Hydrogen Abstraction from Spiro[2.*n*]alkanes

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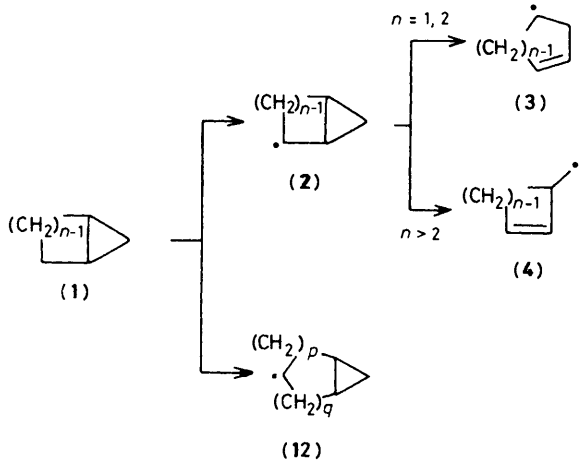
Hydrogen abstraction from spiro[2.3]hexane by t-butoxyl radicals gave spiro[2.3]hex-2-yl radicals; their rearrangement to cyclobutenylethyl radicals was followed by kinetic e.s.r. spectroscopy. Hydrogen abstraction at the methylene groups adjacent to the cyclopropyl rings [cyclopropylmethyl (cpm) sites] in higher spiro[2.*n*]alkanes gave spiro[2.*n*]alk-2-yl radicals, which rearranged to cycloalkenylethyl radicals too rapidly for detection, together with secondary radicals from abstraction at the other methylene groups in the larger ring. From the measured concentrations of the cycloalkenylethyl and secondary radicals the rate of hydrogen abstraction at the cpm sites relative to the rate of hydrogen abstraction at the secondary sites was determined; significant activation of the cpm hydrogens was found. This activation was attributed to a pseudo-allyl type of effect, *i.e.*, to delocalisation of the unpaired electron into the Walsh orbitals of the cyclopropane ring of the spiro[2.*n*]alk-2-yl radicals; semi-empirical SCF-MO calculations supported this explanation. Photobromination of spiro[2.3]hexane occurred mainly by S_H2 attack of bromine atoms at the cyclopropane methylene carbons with fission of either C–C bond.

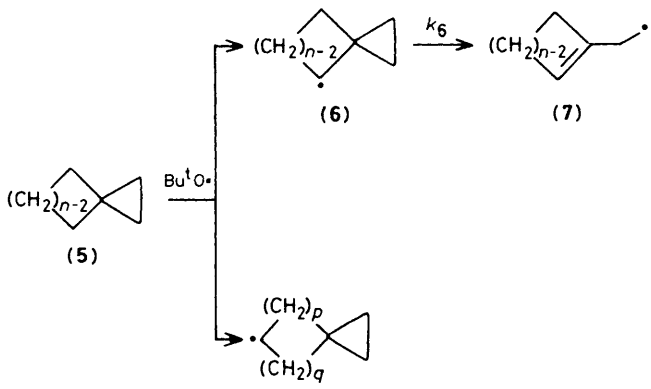
We showed recently [1,2] that the mode and rate of homolytic ring fission in *cis*-bicyclo[*n*.1.0]alk-2-yl radicals (**2**) is controlled by two factors. For the first two members of the series (**1**, $n = 1$ or 2) relief of ring strain outweighs the unfavourable overlap of the SOMO with the orbitals of the inter-ring bond; this bond breaks to give a cycloalkenyl radical (**3**) (Scheme 1). For the higher members of the series (**2**, $n > 2$) stereoelectronic control predominates; *i.e.*, the favourable overlap of the SOMO with the outer cyclopropane bond orbitals ensures that this bond breaks to give cycloalkenylmethyl radicals (**4**).

Hydrogen abstraction from spiro[2.*n*]alkanes (**5**) will occur almost exclusively in the larger ring because of the much higher C–H bond strengths in the cyclopropyl rings. Hydrogen abstraction at C(2) [and C(*n*)] will produce spiro[2.*n*]alk-2-yl radicals (**6**) and hydrogen abstraction at other sites will produce secondary cycloalkyl type radicals (**8**). The radicals (**6**) are of the cyclopropylmethyl type and will rearrange by β-scission of the β,γ-cyclopropane bond to give cycloalkenylethyl radicals (**7**) (see Scheme 2). The spiro[2.*n*]alkyl radicals provide, therefore, a second series in which the interplay of the two effects, relief of ring strain and the stereoelectronic factor, on the ring-opening reaction can be studied. The rate of ring fission will depend on the size of the ring and also on the extent of overlap of the SOMO with the β,γ-bond. The geometry of the system will hold radicals (**6**) in conformation (**9**), but overlap of the SOMO with the cyclopropane bond will depend on the conformation of the larger ring and the *s*/*p* character of the SOMO. The first member of the series (**6a**), *i.e.*, spiropentyl, is a σ-radical;[3] thus this radical centre is not planar as in (**9**) but bent as in (**10**), with consequent poor overlap of the SOMO with the β,γ-bonds. Thus, even though spiropentyl radicals are highly strained, the poor overlap factor and the absence of significant relief of ring strain on β-scission (the rearranged radical, cyclopropenylethyl, is also highly strained) means that they do not readily undergo ring fission. Experimentally it was found that spiropentyl radicals did not rearrange at temperatures below *ca.* 380 K.[3–5]

