The Spiropentyl Radical and Some Homolytic Reactions of Spiropentane

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Spiropentyl radical was generated by hydrogen abstraction from spiropentane by t-butoxyl radical and its e.s.r. spectrum obtained. The experimental e.s.r. parameters were compared with computational results obtained using semi-empirical SCF MO methods. The spiropentyl radicals do not undergo β-scission in the observable temperature range (T < 380 K). The main process in the halogenation of spiropentane at 293 K in CCl_4 solution involves S_H2 attack by the halogen atom to give 1-(halogenomethyl)cyclopropylmethyl radicals. The β-scission of these latter radicals has been investigated by e.s.r. spectroscopy and by the reduction of 1,1-bisbromomethylcyclopropane with tri-n-butyltin hydride.

THE β-scission of cyclopropyl to allyl radicals is strongly exothermic, but in spite of this the activation energy is high and ring fission is not observed in solution under normal conditions.[1] On the other hand, the mildly exothermic ring opening of cyclopropylmethyl to butenyl radicals occurs readily in solution even at 150 K. According to the stereoelectronic explanation of radical reactivity [1] cyclopropylmethyl radicals undergo ready β-scission because the SOMO can assume an eclipsed conformation with respect to a β,γ bond. Cyclopropyl radicals cannot attain this type of conformation without the development of great strain and therefore β-scission requires a much higher activation energy. Spiropentyl radicals (2) derived from spiropentane (1) are an example of a species which is simultaneously a cyclopropyl-type radical and a cyclopropylmethyl-type radical. The rigidity of this radical prevents overlap of the SOMO with the C(1)–C(3) bond, as in cyclopropyl, but there is potential overlap of the SOMO with the C(1)–C(4) and/or the C(1)–C(5) bonds depending on the structure of the radical. The stereoelectronic approach would suggest, therefore, that spiropentyl radicals should undergo β-scission in the second ring and that the process might be observable in solution. The ring strain in spiropentane (265 kJ mol^{-1}) [2] is more than twice that of cyclopropane (115 kJ mol^{-1}) [2] and this factor would also favour ring fission. The study reported in this paper was undertaken with a view to testing this possibility and developing the free-radical chemistry of spiropentane.

Homolytic ring fission in cyclopropanes can also be brought about by S_H2 attack of halogen atoms,[3] which provides a second method of approaching the problem. Applequist and his co-workers [4,5] showed that chlorine atoms attack spiropentane to give a variety of products including those derived from S_H2 attack and hydrogen abstraction. We report here a detailed investigation of the chlorination, bromination, and iodination of spiropentane under much milder conditions than those employed by Applequist. We also report our study of the photochemical reaction of bromotrichloromethane with spiropentane. The thermal decompositions of spiropentane [6] and substituted spiropentanes [7,8] have received a good deal of attention, but apart from the work of Applequist and a brief study of the kinetics of hydrogen abstraction from (1) by CF_3· radicals,[9] very little attention has been given to homolytic reactions involving (1).

RESULTS AND DISCUSSION

Generation of Spiropentyl Radicals.—In initial attempts to observe (2) directly by e.s.r. spectroscopy, (1) and di-t-butyl peroxide in cyclopropane solution were photolysed in the cavity of the spectrometer. Experiments were made with several different concentration ratios of (1) to cyclopropane (in the range 1 : 10—1 : 3) but either no interpretable signal was obtained or cyclopropyl radicals, with e.s.r. parameters identical to those given in the literature,[10,11] were observed. This suggests that the rate of hydrogen abstraction from (1) by t-butoxyl radicals is not greater than that of hydrogen abstraction from cyclopropane. This is in agreement with the data of Whittle and Jones who found (1) and cyclopropane to be of similar reactivity towards hydrogen abstraction by trifluoromethyl radicals.[9] No e.s.r. spectra were obtained from photolysis of solutions of (1) and di-t-butyl peroxide in CF_2Cl_2 or $CFCl_3$. However, when (1) containing *ca.* 20% di-t-butyl peroxide was photolysed without a solvent the spectrum shown in Figure 1 was obtained. The e.s.r. parameters, which

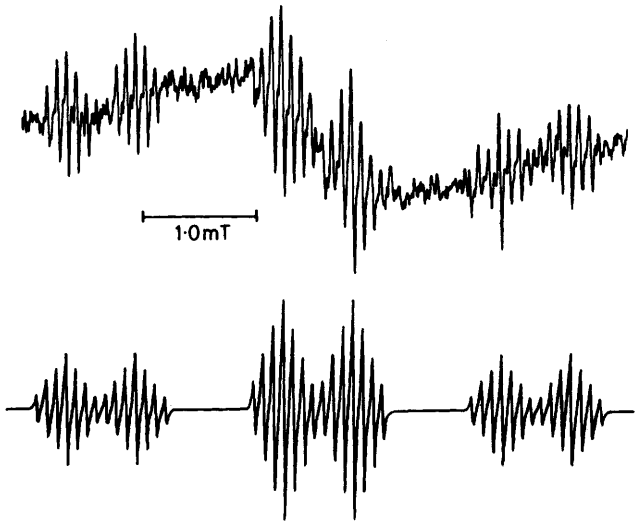


FIGURE 1 E.s.r. spectrum (9.34 GHz) of the spiropentyl radical in neat spiropentane at 161 K. The lower spectrum is the computer simulation

were checked by computer simulation, are given in Table 1. Comparison of these e.s.r. parameters with those of cyclopropyl and 2,2,3,3-tetramethylcyclopropyl radicals (Table 1) confirms that the spectrum corresponds to spiropentyl radicals (2); the comparison also enabled the hyperfine splittings (h.f.s.) to be partly assigned.

