

Homolytic Ring Fission Reactions of Cycloalkylmethyl and Bicycloalkyl Radicals

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The geometries and enthalpies of formation of cyclopropyl, cyclopropylmethyl, cyclobut-2-enylmethyl, cyclobutylmethyl, the isomeric bicyclo[2.1.0]pentyl, bicyclo[1.1.1]pentyl, and spiro-pentyl radicals have been studied by the semi-empirical MINDO/3 method and compared with the calculated and experimental data for the corresponding cyclo- or bicyclo-alkanes. The ring fission reactions of the radicals have been investigated by calculating the energies for successive increments of a chosen reaction co-ordinate. For the cycloalkylmethyl radicals the calculated enthalpies of activation show the same trend as the experimental activation energies for β -scission. The MINDO/3 calculations for the bicycloalkyl radicals are also in agreement with such experimental evidence as is available. For the bicycloalkyl radicals which have not been examined by experiment MINDO/3 suggests that ring fission should be favoured for bicyclo[2.1.0]pent-5-yl radicals. The calculations indicate that overlap of the SOMO with the bond to be broken is usually the most important factor in controlling which bond breaks and the rate of the process. Release of ring strain may, however, oppose and overrule the stereoelectronic effect, *e.g.* with bicyclo[2.1.0]pent-2-yl radicals. If overlap of the SOMO with the β,γ bond is prevented then ring fission is predicted to have a high energy barrier, *e.g.* in cyclopropyl and spiro-pentyl radicals.

The rearrangement of cyclopropylmethyl radicals (1) to but-3-enyl radicals (4) has been well studied¹ and Arrhenius parameters for the ring fission have been determined in solution by kinetic e.s.r. spectroscopy.² The high rate constant for this process is usually understood as resulting from a stereoelectronic effect; β -scission is favoured because the SOMO can assume an eclipsed conformation with respect to a β,γ bond.^{1,3} β -Scission of cyclopropyl radicals to give allyl radicals is slow and cannot be observed in solution under normal conditions in spite of the strong exothermicity of the reaction. In this case the SOMO cannot achieve overlap with the β,γ bond without the development of considerable strain. Cyclobutylmethyl radicals (3) have recently begun to attract attention and rate parameters have been determined for ring fission in (3)^{4,5} and in cyclobutenylmethyl radicals (2).^{5,6} The rearrangements of bicyclopentyl radicals involve similar types of homolytic ring fission. Qualitative experimental evidence which establishes the direction of ring opening has recently been obtained for bicyclo[2.1.0]pent-2-yl radicals (7)^{7,8} and spiro-pentyl radicals (20)^{9,10} and some work has also been published for bicyclo[1.1.1]pentyl radicals (17) and (18).¹¹

These radicals present an interesting situation in which both ring strain and stereoelectronic effects can reinforce or oppose one another. We have made a theoretical study of the radicals mentioned above using semi-empirical SCF MO methods, which throws some light on the interplay of these factors. The ring fission of cyclopropylmethyl radicals has previously been investigated by *ab initio* MO theory employing STO 3G and 4-31G basis sets, but with limited geometry optimisation.¹² The reverse reaction, *i.e.* cyclisation of but-3-enyl radicals has been treated by the MINDO/3¹³ and MINDO/3-UHF methods;¹⁴ the latter report also included studies of the pent-4-enyl and hex-5-enyl cyclisations. Ring opening of cyclopropyl radicals has received intensive theoretical study¹ and *ab initio*^{15,16} as well as MINDO/3 results¹⁷ are available.

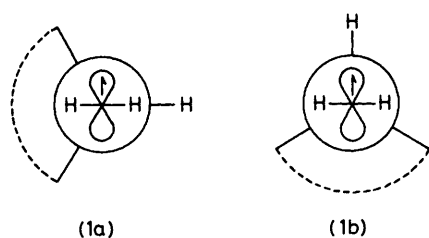
Computational Procedure.—The calculations were carried out using the MINDO/3 procedure of Dewar *et al.*^{18,19} together with the associated Davidson-Fletcher-Powell geometry optimisation programme. The MNDO procedure of Dewar and Thiel^{20,21} gives poorer enthalpies of formation for radicals²⁰ and poorer geometries, in some cases at least,⁹

but some MNDO calculations were also implemented. Unless otherwise stated all equilibrium geometries were found by minimising the energy with respect to all geometrical variables. Reaction co-ordinates were determined by minimising the energy with respect to all other geometrical variables for successive increments of the chosen reaction co-ordinates. Where appropriate, spin densities for the ground state radicals were calculated by the INDO method²² using the optimum geometries derived from the MINDO/3 calculations.