In this paper we report an e.s.r. study of spiro[2.3]hexane (**5b**) and higher members of the series. The chlorination of (**5b** and **c**) was investigated by Applequist and Landgrebe.[5] The rather complex mixtures of products contained some components which indicated that a significant amount of ring opening to give radicals (**7**) had occurred. Suzuki *et al.*[6] generated spiro[2.4]- and spiro[2.5]alk-2-yl radicals from the corresponding azo-alkanes and observed products from β-scission in both cases.

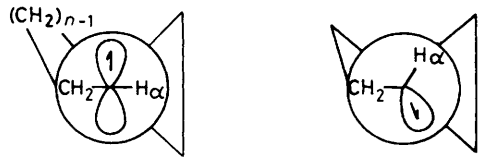


Scheme 1.



a; $n = 2$
b; $n = 3$
c; $n = 4$
d; $n = 5$
e; $n = 6$
f; $n = 11$

Scheme 2.



(9) (10)

Results and Discussion

Spiro[2.3]*hex-2-yl Radicals* (**6b**).—Degassed solutions of spiro[2.3]hexane (**5b**) and di-t-butyl peroxide in dichlorodifluoromethane were photolysed in the cavity of the e.s.r. spectrometer. Samples were also made up in cyclopropane as solvent and, for temperatures above *ca.* 240 K, neat di-t-butyl peroxide was used as solvent. At 140 K the spectrum shown in the Figure was obtained. This consists of a basic double triplet, each component of which is further split into a septet; the central components of each triplet show an additional doublet second order splitting. This spectrum is assigned to the spiro[2.3]hex-2-yl radical (**6b**) with one α-, two equivalent β-, and six fortuitously equivalent γ-hydrogens; the e.s.r. parameters are recorded in Table 1, and the simulation is shown in the Figure. The $a(H_\alpha)$ value (19.6 G) was somewhat low for a planar radical centre; the corresponding $a(H_\alpha)$ in the related cyclobutyl radical, which is generally thought to be planar at C_α, is 21.3 G.[7,8] The low $a(H_\alpha)$ for (**6b**) could indicate a small degree of bending at $\dot{C}_\alpha$ (**2**), as was observed in the spiropentyl radical[3] or alternatively it could be a consequence of some spin delocalisation from the *p*-orbital on C(2) into the Walsh orbitals of the adjacent cyclopropane ring (*vide infra*). The radicals formed on hydrogen abstraction from C(3) could not be detected.

On warming the sample above 140 K the signals from radical (**6b**) decreased in intensity and a new radical appeared with a spectrum consisting of a triplet of triplets. At temperatures above 175 K only this new spectrum, which we assign to the cyclobutenylethyl radical (**7b**), could be detected (e.s.r. parameters in Table 1). On re-cooling the solution to 140 K the spectrum of radical (**7b**) disappeared and that of radical (**6b**) reappeared. Since both the rearranged and unrearranged radicals could be observed the kinetics of the rearrangement were investigated by measuring the concentrations of the two species in cyclopropane solvent over a range of temperatures by the method of Ingold and co-workers.[9,10] The kinetic data are given in Table 2, together with the values of $k_6/2k_t$, where $2k_t$ is the rate constant for bimolecular self-reactions of radicals (**7b**). Least-squares treatment of the data gives equation (1). The

$$\log(k_6/2k_t/\text{mol dm}^{-3}) = (1.48 \pm 0.1) - (1.41 \pm 0.08\ \text{kcal mol}^{-1})/2.3RT^* \quad (1)$$

termination rates of small to moderately sized transient radicals are diffusion controlled in solution and depend on the solution viscosity.[11–13] In order to evaluate $2k_t$ we have used Fischer's accurate data for the self-termination of t-butyl radicals in heptane.[12] At each temperature $2k_t$ was calculated from the Arrhenius equation given by Fischer, equation (2), by correcting for the difference in viscosity of cyclopropane[14] from that of

$$\log[2k_t(\text{Bu}^t\cdot)/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}] = 11.63 - (2.30\ \text{kcal mol}^{-1})/2.3RT \quad (2)$$

n-heptane[12] at each temperature. The rearrangement rate constants (k_6) derived in this way are given in Table 2; least-squares treatment yielded equation (3). The Arrhenius *A*-factor

* 1 cal = 4.18 J.