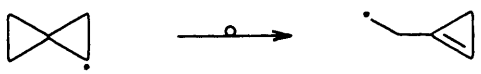
TABLE 1

E.s.r. parameters of spiropentyl and cyclopropyl radicals

Radical	T/K	a/mT (exp)	a/mT (INDO) [c]
[a]	162	$2H_\beta$ 1.91	H_β[3] 2.33, $H_{\beta'}$ 2.83
		H_α 0.62	H_α −0.67
		$2H_\gamma$ 0.173	H_γ[4'] 0.29, H_γ[5] 0.41
		$2H_\gamma$ 0.086	H_γ[4] −0.15, H_γ[5'] −0.21
[b]	151	$4H_\beta$ 2.349	H(*syn*) 2.36, H(*anti*) 2.45
		H_α 0.663	H_α −0.58
[b]		H_α 0.615	
	165	$12H_\gamma$ 0.078	

[a] H.f.s. essentially independent of temperature in the range 160—270 K. [b] Data from refs. 11 and 18. [c] INDO calculated h.f.s. with out of plane angle α of 30°.

The e.s.r. spectrum of (2) could be observed up to temperatures of *ca.* 270 K, but above this temperature the signal was too weak for detection. No spectra of rearranged radicals were observed. The rate constant for the β-scission of the C(1)–C(4) bond in (2) must be $<10^3$ s^{-1} at 270 K which is much slower than the rate constant for the β-scission of the cyclopropylmethyl radical, *viz.*[1] 4.6×10^7 s^{-1}. This result was somewhat unexpected in view of the strain in (2) and the potential overlap of the SOMO with the C(1)–C(4) bond. The product of β-scission in (2) would be the cyclopropenylethyl radical (3). This rearrangement will be approximately thermoneutral (like the cyclopropylmethyl



(2) (3)

rearrangement). However there must be a high activation energy for reaction which will have its origins in the creation of the very strained cyclopropene ring and/or in the fact that there is actually very poor overlap of the SOMO with the C(1)–C(4) bond. Indeed (2) retains its structural integrity even at 370 K.

Semiempirical SCF MO Study of Spiropentyl Radicals.—The structure and enthalpy of formation of (2) were calculated using the MINDO/3 [12,13] and MNDO [14,15] methods of Dewar and his co-workers. Geometries were fully optimised with respect to all bond lengths, bond angles, and dihedral angles. In addition, (2) was also examined using the INDO technique of Pople and Dobosh.[16] The structure of (2) calculated by MINDO/3 is shown in Figure 2. The structure shows a shortening of the C(2)–C(3) and C(2)–C(1) bonds together with a lengthening of the C(3)–C(1) bond, as would be expected for a free radical. The C–H_α bond is predicted to be shorter than the other C–H bonds, again in accord with expectation. The geometry of the second ring, remote from the radical centre, is very little perturbed from that of the rings in (1) for which C(1)–C(4) is 1.510 Å and C(4)–C(5) is 1.483 Å was found by MINDO/3.[12] This indicates that overlap of the SOMO with C(1)–C(4) is not very efficient. This is presumably because spiropentyl is a σ rather than a π radical, *i.e.* the unpaired electron resides in an orbital with appreciable *s* character, which, in turn, helps to explain the lack of rearrangement in (2).

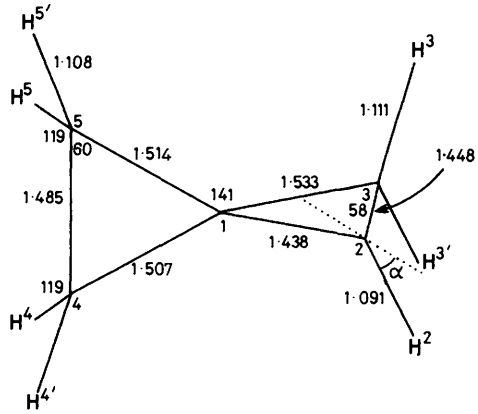


FIGURE 2 Geometry of the spiropentyl radical calculated by MINDO/3

The spiropentyl radical is expected to be non-planar at the radical centre like the cyclopropyl radical. The nearly equal values of $a(H_\alpha)$ for these two radicals (Table 1) implies that they do indeed have very similar configurations. Calculated enthalpies of formation of (2) as a function of the angle α, which measures the deviation of the radical centre from planarity, are plotted in Figure 3. MINDO/3 correctly predicts (2) to be non-planar at the radical centre with an out of plane angle of *ca.* 35°. The enthalpy of formation (ΔH_f 310 kJ mol^{-1}) is *ca.* 8 kJ mol^{-1} lower than in the planar conformation. The MNDO calculations gave rather similar results, except that the radical centre was predicted to be virtually planar (see Figure 3). MNDO gives a better representation of the closed-shell spiropentane [14] than MINDO/3, but has been found to be less successful at predicting the properties of free radicals.[14] The present MNDO results for (2) manifest the same phenomenon.

