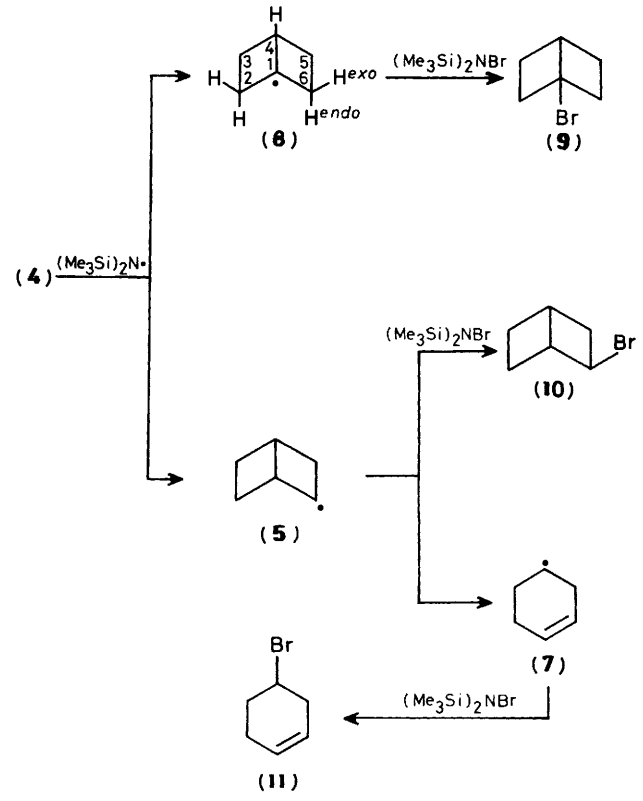
[a] $g = 2.0028$. [b] INDO calculations utilising MINDO/3-optimised geometries; $\langle S^2 \rangle$ values: (**8**) 0.7545; (**5**) 0.7545. [c] INDO calculations utilising MNDO-UHF-optimised geometries; $\langle S^2 \rangle$ values: (**16a**) 0.7608. [d] Long-range hyperfine splittings of 2.6 G (1 H) and 0.8 G (4 H) were partly resolved.

Hyperfine splittings from H_γ at C(3) and C(5) were not resolved, but probably contribute to the fairly large linewidth (ΔH_{pp} *ca.* 1.5 G). INDO calculations on the radical (**8**) (see later) gave hyperfine splittings in reasonable agreement with experiment (Table 1); this provides further support for the proposed identification.

The e.p.r. spectra were too weak for any other radicals to be detected, and obviously the formation of the radical (**5**) to some extent cannot be ruled out. However, the spectroscopic evidence favours hydrogen abstraction from the bridgehead sites in (**4**) as the main reaction with t-butoxyl radicals.

Hydrogen abstraction from a bridgehead site in preference to a methylene site is rare, although not unknown for strained bicycloalkanes,[10,11] and therefore we sought to confirm this result by product studies. Compound (**4**) was treated with *N*-bromobis(trimethylsilyl)amine under radical conditions[12] at 75 °C. The reaction was monitored up to about 50% reactant consumption (62 h) by n.m.r. and g.l.c. analysis; the product mixture then contained about 75% monobromides together with some dibromides. The monobromides were identified by a mixture of techniques (see Experimental section) and the two major monobromides were isolated by preparative g.l.c. The ^{1}H n.m.r. spectrum of the first component was almost identical with that of 1-chlorobicyclo[2.2.0]hexane[13] and the second component had a ^{1}H n.m.r. spectrum similar to those of *exo*-2-chlorobicyclo[2.2.0]hexane[13] and *exo*-bicyclo[2.2.0]hexan-2-ol.[14] The bridgehead bromide (**9**) (46%) and the *exo*-2-bromide (**10**) (46%) were the only products detected, together with 4-bromocyclohexene (**11**) (7%) after 30 h reaction. At longer reaction times dibromides started to appear on the chromatogram, as did small amounts of bromobenzene and some minor unidentified components. The dibromides (16%) were mainly *trans*- and *cis*-1,4-dibromocyclohexane, together with a minor amount of *trans*-1,2-dibromocyclohexane.