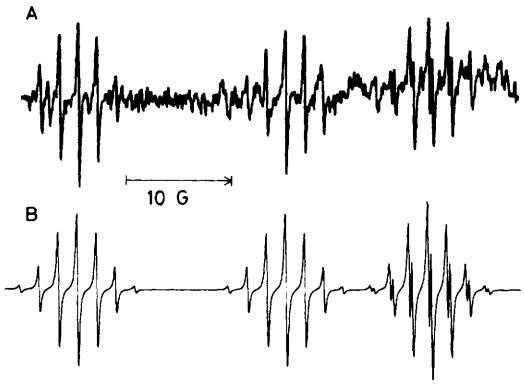


Figure. Low-field halves of 9.4 GHz e.s.r. spectrum of spiro[2.4]hex-2-yl radicals at 140 K. Upper trace (A) experimental; lower trace (B) computer simulation. Some lines from the rearranged radical, cyclobutenylethyl, can also be observed

Table 1. E.s.r. parameters of spiro[2.3]hex-2-yl radicals (**6**) and cycloalkenylethyl radicals (**7**)

Radical	*T*/K	H.f.s.(G)
Spiro[2.3]hex-2-yl (**6b**)	141	$a(H_\alpha)$ 19.6, $a(2H_\beta)$ 33.0, $a(6H_\gamma)$ 1.8
Cyclobutenylethyl (**7b**)	175	$a(2H_\alpha)$ 21.6, $a(2H_\beta)$ 28.2
Cyclopentenylethyl (**7c**)	251	$a(2H_\alpha)$ 21.6, $a(2H_\beta)$ 27.2
Cyclohexenylethyl (**7d**)	240	$a(2H_\alpha)$ 22.5, $a(2H_\beta)$ 27.7
Cycloheptenylethyl (**7e**)	230	$a(2H_\alpha)$ 22.4, $a(2H_\beta)$ 26.7
Cyclododecenylethyl (**7f**)	240	$a(2H_\alpha)$ 22.4, $a(2H_\beta)$ 26.0

Table 2. Kinetic e.s.r. data for the rearrangement of spiro[2.3]hex-2-yl radical (**6b**)

T/K	10^8[(**6b**)]/M	10^8[(**7b**)]/M	$k_6/2k_t$	$10^2k_6/\text{s}^{-1}$
170	1.21	4.07	17.8	17.0
170	1.37	3.99	15.6	14.8
170	1.30	3.90	15.6	14.8
165	1.58	3.26	9.99	8.71
165	2.07	3.13	7.86	6.92
165	1.50	2.85	8.27	7.24
160	1.89	2.60	6.18	5.01
160	3.43	2.08	3.34	2.69
160	1.59	1.47	2.83	2.29
154	2.34	1.68	2.89	2.14
154	3.85	1.37	1.86	1.38
154	1.52	1.08	1.85	1.38
149	4.55	1.08	1.34	0.91
149	2.21	0.64	0.83	0.56
143	2.05	0.37	0.44	0.27

$$\log(k_6/\text{s}^{-1}) = (12.5 \pm 0.1) - (7.2 \pm 0.4\ \text{kcal mol}^{-1})/2.3RT \quad (3)$$

is close to the 'normal' value of *ca.* 10^{13} s^{-1} for unimolecular reactions; the activation energy is discussed below.

Hydrogen Abstraction from Higher Spiro[2.n]*alkanes.*—Hydrogen abstraction by t-butoxyl radicals was also studied for spiro[2.4]heptane (**5c**), spiro[2.5]octane (**5d**), spiro[2.6]nonane (**5e**), and spiro[2.11]tetradecane (**5f**). The first three compounds were examined at temperatures down to 120 K, but in all cases the spiro[2.*n*]alk-2-yl radicals were completely rearranged to cycloalkenylethyl radicals (**7**), which were observed throughout the whole temperature range. Their e.s.r. parameters are

Table 3. Relative rates of hydrogen abstraction by Bu^{t}O· radicals from spiro[2.*n*]alkanes and bicyclo[*n*.1.0]alkanes