The INDO calculations for (2) were carried out using a geometry derived from the MINDO/3 calculations, *viz.* C–C bond lengths, bond angles, and C–H bond lengths, as in Figure 2. The expectation value of S^2, at the energy minimum, was 0.756 which shows that the INDO wave functions are close to the ideal doublet state and contain very little contamination from higher multiplicity spin states. The variation in the INDO-calculated energies of (2) with α (Figure 3) shows that INDO

also predicts (2) to be non-planar, with a minimum-energy structure (−5 kJ mol^{-1} relative to the planar conformation) at α 30°. Thus MINDO/3 and INDO are in good agreement and give a consistent picture of (2). Kochi and his co-workers using the INDO method [17,18] calculated the out of plane angle for the C–H_α bond in cyclopropyl radicals to be 35°. It is clear the spiropentyl and cyclopropyl are closely similar in structure.

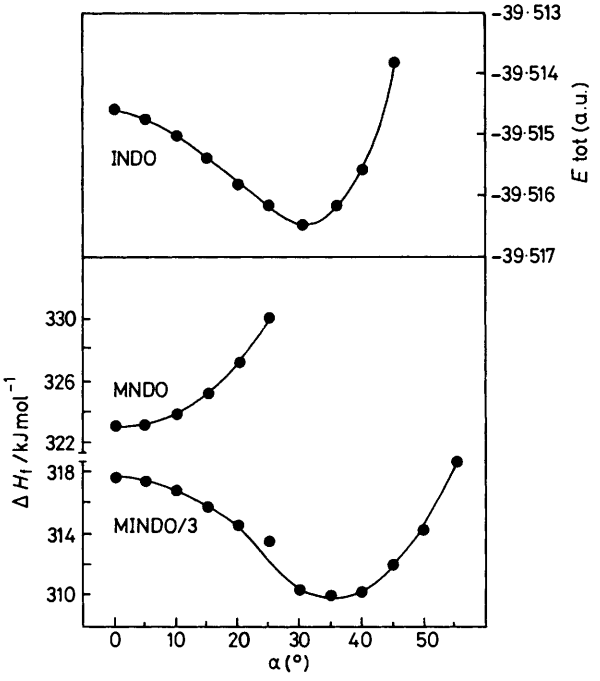


FIGURE 3 Upper: INDO-calculated variation in total energy of the spiropentyl radical as a function of the out of plane angle α. Lower: variation in the enthalpy of formation of the spiropentyl radical as a function of α, calculated by MNDO and MINDO/3

The INDO-calculated h.f.s. for (2) depend strongly on the angle α and are given in Table 1 for the minimum-energy structure. The agreement with experiment is quite good and provides further evidence that (2) is a σ radical. The predicted h.f.s. for the *syn*- and *anti*-β-hydrogens differ by *ca.* 0.5 mT whereas experimentally they are found to be equal. The calculated difference is appreciably larger than was found for the *syn*- and *anti*-β-hydrogens of cyclopropyl,[18] but is really not disturbingly large when the known limitations of the INDO method are taken into account.[19] If this difference is real, however, it indicates that pyramidal inversion at the radical site in (2) occurs at a rate which is fast on the e.s.r. time scale. The INDO calculations suggest that the larger pair of $a(H_\gamma)$ are positive and should be assigned to 4'- and 5-H and that the smaller pair are negative and should be assigned to 4- and 5'-H.

Photochlorination of Spiropentane.—Reaction of (1) with molecular chlorine proceeds rapidly at room temperature in CCl_4 solution. The products identified from reactions with a deficiency of chlorine are given in Table 2. By far the main product is the 1,3-dichloride (5a)

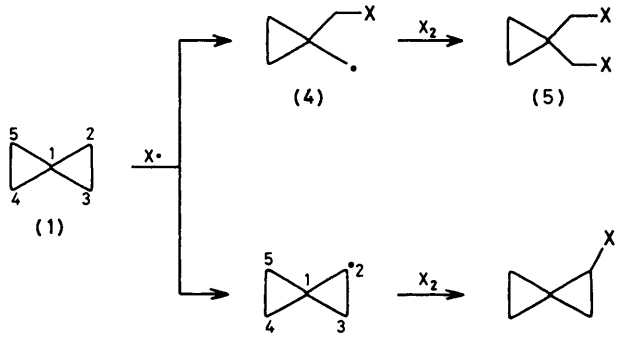
TABLE 2

Products of the photohalogenation of spiropentane in solution [a]

Reagent	Product, yield [b] (5)	(13)	Other
Cl_2–CCl_4 [c]	54.4	14.2	(6a), 3.6, (8), 4.5, (10) 23.0
Br_2–CCl_4	90.1	9.9	(17) ≤ 0.1
CCl_3Br	70.7		(5d),[d] 2.1, $CHCl_3$, 4.7, C_2Cl_6, 19.6
I_2–CCl_4	96.0	4.0	

[a] All reactions at ambient temperature (20 °C). [b] Yields expressed as mol% relative to the total products. [c] Results for reaction with excess of spiropentane. [d] (5d) is 1-bromomethyl-1-chloromethylcyclopropane.

which is almost certainly formed by bimolecular homolytic substitution, S_H2, on (1) (see Scheme 1). Chlorine atoms also abstract hydrogen from (1) giving spiropentyl radicals (2) which in turn abstract chlorine from Cl_2 to produce spiropentyl chloride (6a). Only 3.6% of the reaction proceeds by hydrogen abstraction while nearly 82% goes by way of the S_H2 process to produce (5a) and its further chlorination products (8a) and (10a).