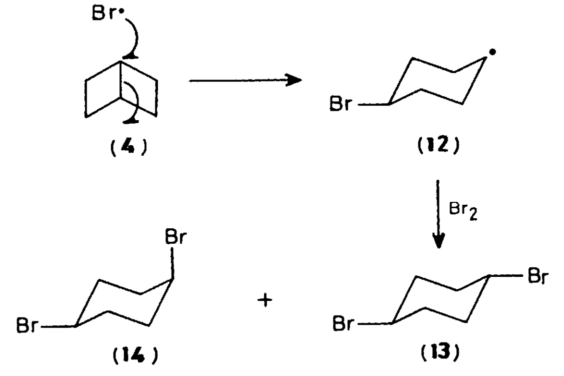
The main process is a radical chain reaction in which the bis(trimethylsilyl)aminyl radical abstracts hydrogen from both the bridgehead and methylene sites in (**4**) (Scheme 1). This result, together with the e.p.r. evidence and the isolation of 1-chlorobicyclo[2.2.0]hexane from the chlorination[13] of (**4**), confirms that radicals abstract hydrogen from the bridgehead site; the relative reactivity of the bridgehead *vs.* methylene hydrogen atoms depends on the nature of the attacking radical and on the temperature.



Scheme 1.

The isolation of (**11**) and the complete absence of the bromide derived from cyclobutenylethyl radicals (**6**) shows that the radical (**5**) rearranges exclusively by β-scission of the C(1)–C(4) (inter-ring) bond. In the chlorination of (**4**) Srinivasan and Sonntag also found the chloro analogues of (**10**) and (**11**) and none of the chloro derivative of (**6**). Thus, there is complete agreement that this rearrangement occurs in the stereo-electronically forbidden mode. It is probable that this unusual mode is favoured because scission of the inter-ring bond leads to relief of virtually all the strain in (**4**) (*i.e. ca.* 50.2 kcal mol^{-1} as judged by the strain in the corresponding hydrocarbons)[15] whereas for scission of the C(1)–C(6) bond the cyclobutene ring strain (29.8 kcal mol^{-1})[16] remains in (**6**). The inter-ring bond scission in (**5**) is therefore about 20 kcal mol^{-1} more exothermic than peripheral bond scission. In addition, recent calculations[17] have indicated that the inter-ring bond in (**4**) is 'bent' out of the line of centres by about 14°. This bending of the orbitals in the inter-ring bond will permit some overlap with the SOMO and this factor should also assist the β-scission of the inter-ring bond.

The photobromination of (**4**) in CCl_4 solution was rapid (reaction complete in less than 3 min) at ambient temperature and gave two main products, *trans*-1,4-dibromocyclohexane (**13**) (57%) and the *cis*-isomer (**14**) (40%), together with a minor amount of *trans*-1,2-dibromocyclohexane (2%). Monobromides amounted to less than 1% of the total products. The very specific formation of 1,4-dibromocyclohexanes points to an S_H2 attack by bromine atoms at the bridgehead carbon atoms to give bromocyclohexyl radicals (**12**) as the first step in the reaction

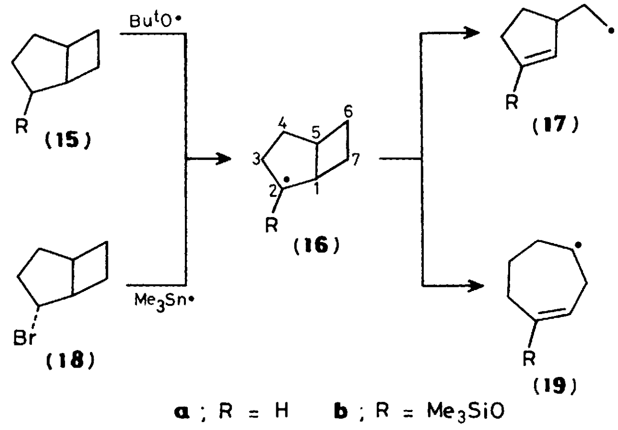


Scheme 2.

(Scheme 2). The fact that the [(**13**)]:[(**14**)] ratio of 1.4:1 obtained from (**4**) was similar to the ratio of about 1.1:1 reported for the photobromination of bromocyclohexane[18] supports the proposed mechanism because the final step in both reactions is the same. Although several alternative routes to the dibromides involving monobromination of (**4**) as the first stage, followed by further bromination, elimination, and hydrogen bromide addition steps can be envisaged, the almost complete absence of monobromides and 1,3-dibromides amongst the products makes these very unlikely. We attribute the small amount of *trans*-1,2-dibromocyclohexane to a minor electrophilic bromination similar to that observed with cyclopropanes.[19] The same dibromides were obtained in the reaction of (**4**) with $(Me_3Si)_2NBr$ (see before); thus the main hydrogen-abstraction reactions are accompanied by a minor amount of S_H2 attack by bromine atoms in that case also.