Compound	*T*/K	[cpm]/[sec.]	*k*(cpm)/*k*(sec.)[a]
Spiro[2.5]octane (**5d**)	240	5.8 ± 0.5	8.6 ± 0.8
	273	4.9 ± 0.5	7.3 ± 0.8
Spiro[2.6]nonane (**5e**)	240	2.3 ± 0.2	4.6 ± 0.4
	256	2.0 ± 0.2	4.1 ± 0.4
	273	1.8 ± 0.2	3.6 ± 0.4
	295	1.8 ± 0.2	3.6 ± 0.4
	317	1.6 ± 0.2	3.2 ± 0.4
Spiro[2.11]tetradecane (**5f**)	240	1.2 ± 0.1	5.2 ± 0.5
Bicyclo[6.1.0]nonane (**1**, $n = 6$)	240	0.75 ± 0.25	1.5 ± 0.5

[a] Statistically corrected for the numbers of hydrogens in each environment.

recorded in Table 1. The archetype radical, cyclopropylmethyl, is not fully rearranged under e.s.r. conditions until *ca.* 160 K,[15] so it follows that the spiro[2.*n*]alkyl radicals rearrange more rapidly.

With spiro[2.4]heptane the only detectable radical was (**7c**), but spiro[2.5]octane gave rise to signals from cyclohexenylethyl radicals (**7d**) together with a set of six very weak lines with spacings of 21.4 and 46.2 G. This spectrum was almost identical with that of cyclohexyl radicals[16] and we attribute it to the substituted cyclohexyl radicals (**8d**) formed on hydrogen abstraction from the methylene groups at C(3) and C(4). Similarly, weak signals from secondary radicals [$a(H_\alpha) = 22.5$, $a(2H_\beta) = 23.8$, $a(2H_\beta) = 27.0$ G] were observed on hydrogen abstraction from spiro[2.6]nonane and spiro[2.11]tetradecane [$a(H_\alpha) = 22.0$, $a(4H_\beta) = 27.5$ G]. Thus for all the spiro-[2.*n*]alkanes hydrogen is abstracted mainly at the sites adjacent to the cyclopropyl ring [the cyclopropylmethyl (cpm) sites, C(2) and C(*n*)] but abstraction from the remaining methylenes is not negligible (see Scheme 2).

The rate of hydrogen abstraction at the cpm sites, relative to the rate of abstraction at the remaining methylenes, *k*(cpm)/k(sec.), was estimated in each case from the concentrations of radicals (**7**) and (**8**), determined by double integration of suitable peaks from the spectra of each radical. The relative concentrations of the two radicals and the *k*(cpm)/*k*(sec.) values derived by correcting for the numbers of hydrogens in each environment are recorded in Table 3. The relative rate *k*(cpm)/*k*(sec.) depends to some extent on the size of the larger ring, which is not surprising because the rate of hydrogen abstraction from cycloalkanes varies with ring size.[17] Spiro-[2.11]tetradecane (**5f**) probably gives the nearest approximation to 'normal' secondary hydrogens, and the result here indicates that hydrogen is abstracted from the cpm sites about five times more rapidly. As would be expected, the cpm site is less activated towards Bu^{t}O· radical attack than the allyl site for which *k*(allyl)/*k*(sec.) = 36 or the propynyl (propargyl) site for which *k*(propynyl)/*k*(sec.) = 18 at 293 K.[18] The relative rate of hydrogen abstraction at the cpm sites decreases with increasing temperature (Table 3), *i.e.*, the reaction becomes less selective.

The highest occupied of the Walsh orbitals of cyclopropane consists of a degenerate pair constructed from *p*-orbitals in the plane of the cyclopropyl ring.[19–21] In the spiro[2.3]hex-2-yl radicals (**6b**) the *p*-orbital at C(2) is held in the ideal orientation for interaction with either member of this cyclopropyl HOMO. The main contributions to the resultant SOMO of radicals (**6b**) are illustrated in (**11**); semi-empirical calculations support this representation (*vide infra*). The MO in (**11**) is similar to the SOMO of allyl radicals except that one of the terminal *p*-orbitals in allyl is replaced by the pair of orbitals on the cyclopropyl methylene groups. The activation towards hydrogen abstraction at the cpm sites can therefore be attributed to

(**11**)

this pseudo-allyl delocalisation. The less favourable overlap in (**11**) as compared with allyl accounts for the smaller activation at cpm as compared with allyl sites.