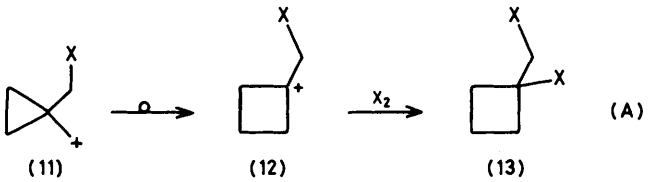


SCHEME 1

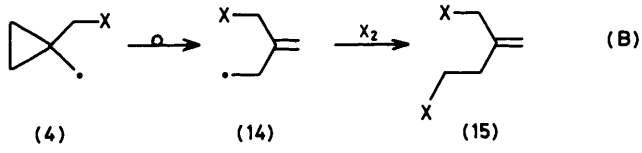
The remainder of the reaction produces 1-chloro-1-chloromethylcyclobutane (13a). The spiropentane used here was not contaminated with methylenecyclobutane so this last product could not have been formed by halogen addition to that olefin, nor is it reasonable to suggest that there could be significant thermal decomposition (which produces methylenecyclobutane [6]) at 20 °C. It is most probable therefore that (13a) was formed by a small amount of ionic chlorination which accompanied the main radical processes. The intermediate primary carbonium ion (11a) would readily ring expand to give the tertiary carbonium ion (12a) thus leading to product (13a) [reaction (A)]. Shea and Skell also found *ca.* 10% ionic reaction accompanying the radical halogenation of alkylcyclopropanes in CCl_4 solution.[20]

Applequist and his co-workers found (6a) and the unsaturated dichloride (15a) [together with the tetrachloride from chlorine addition to (15a)] to be the major products in the gas-phase photochlorination of (1) at

ca. 116 °C.[4] Hydrogen abstraction from (1) has a high activation energy and it is quite reasonable therefore that at 116 °C more (6a) should be formed. The observation of (6a) at 116 °C in the gas phase and at 20 °C in solution, and the absence of products derived from the rearrangement of (2), provides further confirmation that

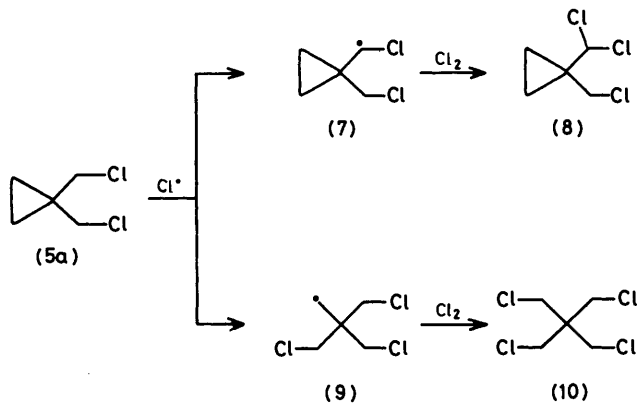


β-scission in (2) is a high activation energy process. The product (15a) is, of course, formed *via* β-scission of the intermediate substituted cyclopropylmethyl radical (4a) [reaction (B)]. Evidently this rearrangement competes effectively with chlorine abstraction by (4a) in the gas phase at 116 °C. However, in solution at 20 °C the halogen concentration was sufficiently high, and the rearrangement (B) was slower, so that the halogen abstraction step leading to (5a) predominated and (15a) was not formed in detectable quantities.



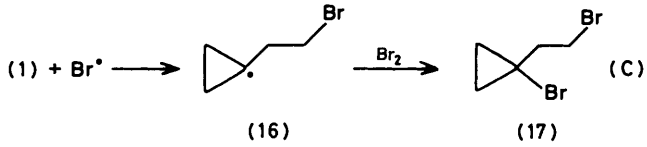
When excess of chlorine was used polychlorination occurred rapidly and tri- and tetra-chlorides were the main products even in reactions lasting no more than 30 min. The main trichloride detected was (8) formed *via* hydrogen abstraction from one of the chloromethyl groups in (5a). However, a second S_H2 attack on (5a) giving pentaerythrityl tetrachloride (10) (see Scheme 2) took place even more rapidly, as is shown by the relative yields of (8) and (10) in Table 2.