This is the first time than an S_H2 reaction has been observed for a cyclobutane ring. The reaction is well known for cyclopropane halogenation[20] and for the cyclopropane reaction with bis(trifluoromethyl)aminoxyl,[21] and it has been utilised to show that homolytic displacement on carbon involves inversion of configuration.[19,22] The ring strain of cyclobutane (26.2 kcal mol^{-1})[16] is only slightly less than that of cyclopropane (27.6 kcal mol^{-1}),[16] but chlorination[23] and bromination[24] of cyclobutane and its derivatives[25—27] occur by straightforward hydrogen abstraction. The inter-ring bond in (**4**) is unusually long (an electron diffraction study gave 1.577 Å)[28] and this, coupled with the release of nearly 50 kcal mol^{-1} of strain energy, is enough to tip the balance in favour of the S_H2 process for (**4**) and probably for other molecules containing fused cyclobutane rings.

The photochemical reaction of (**4**) with an excess of bromotrichloromethane at 20 °C gave the following products: $CHCl_3$ (12%), (**9**) (2%), (**10**) (4%), (**11**) (2%), C_2Cl_6 (32%), (**13**) (33%), (**14**) (14%), and *trans*-1,2-dibromocyclohexane (<1%). Photolysis of CCl_3Br produces both trichloromethyl radicals and bromine atoms. We would expect the $CCl_3^{\bullet}$ radicals to abstract hydrogen from (**4**) and the bromine atoms to react by homolytic substitution. The presence of chloroform and the monobromides indicates that $CCl_3^{\bullet}$ radicals do indeed abstract hydrogen, although there is a lower proportion of bridgehead attack. In fact the proportion of bridgehead hydrogen abstraction from (**4**) decreases along the series of radicals $Bu^tO^{\bullet} > (Me_3Si)_2N^{\bullet} > CCl_3^{\bullet}$. The same dibromides were obtained as in the bromination of (**4**), *i.e.* this is consistent with S_H2 attack by the primary bromine atoms from CCl_3Br. The [(**13**)]:[(**14**)] ratio of 2.4:1 in this case is *not* the same as in the photobromination because the intermediate bromocyclohexyl radicals (**12**) abstract bromine from CCl_3Br rather than from molecular bromine, *i.e.* the final steps are not the same in the two reactions.



Scheme 3.

Table 2. E.p.r. parameters for 2-(cyclopent-2-enyl)ethyl radicals (**17**)

		H.f.s./G		
Radical	T/K	$2H_{\alpha}$	H_{β}	H_{β}
(**17a**)	323	22.6	26.5	28.7
(**17b**)	317	22.2	26.5	29.5

cis-*Bicyclo*[3.2.0]*heptane* (**15**).—Hydrogen abstraction from (**15a**) by t-butoxyl radicals was monitored at 200 K by e.p.r. spectroscopy, which showed a weak, not readily identifiable spectrum with broad lines. Exactly the same spectrum, but rather more intense, was obtained by bromine abstraction from *trans*-2-bromobicyclo[3.2.0]heptane (**18**), using photochemically generated trimethyltin radicals. This spectrum showed two doublet and one triplet hyperfine splittings together with some small, partly resolved, long-range splittings (Table 1) and it clearly corresponds to the bicyclo[3.2.0]heptan-2-yl radical (**16a**).

The analogous trimethylsilyloxyl radical (**16b**) was generated by hydrogen abstraction from the silyl ether (**15b**). The spectrum of (**16b**) was similar to that of (**16a**), except for the absence of the H_{α} h.f.s. and the smaller magnitude of the h.f.s. from H(1) (Table 1). The H_{β} h.f.s. values for (**16a** and **b**) are rather similar to those observed for the cyclopentyl radical when its ring motion is 'frozen' at 77 K, *viz.* [29] $a(H_{\beta}, 2\ H) = 23$ G; $a(H_{\beta}, 2\ H) = 46$ G. Evidently, the cyclobutane ring effectively prevents pseudorotation of the cyclopentane ring in (**16**). Models indicate that the large trimethylsilyloxy substituent at C(2) in (**16b**) will experience steric repulsion from the methylene groups of the cyclobutane ring. This will tend to push the C_5 ring into a conformation with the pucker at C(2) which minimises steric repulsion, but also moves H(1) towards the nodal plane of the SOMO at C(2). This accounts for the lower h.f.s. from H(1) in (**16b**) as compared with (**16a**) (Table 1).