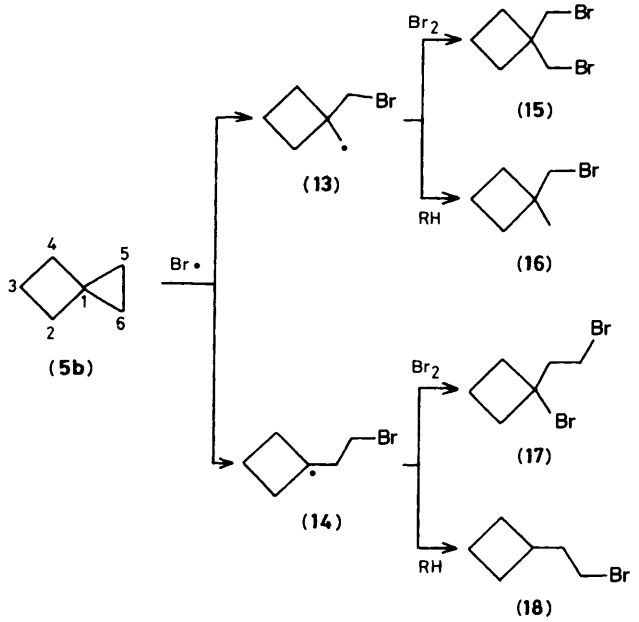
We previously examined hydrogen abstraction from *cis*-bicyclo[*n*.1.0]alkanes (**1**).[2] The bicyclo[*n*.1.0]alk-2-yl radicals (**2**) also rapidly rearrange under e.s.r. conditions to give cycloalkenyl, or cycloalkenylmethyl radicals (see Scheme 1).[1,2] Hydrogen abstraction from the methylene groups in the larger ring that are not adjacent to the cyclopropyl ring will give secondary radicals (**12**). In principle the relative rate of hydrogen abstraction at C(2) could be determined from measurements on the concentrations of the two radicals (**4**) and (**12**). In practice, for the lower members of this series (**1**, $n \leqslant 4$) the only detectable radicals were (**3**) or (**4**); but minor amounts of (**12**) could have escaped detection because of overlapping spectra.[2] For the higher members of this series the e.s.r. spectra were weak and poorly resolved. Re-examination of the reactions using bicycloalkanes carefully repurified by preparative g.l.c. gave similarly poor spectra; in one case, that of *cis*-bicyclo[6.1.0]nonane both radicals (**4**) and (**12**) were sufficiently well marked for their relative concentrations to be determined. The relative rate (Table 3) shows that there is little, if any, activation at the cpm sites in bicyclo[6.1.0]nonane. In the radicals (**2**) the axis of the *p*-orbital at C(2) containing the unpaired electron is tilted out of the orientation parallel to the cyclopropyl ring [*cf.* (**11**)] by an angle that depends on the size and conformation of the ring. Assuming that the conformation of the radical (**2**, $n = 6$) resembles the most stable conformation of bicyclo[6.1.0]nonane,[22,23] the axis of the *p*-orbital at C(2) will be almost perpendicular to the plane of the cyclopropyl ring and pseudo-allyl interaction of the type shown in (**11**) is not possible. The lack of activation at the cpm sites in *cis*-bicyclo[6.1.0]nonane is therefore consistent with this explanation. For the smaller members of this series, models suggest that the axis of the *p*-orbital at C(2) will be between the parallel [as in (**11**)] and perpendicular orientations. Some overlap, and hence some activation, can be expected and this accounts for the preferential attack observed at C(2) in the smaller bicyclo[*n*.1.0]alkanes for both t-butoxyl radicals[2] and chlorine atoms.[24,25]

β-*Scission of Spiro*[2.n]*alk*-2-*yl Radicals.*—Spiropentyl radicals (**6a**) do not undergo β-scission to give cyclopropenylethyl radicals (Scheme 2) at temperatures up to 270 K under e.s.r.

Table 4. β-Scission of spiro[2.*n*]alk-2-yl and related radicals

Radical	k(25 °C)/s^{-1}	log A/s^{-1}	E/kcal mol^{-1}	ΔRS[a]
Spiro[2.2]pent-2-yl (**6a**)	$<10^4$	[13]	>12	10
Spiro[2.3]hex-2-yl (**6b**)	1.1×10^7	12.5	7.2	24
Spiro[2.4]hept-2-yl (**6c**)	$>10^{8.5}$	[13]	<6.5	28
Spiro[2.5]oct-2-yl (**6d**)	$>10^{8.5}$	[13]	<6.5	26
Cyclopropylmethyl[b]	1.3×10^8	12.5	5.9	26

[a] Estimated difference in ring strain (RS) between the unrearranged and rearranged radicals; the RS in radicals (**6**) was assumed to be about the same as that of the corresponding hydrocarbon. [b] Results from reference 15.