Photobromination of (1).—Reaction of (1) with a slight deficiency of bromine in CCl_4 solution gave rise to a very clean product mixture in which by far the main product

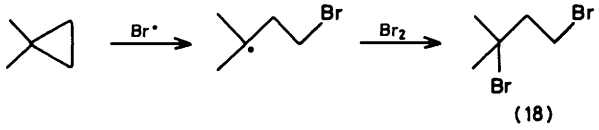


SCHEME 2

was (5b) formed by S_H2 attack of bromine atoms with cleavage of the C(2)–C(3) bond. The product yields are listed in Table 2. The small percentage of (13b) is probably formed by ionic bromination as shown in reaction (A). A third dibromide, of formula $C_5H_8Br_2$, was also detected in *ca.* 0.1% yield. This was eluted close to (5b) and was collected together with (5b) during preparative g.l.c. The ^1H n.m.r. of the resulting material showed no olefinic hydrogens but was not sufficiently strong to enable the structure of the minor component to be elucidated. The most likely structure is (17), and if this identification is correct it indicates that cleavage of the C(1)–C(2) bond is *ca.* 1 000 times slower than cleavage of the C(2)–C(3) bond in S_H2 attack by bromine [reaction (C)]. According to the electron diffraction measurements of



Dallinga *et al.*[21] the C(1)–C(2) bond length is 1.469 Å as compared with 1.519 Å for the C(2)–C(3) bond. The longer C(2)–C(3) bond is presumably weaker which would explain its more facile homolytic fission. 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, *e.g.* bromination of 1,1-dimethylcyclopropane led exclusively to the formation of (18).[20] The same is true



for spiropentane since the cyclopropyl radical (16) will be less stabilised than the primary alkyl radical (4b).

Competitive photobrominations were carried out with cyclopropane and (1) to determine the relative rates of S_H2 attack on the two molecules. The mechanism may be represented as follows, where S is (1) and C is cyclopropane:

$$Br_2 + h\nu \longrightarrow 2Br\cdot$$
$$Br\cdot + C \longrightarrow BrC\cdot \quad k_1^c$$
$$Br\cdot + S \longrightarrow BrS\cdot \quad k_1^s$$
$$BrC\cdot + Br_2 \longrightarrow BrCBr \quad k_2^c$$
$$BrS\cdot + Br_2 \longrightarrow BrSBr \quad k_2^s$$

Since *ca.* 50% of the spiropentane was consumed it was necessary to use an integrated rate expression, and equation (D) can readily be derived if the very small amounts of the reactants used up in termination and ionic reactions are neglected. S_o and C_o are the initial

$$k_1^s/k_1^c = \ln(1-[BrSBr]/S_o)/\ln(1-[BrCBr]/C_o) \quad (D)$$

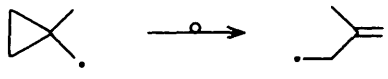
reactant concentrations. Using this expression with the experimental data, k_1^s/k_1^c (20 °C) = 122, *i.e.* spiropentane

is over 100 times as reactive to S_H2 attack by bromine as cyclopropane. This is consistent with the fact that the C(2)–C(3) bond length in (1) (1.519 Å) is somewhat longer than the C–C bond length in cyclopropane (1.510 Å),[22] and so is probably weaker.

Photochemical Reaction of (1) *with Bromotrichloromethane.*—The products of the photochemical reaction of (1) with neat CCl_3Br at room temperature are given in Table 2. The reaction was stopped at <50% consumption of the spiropentane. The main product (5b) was again formed by S_H2 attack of bromine atoms, generated in the initial photolytic step with (1) and subsequent bromine transfer from CCl_3Br by the intermediate radicals (4b). The 1-chloromethyl-1-bromomethylcyclopropane could have been formed by the radicals (4b) abstracting chlorine from CCl_3Br, or by initial chlorine atom attack on (1) followed by bromine atom transfer. Chlorine atoms are not formed in significant amounts in the primary photolysis of CCl_3Br [23] but they can arise from photolysis of the product C_2Cl_6. The presence of $CHCl_3$ indicates that the CCl_3· radicals abstract hydrogen, as well as combining to give C_2Cl_6. No peaks were visible in the monobromide region of the product chromatogram and (6b) was not detected. It is likely therefore that all or part of the $CHCl_3$ is formed by CCl_3· radicals abstracting hydrogen from the products; in any case it is clear that hydrogen abstraction from (1) by CCl_3· radicals occurs only with difficulty.

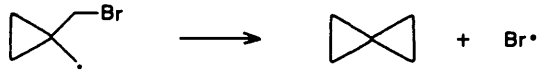
Photoiodination of (1).—Reaction of (1) with molecular iodine proceeded much more slowly in CCl_4 at ambient temperature and reaction was incomplete in 24 h. The reaction was otherwise analogous to photobromination, the main product being (5c); yields are recorded in Table 2. The presence of the 1,2-di-iodide (13c) indicated again that the radical reaction was accompanied by a minor ionic process.