When the temperature was increased the spectra from both radicals (**16a** and **b**) weakened in intensity in the temperature range 250—290 K and were replaced by the spectra of 2-(cyclopent-2-enyl)ethyl radicals (**17a** and **b**), respectively. When the temperature was lowered the spectra of radicals (**16**) reappeared, *i.e.* this was a reversible phenomenon. The e.p.r. parameters of the radicals (**17**) are given in Table 2. Both (**17a** and **b**) showed non-equivalent h.f.s. from the β-hydrogen atoms and the selective line broadening indicated that this was due to restricted rotation about the C_{β}–C_{γ} bonds. The e.p.r. spectra show that the main site for hydrogen abstraction by t-butoxyl radicals is C(2) in the cyclopentane ring of (**15a**), *i.e.* in this case

Table 3. Calculated enthalpies, reaction enthalpies, and enthalpies of activation for bicyclo[2.2.0]hexyl and bicyclo[3.2.0]heptyl rearrangements[a]

	ΔH_f			ΔH°		$\Delta H^{\ddagger}$	
Radical	MINDO/3	MNDO	Reaction	MINDO/3	MNDO	MINDO/3	MNDO
(8)	53.3	49.7	**(5)** $\longrightarrow$ **(6)**	11.8	17.1	35.8	44.3
(5)	53.8	36.7	**(5)** $\longrightarrow$ **(7)**	−31.4	−20.5	*b*	*b*
(6)	65.6	53.8	**(16a)** $\longrightarrow$ **(17a)**	12.9	16.5		
(7)	22.4	16.2	**(16a)** $\longrightarrow$ **(19a)**	−11.2	6.6		
(16a)	27.1	8.1					
(17a)	40.0	24.6					
(19a)	15.9	14.7					

[a] In kcal mol^{-1}; 1 kcal = 4.18 kJ. [b] Catastrophic descents observed in the calculated energies.

bridgehead attack is not favoured. The radicals **(16)** rearrange by scission of the C(1)–C(7) bond, *i.e.* by the stereoelectronically allowed mode (Scheme 3). The temperature range in which this rearrangement was observed by e.p.r. spectroscopy is the same as that for the archetype cyclobutylmethyl radicals,[5] so that the rate and activation parameters must be similar, *i.e.* the Arrhenius activation energy for β-scission in **(16)** will be *ca.* 12 kcal mol^{-1}. It is interesting that bicyclo[2.2.0]hexan-2-yl radicals **(5)** rearrange by inter-ring bond scission, but that increasing the ring size by one carbon atom leads to a change in the rearrangement mode. The bicyclo[3.2.0]heptan-2-yl radical **(16)** gives the thermodynamically less stable primary radical **(17)** in preference to the secondary radical **(19)**. The relief of ring strain in the two rearrangement modes is approximately the same in this case, but the SOMO overlaps more effectively with the orbitals of the C(1)–C(7) bond in **(16)** and hence this stereoelectronically allowed mode is preferred.

The photobromination of **(15a)** in CCl_4 solution at ambient temperature was slow (incomplete in 6 h) and, when an excess of **(15a)** was used, gave mainly monobromides (88%), together with dibromides (7%). The main monobromide was *trans*-2-bromobicyclo[3.2.0]heptane **(18)** (44%), accompanied by the *cis*-isomer (9%) and two unidentified monobromides. These monobromides were not sufficiently well resolved on g.l.c. for isolation by preparative g.l.c., but the mass spectrum of the major unidentified component (27%) showed fragment ions formed by the loss of 28 units. This is characteristic of compounds containing cyclobutane rings and it is probable that the two unidentified monobromides are the *trans*- and *cis*-3-bromobicyclo[3.2.0]heptanes. Retention time comparisons with authentic dibromocycloheptanes showed differences from all three of the dibromides formed from **(15a)**. The mass spectra showed that these three dibromides all had the molecular formula $C_7H_{10}Br_2$, *i.e.* they cannot be the products of an S_H2 reaction. The mass spectra also showed prominent fragmentation by loss of 28 units; thus they are probably the products of radical chain bromination of the monobromides. Bromination of **(15a)** occurs exclusively by the normal hydrogen-transfer mechanism and the S_H2 reaction does not take place for a cyclobutane ring condensed with a cyclopentane ring.

The reaction of **(15a)** with *N*-bromobis(trimethylsilyl)amine gave a complex product mixture containing at least five monobromides, four of which were the same as those obtained in the photobromination. Thus $(Me_3Si)_2N^{\bullet}$ radicals also mainly abstract hydrogen from the methylene groups of the C_5 ring.