Scheme 3.

conditions.[3] The rate constant for this rearrangement must be $<10^3$ s^{-1} at 270 K.[3,26] The upper limit for the rate constant at 298 K together with the corresponding lower limit for the activation energy based on an assumed A-factor of 10^{13} s^{-1}, are compared in Table 4 with the measured Arrhenius parameters for spiro[2.3]hex-2-yl radicals (**6b**). Spiro[2.4]hept-2-yl radicals (**6c**) and higher homologues are fully rearranged under e.s.r. conditions at 120 K. The lower limits for the rearrangement rate constants and corresponding upper limits for the activation energies are given in Table 4, together with the Arrhenius parameters for β-scission of cyclopropylmethyl radicals.[15] Spiropentyl radicals (**6a**) rearrange much more slowly than cyclopropylmethyl radicals because β-scission leads to the creation of the very strained cyclopropene ring, and/or because there is actually very poor overlap of the σ-orbital at C(2) with the orbitals of the β,γ-bond.[3]

The rate constant for rearrangement of radicals (**6b**) is about an order of magnitude less than that of cyclopropylmethyl radicals at 298 K, and the activation energy is 1.3 kcal mol^{-1} higher. β-Scission of (**6b**) leads to the creation of the rather strained cyclobutene ring so that relief of ring strain (ΔRS) is less in this reaction than for cyclopropylmethyl radicals (Table 4). In addition, the p-orbital at C(2) in radical (**6b**) is held rather rigidly in the cyclobutane ring whereas in cyclopropylmethyl radicals it is free to attain optimum overlap with the orbitals of the β,γ-bond. Either or both these factors may explain the slower rate of rearrangement of radical (**6b**).

Spiro[2.4]hept-2-yl radicals (**6c**) and the higher homologues undergo β-scission more rapidly than cyclopropylmethyl radicals. The relief of ring strain on ring-opening in radicals (**6c**) is greater than that in cyclopropylmethyl radicals and may be slightly greater for the higher homologues. The extent of overlap of the p-orbital at C(2) with the β,γ-bond in the cyclopropane ring will depend on the conformation of the ring for the larger spiro[2.*n*]alk-2-yl radicals. It is clear, however, that an orientation favourable to β-scission can be achieved, especially in the larger and more flexible rings.

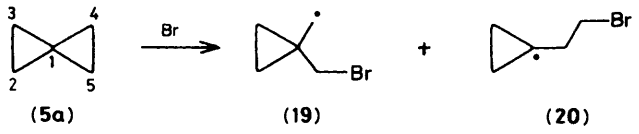
The spiro[2.3]hex-2-yl radical (**6b**) was investigated by MINDO/3[27,28] and MNDO[29,30] semi-empirical SCF-MO methods. The configuration at the radical centre [C(2)] was established by optimising with respect to all geometrical variables for a series of out-of-plane angles of the C(2)–H bond: both methods gave minimum-energy structures with planar radical centres. Both methods also predicted that the main contributions to the SOMO are essentially as shown in structure (**11**); *i.e.*, they indicate significant delocalisation into the cyclopropane ring. INDO[31] calculations using the optimum geometry derived from the MNDO method gave −16.8 G for $a(H_\alpha)$; an identical value was obtained using the MINDO/3 calculated geometry. This calculated value is somewhat less than the experimental $a(H_\alpha)$ (19.6 G, Table 1) but it shows that the lowering of $a(H_\alpha)$ as compared with the value for cyclobutyl radicals can probably be attributed to delocalisation of the unpaired electron into the Walsh orbitals of the cyclopropane ring rather than to non-planarity at the radical centre.

An MNDO study of the β-scission of radicals (**6b** and **c**) was carried out by optimising with respect to all other geometrical variables for successive increments (0.05 Å) of one of the β,γ-bonds. The calculated enthalpies of reaction and activation were:

	ΔH°/kcal mol^{-1}	ΔH^+/kcal mol^{-1}
(**6b**) ⟶ (**7b**)	0	24
(**6c**) ⟶ (**7c**)	−6	21

The MNDO calculations correctly predict β-scission in radical (**6c**) to be more exothermic and to have a lower enthalpy of activation than in radical (**6b**). However, the absolute magnitudes of the activation enthalpies are overestimated by a factor of between three and four. Similar overestimation by the MNDO method of the energy barriers to β-scission was observed for bicyclo[*n*.1.0]alk-2-yl radicals.[2]