Rearrangement of 1-*Bromomethylcyclopropylmethyl Radicals* (4b).—The radicals (4b) were generated directly in the cavity of the e.s.r. spectrometer by photolysis of a solution of (5b), Et_3SiH, and di-t-butyl peroxide in cyclopropane. At 130 K a weak spectrum consisting of a triplet [*g* 2.0026, *a*(2H) 2.15 mT] probably due to (4b) was observed. The components of the triplet showed evidence of γ-structure, but the signal was too weak to allow this to be analysed. At higher temperatures this signal disappeared and a new spectrum



(19) (20)

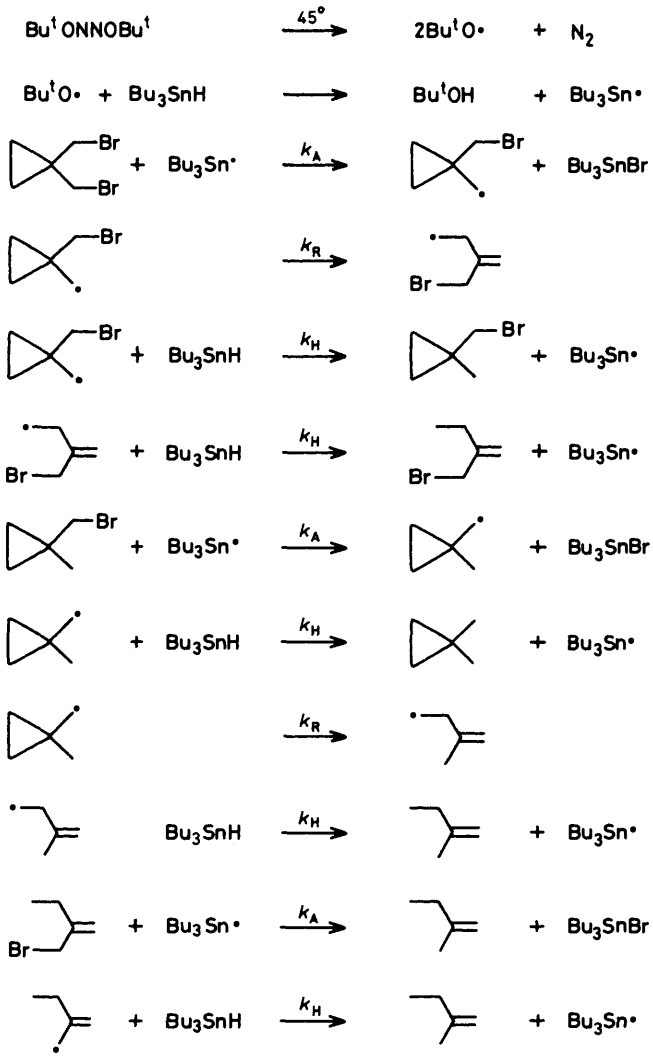
appeared becoming stronger until at 170 K only the new radical could be detected. This spectrum consisted of a triplet of triplets [*g* 2.0026, *a*(2H) 2.16, *a*(2H) 2.70 mT]. These e.s.r. parameters are essentially the same as those of the 3-methylbutenyl radical (20),[24] hence the spectrum can be assigned to (14b). We find therefore that radical (4b) rearranges in the same temperature range as 1-methylcyclopropylmethyl (19) and cyclopropylmethyl radicals under e.s.r. conditions.[24,25] Kinetic e.s.r. measurements on the β-scission of cyclopropylmethyl radicals [26] yielded the Arrhenius parameters $\log(A/s^{-1})$ 12.48, E 24.9 kJ mol^{-1}. The rate parameters for β-scission of (4b) must be approximately the same.



(4b) (1)

After the photolyses the e.s.r. tubes were opened and the products were examined by g.l.c. and g.l.c.–m.s. The only hydrocarbon product which could be detected was (1) formed in trace amounts. It is possible therefore that a small proportion of the radicals (4b) undergo an intramolecular cyclization to reform spiropentane. A similar but more efficient process was observed by Kaplan in the cyclization of 1,3-di-iodopropane.[27]

Reaction of (5b) with neat tri-n-butyltin hydride at 45 °C using di-t-butyl hyponitrite as a thermal initiator



SCHEME 3

gave 1,1-dimethylcyclopropane (21) and 2-methylbut-1-ene (22) as the only detectable C_5 hydrocarbon products. No spiropentane was formed and no monobromohydrocarbons. The mechanism can be written as shown in Scheme 3. Primary alkyl radicals abstract hydrogen from Bu_3SnH at essentially the same rate,[28] the recommended temperature dependence of the rate constant for this reaction being $\log(k_H/l\ mol^{-1}\ s^{-1}) = 9.07 - 15.4/2.3RT$. The e.s.r. evidence described above indicates that the substituted cyclopropylmethyl radicals (4b) and (19) undergo rearrangement at the same rate. We can therefore make the approximation that all the k_H values in Scheme 3 are equal and that both the k_R values are equal. Applying the steady-state approximation we obtain equation (E). From the experimentally

$$\frac{[(22)]}{[(21)]} = \frac{k_R}{k_H[Bu_3SnH]}\left(2 + \frac{k_R}{k_H[Bu_3SnH]}\right) \quad (E)$$

determined final concentrations of (21) and (22), the known Bu_3SnH concentration, and a value of k_H of $3.4 \times 10^6\ s^{-1}$ at 45 °C,[28] the following value of k_R is obtained on taking the positive root in the quadratic for k_R defined by (E): k_R (45 °C) $= 2.6 \times 10^8\ s^{-1}$. In this connection we note that extrapolation of the Arrhenius parameters for cyclopropylmethyl ring fission, determined at low temperatures by Maillard *et al.*,[26] to 45 °C gives k_R $2.4 \times 10^8\ s^{-1}$.