Semi-empirical SCF MO Calculations.—The geometries and enthalpies of formation (ΔH_f) of the radicals **(5)**, **(8)**, and **(16a)** and their rearrangement products were calculated by MNDO[30,31] and MINDO/3;[31,32] some of the results are in Table 3. The calculated geometries of the radical **(5)** were quite reasonable in the light of expectation based on the structure of **(4)** elucidated by electron diffraction.[28] The long inter-ring bond was correctly calculated (1.58 Å by the MNDO method), the main difference being that, as expected, the calculated radical structure showed shorter C_{β}–$C_{\alpha}^{\bullet}$ bonds. The calculated angle between the rings (118°) was also somewhat larger than the experimental value for the parent molecule (113.5°). The calculated ΔH_f values of the radicals **(5)** and **(8)** are quite close (Table 3), and this is in accord with the relatively easy hydrogen abstraction from the bridgehead position to give **(8)**. The calculations correctly predict that β-scission of **(5)** will be much more exothermic for inter-ring bond fission, *i.e.* the calculations support the idea that this β-scission is favoured because of its high exothermicity. The enthalpies of activation were investigated for both rearrangement modes. The MINDO/3 and MNDO $\Delta H^{\ddagger}$ values were very high for the C(1)–C(6) bond scission, as would be expected (Table 3). Neither method was successful in following the reaction co-ordinate for inter-ring bond scission. Extending the C(1)–C(4) bond led to large energy increases followed by catastrophic descents; similar difficulties were encountered in semi-empirical MO studies of related radicals such as bicyclo[2.1.0]pentan-2-yl.[2] Agreement with experiment is poor in the case of bicyclo[3.2.0]heptan-2-yl radicals. There are serious differences in the enthalpies of formation calculated by the two methods (Table 3) and the calculated reaction enthalpies favour inter-ring bond scission rather than the observed peripheral bond fission.

The MINDO/3 optimum geometries were used in INDO calculations[33] on the radicals **(5)**, **(8)**, and **(16a)**; the theoretical hyperfine splittings are compared with experiment in Table 1. The calculated values are in reasonably good agreement with experiment for the radical **(8)**. Furthermore, the calculated hyperfine splittings of the radical **(5)** are entirely different from the experimental observations, *i.e.* these results support the identification of the radical observed by e.p.r. spectroscopy as the bridgehead radical **(8)**. The calculated splittings for the radical **(16a)** are in poor agreement with experiment, especially for the *exo*- and *endo*-hydrogen atoms at C(3). It is likely that the calculated conformation of the C_5 ring does not reproduce the true location or the magnitude of the pucker. Equally poor agreement was observed when the optimum MNDO geometry of **(16a)** was used in INDO calculations.

Conclusions

Bicyclo[2.2.0]hexan-2-yl radicals **(5)** rearrange by β-scission of the inter-ring bond because this is a much more exothermic process than the alternative β-scission of the C(1)–C(6) bond. On the other hand, bicyclo[3.2.0]heptan-2-yl radicals **(16a)** prefer the usual stereoelectronically allowed β-scission to give 2-(cyclopent-2-enyl)ethyl radicals. There is therefore a close analogy between this series of bicyclo[*n*.2.0]alkan-2-yl radicals and the bicyclo[*n*.1.0]alkan-2-yl radicals (**1**). In the latter case the rearrangement mode also switches from inter-ring bond scission to peripheral bond scission when the ring containing the SOMO becomes five-membered or larger.

Bicyclo[2.2.0]hexane is unique in that at present it is the only cyclobutane derivative known to undergo an S_H2 reaction with bromine atoms. Cyclobutanes condensed with larger rings, *e.g.* bicyclo[3.2.0]heptane, undergo normal hydrogen abstraction with bromine atoms. This novel reaction of (**4**) is probably a result of its unusually long and 'bent' inter-ring bond.

Experimental

E.p.r. spectra were recorded with a Bruker ER 200D spectrometer on degassed samples, sealed in Spectrosil tubes, irradiated with light from a 500 W super-pressure Hg arc. N.m.r. spectra were obtained with a Bruker WP 80 instrument for $CDCl_3$ solutions at ambient temperature with Me_4Si as internal standard. G.l.c.–mass spectrometric analyses were carried out with a Finnegan Incos instrument. For preparative g.l.c. a Pye-Unicam 105 chromatograph was used, with 5 m × 1 cm glass columns packed with Carbowax 20 M or FFAP.

Bicyclo[2.2.0]*hexane*[8] (**4**).—The vapour from refluxing hexa-1,5-diene (50 g) and mercury (1.0 g) was allowed to rise into a large quartz Applied Photophysics reactor where it was irradiated for 96 h with light from a 16 W low-pressure Hg lamp. The liquid from the distillation flask was fractionally distilled through a 20 cm column packed with glass helices until the vapour temperature had risen to 60 °C. This fraction was mainly unchanged hexa-1,5-diene. The residue was distilled (Kugelrohr) at 90 °C to give a second fraction (2 g) which contained hexadiene, allylcyclopropane, bicyclo[2.1.0]hexane, bicyclo[2.2.0]hexane, and some unidentified components. Pure (**4**) was separated by preparative g.l.c. using a 10 m column, packed with Carbowax 20 M, at 40 °C; yield 150 mg; ^1H n.m.r. spectrum identical with that given in the literature.[8]