Photobromination of Spiro[2.3]*hexane.*—Reaction of (**5b**) with molecular bromine in CCl_4 solution at 293 K proceeded rapidly on illumination and was complete in *ca.* 10 min. The main products were identified as 1,1-di(bromomethyl)cyclobutane (**15**) (25%), 1-bromo-1-(2-bromoethyl)cyclobutane (**17**) (63%), and two monobromides $C_6H_{11}Br$, tentatively identified as 1-bromomethyl-1-methylcyclobutane (**16**) (5%) and 1-(2-bromoethyl)cyclobutane (**18**) (5%). The main reaction pathways are indicated in Scheme 3. S_H2 attack of bromine atoms at C(5) or C(6) leads to radical (**13**) by fission of the C(5)–C(6) bond, or radical (**14**) by fission of the C(1)–C(5) or C(1)–C(6) bonds. These intermediate radicals then abstract bromine to



(5a) (19) (20)

produce the major dibromides, or hydrogen (probably from the substrate) to give the monobromides (**16**) and (**18**). The mechanism is analogous to that found for spiro[2.2]pentane,[3] except that cleavage of C(1)–C(5) takes place much more readily in (**5b**) than does the analogous cleavage of C(1)–C(4) in (**5a**). The proportions of the two dibromides indicate that C(5)–C(6) cleavage occurs about 0.4 times as rapidly as C(1)–C(5) cleavage in (**5b**) whereas in (**5a**) the analogous relative rate is *ca.* 1 000. In the photobromination of alkyl-substituted cyclopropanes the direction of ring fission was found to be always in favour of generating the thermodynamically preferred product radical.[32] With spiropentane the cyclopropyl radical (**20**) is much less stabilised than the primary radical (**19**). With spirohexane (**5b**) the cyclobutyl radical (**14**) is more stabilised than the primary radical (**13**). [N.B. The D(C–H) values are 106 (cyclopropyl), 98 (primary), 96.5 (cyclobutyl) (kcal mol^{-1}).[33]] The larger proportion of C(1)–C(5) cleavage in (**5b**) is therefore consistent with this explanation. The main difference between the photobromination of (**5b**) and the photochlorination[5] is that in the latter, products from hydrogen abstraction at C(2) were important. In the photobromination of (**5b**) no products from hydrogen abstraction at C(2) or C(3) were detected, although there were a few minor (< 1%) unidentified components. This difference is not surprising in view of the known greater selectivity of bromine atoms.

Experimental

^{1}H N.m.r. spectra were recorded on a Bruker WP80 instrument in $CDCl_3$ solutions at ambient temperature with Me_4Si as internal standard. Mass spectra were obtained with an AEI MS 902 spectrometer. E.s.r. spectra were run with a Bruker ER 200D instrument, samples being degassed, sealed in Spectrosil tubes and photolysed directly in the cavity with light from a 500-W medium-pressure mercury arc.

Spiro[2.3]hexane (**5b**) was prepared from 1,1-bis(bromomethyl)cyclobutane (**14**) by the method of Buchta and Merck.[34] The crude material was distilled, then small samples were purified by preparative g.l.c. on a 7 ft. column packed with 10% SE30 on Chromosorb W. The ^{1}H n.m.r. spectrum was identical with that given in the literature.[5]

Spiro[2.4]heptane (**5c**) was prepared by hydrogenation of spiro[2.4]hepta-4,6-diene over platinum(IV) oxide.[35] The product was distilled and small samples were purified by preparative g.l.c. on a 20 ft. column packed with 10% Carbowax 20 M on Chromosorb W. The ^{1}H n.m.r. spectrum was identical with that given in the literature.[5] Two impurities were separated and shown to be ethylcyclopentane, δ_H 1.25 (3 H, t, J 7 Hz), 1.5—1.8 (9 H, m), and 3.55 (2 H, q, J 7 Hz), and 1,1-dimethylcyclopentane, δ_H 2.0 (6 H, s) and 2.2—2.8 (8 H, m).

cis-Spiro[2.5]octane (**5d**) was prepared from methylenecyclohexane and CH_2I_2,[36] b.p. 119 °C at 760 mmHg. Small samples were separated from unchanged substrate by preparative g.l.c. on a 15 ft. column packed with 10% BMEA on Chromosorb P operated at 95 °C. The ^{1}H n.m.r. spectrum agreed with the literature; M^+ found 110.1091, calculated for C_8H_{14}: 110.1095; δ_C 12.16, 25.74, 26.30, and 36.00 (quaternary carbon not observed).

cis-Spiro[2.6]nonane (**5e**) was prepared from methylenecycloheptane in a similar way,[36] b.p. 145—148 °C at 760 mmHg. Small samples were separated from unchanged methylenecycloheptane by preparative g.l.c. using a 15 ft column packed with 10% MS 200/500 on Chromosorb G at 145 °C. The ^{1}H n.m.r. spectrum agreed with the literature; M^+ found 124.1247, calculated for C_9H_{16}: 124.1252; δ_C 14.18, 20.50 (quaternary), 26.64, 28.23, and 38.46.