EXPERIMENTAL

^1H N.m.r. spectra were recorded on Varian EM 360 and/or Bruker WP 80 instruments in $CDCl_3$ solutions at room temperature with tetramethylsilane as internal standard. Mass spectra were obtained with a Hewlett–Packard 5992 g.l.c.–m.s. system. G.l.c. analyses were carried out on Pye 105 and Varian 3700 instruments with columns packed with 15% tritolyl phosphate, 12% OV 101, and 12% ββ′-oxydipropionitrile on Chromosorb G as solid support. E.s.r. spectra were obtained at X-band frequency with a Bruker ER 200 D and/or a Varian E 104 instrument.

Spiropentane (1) was prepared from pentaerythrityl tetrabromide and sodium by the method of House *et al.*[29] It was separated from 2-methylbut-1-ene and methylenecyclobutane by preparative g.l.c. using a 30 ft column packed with 12% ββ′-oxydipropionitrile operated at 30 °C. The n.m.r. and mass spectra agreed with the literature and g.l.c. analysis indicated a purity of 99.9%.

Photochlorination of (1).—(i) *With excess of chlorine.* Carbon tetrachloride was deoxygenated by bubbling nitrogen through it for *ca.* 10 min. CCl_4 (1 ml) was saturated with chlorine by passing the gas through the liquid. This solution (0.25 ml) was then added to a deoxygenated solution of spiropentane (30 μl) in CCl_4 (0.25 ml). The mixture, in a thin-walled Pyrex tube, was then photolysed with 300 nm light from a Rayonet tube for 30 min at ambient temperature (19 °C). G.l.c. analysis of the product mixture indicated six main chlorinated products. These were shown by g.l.c.–mass spectrometry to be: peak 1, $C_5H_8Cl_2$ (7.4%); peak 2, $C_5H_7Cl_3$ (28.0%); peak 3, $C_5H_6Cl_4$ (19.0%); peak 4, $C_5H_8Cl_4$ (20.0%); peak 5, $C_5H_8Cl_4$ (10.6%), and peak 6, $C_5H_6Cl_4$ (15.0%). The retention time and mass spectrum of the dichloride were identical to those of 1,1-bischloromethylcyclopropane (see below) and the mass spectra suggested structures (8) and (10) for the trichloride and first tetrachloride respectively. The remaining tetrachlorides were not structurally characterised.

(ii) *With excess of spiropentane.* Several experiments with lower chlorine concentrations were carried out under otherwise identical conditions. In one experiment 71% of the spiropentane remained unchanged at the end of the photolysis. G.l.c. analysis of this mixture indicated five main products: peak 1 (3.6%), M^+ 102, 104, fragmentation pattern consistent with chlorospiropentane (6a); peak 2 (54.4%), M^+ 138, 140, 142, which was identical to peak 1 in (i) above [the ^1H n.m.r. of the mixture confirmed this as 1,1-bischloromethylcyclopropane (5a), δ_H 0.79 (4 H, s) and 3.57 (4 H, s)]; peak 3 (14.2%), M^+ 138, 140, 142, fragmentation pattern consistent with 1-chloro-1-chloromethylcyclobutane (13a); peak 4 (4.5%), M^+ 172, 174, 176, 178, which was identical to peak 2 in (i) above, *i.e.* structure (8); and peak 5 (23.0%), M^+ absent but the mass spectrum showed fragment ions for successive loss of chlorine from $C_5H_8Cl_4$, identical to peak 4 in (i) above, *i.e.* pentaerythrityl tetrachloride (10).

Photobromination of (1).—Spiropentane (2.9 mmol) in CCl_4 (0.5 ml) was added to bromine (0.75 mmol) in CCl_4 (0.5 ml) and the solution photolysed at ambient temperature with light from a tungsten lamp for 40 min; all the bromine colour had then been discharged. G.l.c. and g.l.c.–m.s. analysis showed two product peaks in addition to unchanged (1); peak 1 (9.9%), M^+ absent but fragment ions for successive loss of bromine from $C_5H_8Br_2$; peak 2 (90.1%), M^+ (very weak) 226, 228, 230, the fragmentation pattern was consistent with the structure 1,1-bisbromomethylcyclopropane (5b). The two peaks were separated by preparative g.l.c. on the tritolyl phosphate column. Peak 1 gave δ_H 2.0 (2 H, m), 2.65 (4 H, m), and 3.8 (2 H, s) which shows the structure to be 1-bromo-1-bromomethylcyclobutane (13b). The ^1H n.m.r. and retention time were identical to those obtained from authentic (13b) prepared by adding 1 mol. equiv. of bromine to methylenecyclobutane in CCl_4 solution. The ^1H n.m.r. of peak 2, δ_H 0.5 (4 H, s) and 3.5 (4 H, s), confirmed the structure as (5b).