4-*Bromocyclohexene* (**11**).[34]—Phosphorus tribromide (51.5 g) was added dropwise to a refluxing solution of cyclohexane-1,4-diol (29.0 g) in benzene (150 ml). The HBr was absorbed by a 20% solution of KOH. The mixture was refluxed for 12 h, then poured into ice–water, and the benzene layer was washed with 10% Na_2CO_3 and water and then dried (K_2CO_3). The benzene was removed by distillation at atmospheric pressure and the bromide distilled. It was dissolved in MeOH (45 ml) and refluxed with $CaCO_3$ (1 g) for 0.5 h; the solution was then filtered. Dichloromethane (20 ml) was added and the solution was washed with water (3 × 40 ml), dried (Na_2SO_4), and distilled; b.p. 53—55 °C at 25 Torr (lit.,[34] 49—52 °C at 28 Torr); yield 31%; δ_H 1.9—2.2 (4 H, m), 2.5 (2 H, br s), 4.35 (1 H, m), and 5.4—5.9 (2 H, m).

Reaction of Bicyclo[2.2.0]*hexane* (**4**) *with* N-*Bromobis-(trimethylsilyl)amine*.—Compound (**4**) (24 mg), $(Me_3Si)_2NBr$ (71 mg), $Bu^tCH{=}CH_2$ (1.5 mg), and azobisisobutyronitrile (1 mg) were dissolved in perdeuteriobenzene (0.36 ml) and the mixture was heated at 75 °C. The reaction was monitored from time to time by n.m.r. spectroscopy and g.l.c. and stopped after 62 h, when most of the reactant had been consumed. Apart from $(Me_3Si)_2NH$ the chromatogram showed seven products. The first peak (32%) had *m/z* (%) 162 (1), 160 (1), 134 (2), 132 (2), 121 (1), 119 (1), 81 (100), 80 (9), 79 (27), 77 (6), 76 (5), 75 (36), 55 (5), 54 (5), 53 (14), and 51 (45), as expected for C_6H_9Br. It was isolated by preparative g.l.c. on a Carbowax 20 M column operated at 140 °C [δ_H 1.7—2.1 (2 H, m), 2.2—3.0 (6 H, m), and 3.0—3.3 (1 H, m)] and identified as 1-bromobicyclo[2.2.0]hexane (**9**). The second peak (35%) had *m/z* (%) 121 (16), 119 (16), 82 (5), 81 (100), 80 (12), 79 (26), 78 (3), 77 (8), 76 (4), 75 (55), 67 (10), 65 (3), 55 (3), 54 (5), 53 (14), 52 (3), and 51 (5), also in agreement with C_6H_9Br. It was isolated by preparative g.l.c. [δ_H 2.0 (2 H, d, *J* 10 Hz), 2.4 (2 H, m), 2.8—3.2 (4 H, m), and 4.55 (1 H, t, *J* 6 Hz)] and identified as *exo*-2-bromobicyclo-[2.2.0]hexane (**10**). Peaks 3 (3%) and 4 (1%) were shown to be 4-bromocyclohexene (**11**) and bromobenzene by comparison of their retention times and mass spectra with those of authentic materials. The chromatogram showed several trace (< 1%) unidentified products together with three dibromides $C_6H_{10}Br_2$. Comparison of their retention times (on several columns) and mass spectra with those of authentic materials showed these to be *trans*-1,2-dibromocyclohexane (5%), *trans*-1,4-dibromocyclohexane (**13**) (8%), and *cis*-1,4-dibromocyclohexane (**14**) (3%).

Photobromination of Bicyclo[2.2.0]*hexane* (**4**).—To compound (**4**) (18 mg) in CCl_4 (0.3 ml) was added bromine (35 mg), and the solution was irradiated with light from a tungsten lamp for 3 min at 20 °C. The chromatogram showed only three products above the 1% level which were identified as already described; peak 1, *trans*-1,2-dibromocyclohexane (2%); peak 2, *trans*-1,4-dibromocyclohexane (57%); peak 3, *cis*-1,4-dibromocyclohexane (40%).

Photochemical Reaction of Bicyclo[2.2.0]*hexane* (**4**) *with* CCl_3Br.—Compound (**4**) (30 mg) in CCl_3Br (0.45 ml) was irradiated in a thin-wall Pyrex tube by light from a 250 W medium-pressure mercury lamp at 20 °C for 23 h. The following products were identified by g.l.c.–mass spectrometry and retention time comparisons as already described: $CHCl_3$ (12%), 1-bromobicyclo[2.2.0]hexane (**9**) (2%), *exo*-2-bromobicyclo-[2.2.0]hexane (**10**) (4%), 4-bromocyclohexene (**11**) (2%), C_2Cl_6 (32%), *trans*-1,2-dibromocyclohexane (0.1%), *trans*-1,4-dibromocyclohexane (**13**) (33%), and *cis*-1,4-dibromocyclohexane (**14**) (14%).