cis-Spiro[2.11]tetradecane (**5f**) was prepared in a similar way; b.p. 138—142 °C at 15 mmHg. Pure (**5f**) was separated from unchanged methylenecyclododecane by preparative g.l.c. using a 3 ft column packed with 10% APL on Chromosorb W at 160 °C. The pure material had a m.p. of 29 °C; M^+ found 194.2027, calculated for $C_{14}H_{26}$: 194.2034; δ_H 0.17 (4 H, s), 1.38 (22 H, br s); δ_C 11.98, 20.10 (quaternary), 21.67, 22.60 (×2), 26.08, 26.40, and 32.54.

Bromination of Spiro[2.3]*hexane* (**5b**).—Bromine (60 μl) in deaerated CCl_4 (250 μl) was added slowly to a deaerated solution of (**5b**) (20 μl) in CCl_4 (250 μl). On illumination with a tungsten lamp the bromine colour was discharged in *ca.* 10 min. The mixture was analysed by g.c.–m.s. and found to contain two minor monobromides $C_6H_{11}Br$ and two major dibromides $C_6H_{10}Br_2$ together with unchanged (**5b**). The ^{1}H n.m.r. spectrum showed the first eluted dibromide to be 1,1-bis(bromomethyl)-cyclobutane (**14**) (25%) and the second to be 1-bromo-1-(2-bromoethyl)cyclobutane (**16**) [δ_H 2.3—2.8 (8 H, m), 3.5 (2 H, dd)] (63%). The identity of the first dibromide was confirmed by retention time comparisons with authentic material.

References

1 C. Jamieson, J. C. Walton, and K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1366.
2 C. Roberts and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1983, 879.
3 A. J. Kennedy, J. C. Walton, and K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, 1982, 751.
4 D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Am. Chem. Soc.*, 1960, **82**, 2368.
5 D. E. Applequist and J. A. Landgrebe, *J. Am. Chem. Soc.*, 1964, **86**, 1543.
6 M. Suzuki, S. I. Murahashi, A. Sonada, and I. Moritani, *Chem. Lett.*, 1974, 267.
7 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1968, **90**, 7155.
8 J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Am. Chem. Soc.*, 1969, **91**, 1877.
9 G. B. Watts, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, 1972, **94**, 8784.
10 D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, 1974, **96**, 6356.
11 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 193.
12 H. Schuh and H. Fischer, *Int. J. Chem. Kinet.*, 1976, **8**, 341.
13 C. Huggenberger and H. Fischer, *Helv. Chim. Acta*, 1981, **64**, 338.
14 R. W. Gallant, *Hydrocarbon Processing*, 1970, **49**, 137.
15 B. Maillard, D. Forrest, and K. U. Ingold, *J. Am. Chem. Soc.*, 1976, **98**, 7024.
16 R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.
17 J. M. Tedder and J. C. Walton, *Adv. Free-Radical Chem.*, 1980, **6**, 155.
18 E. Bascetta, F. D. Gunstone, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1983, 603.
19 A. D. Walsh, *Trans. Faraday Soc.*, 1949, **45**, 179.
20 R. Hoffmann, *J. Am. Chem. Soc.*, 1968, **90**, 1475.
21 P. Hemmersbach and M. Klessinger, *Tetrahedron*, 1980, **36**, 1337.
22 R. P. Corbally, M. J. Perkins, A. S. Carson, P. G. Laye, and W. V. Steele, *J. Chem. Soc., Chem. Commun.*, 1978, 778.
23 W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, 1967, **32**, 2976.
24 P. F. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *J. Org. Chem.*, 1968, **33**, 1448.
25 R. S. Boikess, M. MacKay, and D. Blithe, *Tetrahedron Lett.*, 1971, 401.
26 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317.
27 R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285.

28 M. J. S. Dewar, Quantum Chemistry Program Exchange No. 309, University of Indiana, Indiana, 1976.
29 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899, 4907.
30 W. Thiel, Quantum Chemistry Program Exchange, No. 353, University of Indiana, Indiana, 1978.
31 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.
32 K. J. Shea and P. S. Skell, *J. Am. Chem. Soc.*, 1973, **95**, 6728.
33 D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, 1982, **33**, 493.
34 E. Buchta and W. Merck, *Chimia*, 1968, **22**, 193.
35 C. F. Wilcox and R. R. Craig, *J. Am. Chem. Soc.*, 1961, **83**, 3866.
36 E. LeGoff, *J. Org. Chem.*, 1964, **29**, 2048.

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