Competitive Photobromination of Spiropentane and Cyclopropane.—Cyclopropane was bubbled through deoxygenated CCl_4 and then spiropentane (0.188 mmol) was added to the resulting solution (1 ml). The concentrations of the two reactants were monitored by n.m.r. and cyclopropane was blown off, by bubbling nitrogen, until there was 0.43 mmol present. Then bromine (0.094 mmol) was added and the solution was photolysed in the n.m.r. tube for 30 min at 20 °C. Analysis of the products by g.l.c.–m.s. showed four peaks in addition to unchanged starting materials. These were shown to be $CH_2BrCHBrCH_3$ (0.3%), CH_2BrCH_2-CH_2Br (2.3%), 1-bromo-1-bromomethylcyclobutane (6.7%), and 1,1-bisbromomethylcyclopropane (90.5%). The mixtures were quantitatively analysed before and after reaction by n.m.r. for cyclopropane, spiropentane, and 1,1-bisbromomethylcyclopropane and by g.l.c. for the products given above. The final [1,1-bisbromomethylcyclopropane] to initial [spiropentane] ratio was found to be 0.531 and the final [$CH_2BrCH_2CH_2Br$] to initial [cyclopropane] ratio was found to be 0.0062.

Photochemical Reaction of Bromotrichloromethane with (1).—Spiropentane (0.28 mmol) was added to deoxygenated CCl_3Br (0.5 ml) in an n.m.r. tube; the solution was photolysed at 20 °C with light from a 300 nm Rayonet lamp and

monitored periodically by n.m.r. and g.l.c. After 60 h *ca.* 46% of the spiropentane had reacted. Analysis by ^1H n.m.r. showed the presence of $CHCl_3$ and 1,1-bisbromomethylcyclopropane and analysis by g.l.c.–m.s. confirmed the following products: $CHCl_3$ (4.7%), 1-chloromethyl-1-bromomethylcyclopropane (2.1%), C_2Cl_6 (19.6%), and 1,1-bisbromomethylcyclopropane (70.7%) together with minor unidentified products amounting in total to *ca.* 3.0%.

Reaction of 1,1-*Bisbromomethylcyclopropane with Silyl and Stannyl Radicals.*—Compound (5b) was obtained by bromination of (1) on a 0.5 g scale followed by preparative g.l.c. on a 5 ft 5% OV 101 column operated at 80 °C, *ca.* 0.1 g of product being obtained. G.l.c. analysis of this indicated 95.8% purity with the main contaminant being (13b) (3.6%), together with a third dibromide $C_5H_8Br_2$ (0.1%). The ^1H n.m.r. of the product showed no sign of olefinic protons and the mass spectrum was consistent with this latter product being (17). Compound (5b) (0.02 ml), triethylsilane (0.02 ml), and di-t-butyl peroxide (0.02 ml) were dissolved in cyclopropane (*ca.* 0.25 ml) degassed on a vacuum line and sealed into a Spectrosil tube. The tube was irradiated for 15 min by light from a 500 W Wotan super pressure mercury arc directly in the cavity of the e.s.r. spectrometer. E.s.r. signals were observed and these are described in the text. After the photolysis the tube was opened and the cyclopropane slowly blown off in a stream of nitrogen. CCl_4 was added and the products examined by g.l.c.–m.s. and n.m.r. Compound (5b) was largely unchanged and the only significant hydrocarbon product was spiropentane which amounted to 1.9% of the remaining (5b).

Photolysis under the same conditions was carried out with (5b), (0.02 ml), $Me_3SnSnMe_3$ (0.02 ml), and di-t-butyl-peroxide (0.02 ml) in cyclopropane (*ca.* 0.25 ml). No e.s.r. signals were observed and the (5b) was largely unchanged. Spiropentane amounting to 1.2% of unchanged (5b) was identified among the products from its mass spectrum and by retention time comparisons.

Thermal Reaction of (5b) *with Tri-*n*-butyltin Hydride.*—A solution of t-butyl hyponitrite (0.2 mg) in Bu^n_3SnH (0.25 ml, 3.79M) was made up and to it was added 20 μl of a solution of (5b) (0.16M) in benzene. The mixture was degassed, sealed in a Spectrosil tube and heated at 45 °C for 6 h. G.l.c.–m.s. analysis of the mixture showed 1,1-dimethylcyclopropane (0.044% of benzene standard) and 2-methylbut-1-ene (17.45% of benzene standard) to be the only hydrocarbon products. No spiropentane was detected. The identities of the two products were confirmed by retention time comparisons with authentic materials.

Photoiodination of (1).—Iodine (0.68 mmol) was added to a solution of (1) (0.75 mmol) in CCl_4 (1 ml) and the Pyrex tube was photolysed in sunlight for 24 h. After taking the ^1H n.m.r. spectrum the solution was freed from unchanged iodine by adding $CHCl_3$ and washing with sodium thiosulphate solution. The mixture was dried (Na_2SO_4) and the solvent removed on a rotary evaporator. The residue was taken up in ether and examined by g.l.c.–m.s. There were only two detectable products: peak 1, 1,1-bisiodomethylcyclopropane (96.0%) ($M - I)^+$, I^+, $C_5H_8^+$ *etc.* present, δ_H 1.05 (4 H, s) and 3.35 (4 H, s); peak 2, $C_5H_8I_2$ (4.0%); the mass spectrum was consistent with the structure 1-iodo-1-iodomethylcyclobutane.

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