Bicyclo[3.2.0]*heptane* (**15a**).—A solution of bicyclo-[3.2.0]heptan-2-one[35] (3 g), 90% hydrazine hydrate (3 ml), and KOH (4 g) in diethylene glycol (30 ml) was heated under reflux for 5 h and then distilled until the temperature of the liquid reached 175 °C. The hydrocarbon was separated from the aqueous distillate, dried ($CaCl_2$), and distilled; b.p. 110 °C; yield 23%; δ_H 1.2—1.6 (6 H, m), 1.6—1.9 (2 H, m), 1.9—2.4 (2 H, m), and 2.5—2.9 (2 H, m).

trans-2-*Bromobicyclo*[3.2.0]*heptane* (**18**).—2-Hydroxybicyclo[3.2.0]heptane was made by reduction ($LiAlH_4$) of bicyclo[3.2.0]heptan-2-one[35] and shown to consist of a mixture of the *cis*- (95%) and *trans*- (5%) isomers. The alcohol (1.0 g) and pyridine (0.17 g) in diethyl ether (10 ml) were cooled in ice–salt and PBr_3 (1.0 g) was added dropwise. The mixture was stirred for 60 min, water was added, and the separated ether layer was washed with $NaHCO_3$ and water, then dried (Na_2SO_4) and distilled; b.p. 140 °C at 15 Torr; yield 10%; δ_H 1.3—1.8 (4 H, m), 1.8—2.5 (4 H, m), 2.5—3.2 (2 H, m), and 4.3 (1 H, d, *J* 4 Hz); *m/z* (%) 176 (2), 174 (2), 148 (6), 146 (6), 95 (65), 94 (8), 83 (8), 78 (16), 77 (100), 76 (10), 57 (5), and 55 (11). G.l.c. analysis showed two components, which were assigned *trans*- (95%) and *cis*- 5(%) structures by comparison of the n.m.r. spectra with those of the alcohols.[35]

2-(*Trimethylsilyloxy*)*bicyclo*[3.2.0]*heptane* (**15b**).—To the alcohol (0.8 g) and pyridine (0.56 g) in n-pentane (10 ml) was added trimethylsilyl chloride (0.77g), and the mixture was stirred for 15 min. The solution was filtered and distilled; b.p. 110 °C at 15 Torr; yield 84%; δ_H 0.1 (9 H, s), 1.1—2.3 (8 H, m), 2.3—2.7 (2 H, m), and 4.1 (1 H, m).

Photobromination of Bicyclo[3.2.0]*heptane* (**15a**).—To compound (**15a**) (42 mg) in CCl_4 (0.5 ml) was added bromine (46 mg), and the solution was irradiated with light from a tungsten lamp at 20 °C for 6 h. Analysis of the products by g.l.c.–mass spectrometry showed four main monobromides together with three dibromides. Comparison of their retention times and mass spectra with those of authentic materials showed that peaks 1 (9%) and 3 (44%) were the *cis*- and *trans*-2-bromobicyclo[3.2.0]heptanes. The mass spectra of the other two monobromides indicated the molecular formula $C_7H_{11}Br$, and the presence of appreciable $(M - 28)^+$ fragment ions suggested that they contained cyclobutane rings. Most probably these are *cis*- (8%) and *trans*-3-bromobicyclo[3.2.0]-heptanes (27%). Individual peaks were not well enough resolved for preparative g.l.c. The dibromides were formed in greater yield in a second photobromination with twice as much bromine. The molecular ions and the fragmentation patterns all indicated the molecular formula $C_7H_{10}Br_2$. The first two also showed $(M - 28)^+$ ions, *i.e.* these contain cyclobutane rings.

Reaction of Bicyclo[3.2.0]*heptane* (**15a**) *with* N-*Bromobis*(*trimethylsilyl*)*amine*.—The hydrocarbon (85 mg) with $(Me_3Si)_2NBr$ (211 mg), $Bu^tCH=CH_2$ (5 mg), and azobisisobutyronitrile (5 mg) in perdeuteriobenzene (0.5 ml) was heated at 75 °C for about 6 h. G.l.c.–mass spectrometry of the products showed a complex mixture containing at least five monobromides, four of which were the same as those obtained in the photobromination. Other products included $(Me_3Si)_2NH$ and $C_6D_6Br_2$, but no C_7 dibromides were detected.

References

1 K. U. Ingold and J. C. Walton, *Acc. Chem. Res.*, 1986, **19**, 72.
2 C. Roberts and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1983, 879.
3 C. Jamieson, J. C. Walton, and K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1366.
4 A. L. J. Beckwith and G. Moad, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1083.
5 K. U. Ingold, B. Maillard, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1981, 970.
6 A. L. J. Beckwith and K. U. Ingold in 'Rearrangements in Ground and Excited States,' ed. P. de Mayo, Academic Press, New York, 1980, vol. 1, p. 161.
7 J. C. Walton, *J. Chem. Soc., Chem. Commun.*, 1987, 1252.
8 S. Cremer and R. Srinivasan, *Tetrahedron Lett.*, 1960, 24; R. Srinivasan, *J. Am. Chem. Soc.*, 1961, **83**, 4923.
9 C. E. Griffin, N. F. Hepfinger, and B. L. Shapiro, *J. Am. Chem. Soc.*, 1963, **85**, 2683.
10 K. B. Wiberg and V. Z. Williams, *J. Org. Chem.*, 1970, **35**, 369.
11 B. Maillard and J. C. Walton, *J. Chem. Soc., Chem. Commun.*, 1983, 900.
12 B. P. Roberts and C. Wilson, *J. Chem. Soc., Chem. Commun.*, 1978, 752.
13 R. Srinivasan and F. I. Sonntag, *Tetrahedron Lett.*, 1967, 603.
14 R. N. McDonald and C. E. Reinke, *J. Am. Chem. Soc.*, 1965, **87**, 3020.
15 W. F. Maier and R. von R. Schleyer, *J. Am. Chem. Soc.*, 1981, **103**, 1891.
16 S. W. Benson in 'Thermochemical Kinetics,' 2nd edn., Wiley, New York, 1976, p. 273.
17 K. B. Wiberg and J. J. Wendoloski, *J. Am. Chem. Soc.*, 1982, **104**, 5679.
18 D. S. Ashton, J. M. Tedder, and J. C. Walton, *J. Chem. Soc., Chem. Commun.*, 1971, 1481; D. S. Ashton, J. M. Tedder, J. C. Walton, A. Nechvatal, and I. K. Stoddart, *J. Chem. Soc., Perkin Trans. 2*, 1973, 846; W. Thaler, *J. Am. Chem. Soc.*, 1963, **85**, 2607.
19 K. J. Shea and P. S. Skell, *J. Am. Chem. Soc.*, 1973, **95**, 6728.
20 For reviews see: J. M. Tedder and J. C. Walton, *Adv. Free Radical Chem.*, 1980, **6**, 1955; W. A. Thaler, *Methods Free-Radical Chem.*, 1969, **2**, 121; M. L. Poutsma, *ibid.*, 1969, **1**, 79.
21 M. Anpo, C. Chatgilialoglu, and K. U. Ingold, *J. Org. Chem.*, 1983, **48**, 4104.
22 J. H. Incremona and C. J. Upton, *J. Am. Chem. Soc.*, 1972, **94**, 301; C. J. Upton and J. H. Incremona, *J. Org. Chem.*, 1976, **41**, 523; G. G. Maynes and D. E. Applequist, *J. Am. Chem. Soc.*, 1973, **95**, 6728.
23 C. Walling and F. Mayahi, *J. Am. Chem. Soc.*, 1959, **81**, 1485.
24 K. C. Ferguson and E. Whittle, *Trans. Faraday Soc.*, 1971, **67**, 2618.
25 W. A. Nevill, D. A. Frank, and R. D. Trepka, *J. Org. Chem.*, 1962, **27**, 422.
26 D. S. Ashton and J. M. Tedder, *J. Chem. Soc., Perkin Trans. 2*, 1972, 2965.
27 D. S. Ashton, H. Singh, J. M. Tedder, J. C. Walton, and E. A. Watt, *J. Chem. Soc., Perkin Trans. 2*, 1973, 125.
28 B. Andersen and R. Srinivasan, *Acta Chem. Scand.*, 1972, **26**, 3468.
29 J. E. Bennett and A. Thomas, *Proc. Roy. Soc.* (*Lond.*), *Ser. A*, 1964, **68**, 3889; D. Greatorex and T. J. Kemp, *Trans. Faraday Soc.*, 1971, **67**, 1576; T. Migazaki, T. Wakayama, M. Fukaya, Y. Saitake, and Z. Kuri, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1030.
30 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899, 4907.
31 J. J. P. Stewart, Quantum Chemistry Program Exchange, No. 455, University of Indiana, 1983.
32 R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285.
33 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.
34 R. H. Fish and B. M. Broline, *J. Organomet. Chem.*, 1978, **159**, 255.
35 T. S. Cantrell and J. S. Solomon, *J. Am. Chem. Soc.*, 1970, **92**, 4656; T. Svenson, *Chem. Scripta*, 1973, **3**, 171.

Received 12*th October* 1987; *Paper* 7/1824