Cycloalkylmethyl Radicals.—There are two limiting conformations about the C_α - C_β bond for cycloalkylmethyl radicals, *i.e.* (1a) and (1b). It has previously been shown that MNDO predicts (1b) as the preferred conformation for cyclobutylmethyl radicals²³ and we also find that both the MINDO/3 and MNDO methods predict (1b) as the preferred conformation for cyclopropylmethyl and cyclobutenylmethyl radicals. The calculated energy differences between the two conformers are small [9 kJ mol⁻¹ for (1) and 7 kJ mol⁻¹ for (2)]. Danen's INDO calculations on (1) with partial geometry optimisation predicted (1a) as the preferred conformation,²⁴ as did the INDO calculations of Stock and Young.²⁵ When the MINDO/3 optimum geometrical parameters are used as input for INDO calculations on (1) lower total energies are found than those reported by previous workers, *i.e.* the MINDO/3 structures represent points closer to the true minima of the INDO potential energy surface. However, again our INDO calculations predicted (1a) to be the preferred conformation.

The e.s.r. spectral data on radicals (1),²⁶ (2),⁶ and (3)^{23,27} established (1a) as the preferred conformation in each case. Thus INDO is more successful than MINDO/3 or MNDO in determining the radical conformations. The potential barrier in (3) was found from e.s.r. measurements²³ to be *ca.* 4 kJ mol⁻¹ and barriers of similar magnitude are expected for radicals (1) and (2). It is a severe test of any theory to calculate such small barriers from first principles and the failure of the MINDO/3 method in this respect is not surprising.

Partial structures for radicals (1)–(3), as calculated by MINDO/3, are compared in Figure 1 with the calculated structures of the corresponding methylcycloalkanes. The geometries were insensitive to the dihedral angle about the



The computed enthalpies of activation (ΔH^\ddagger) are compared with the experimental activation energies in the Table. The experimental activation energies do not correlate with the reaction enthalpies or with the ring strain. [Conventional ring strain terms are³⁰ 115, 125, and 110 kJ mol⁻¹ for (1)–(3), respectively.] The ring opening of (2) is by far the most exothermic of the cycloalkylmethyl radical rearrangements due to the higher strain of the cyclobutenyl ring and the production of the resonance stabilised pentadienyl radical (5)

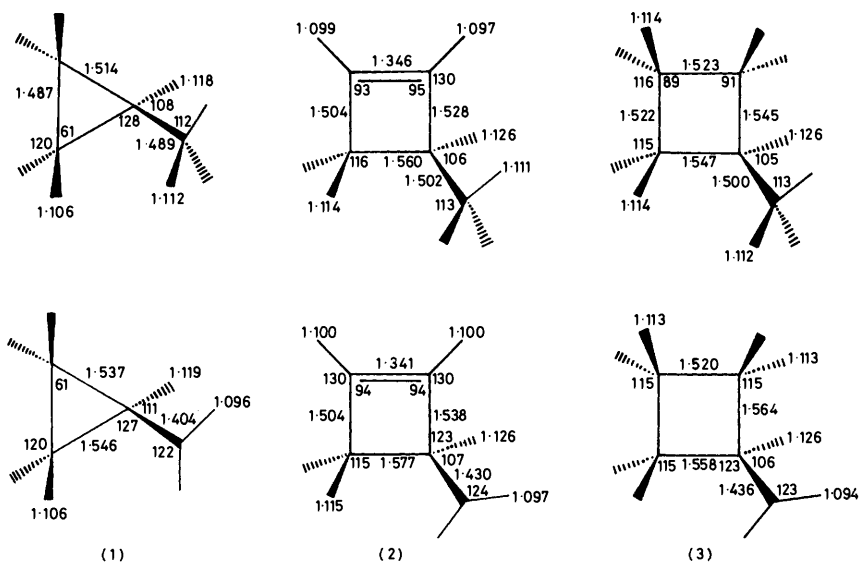
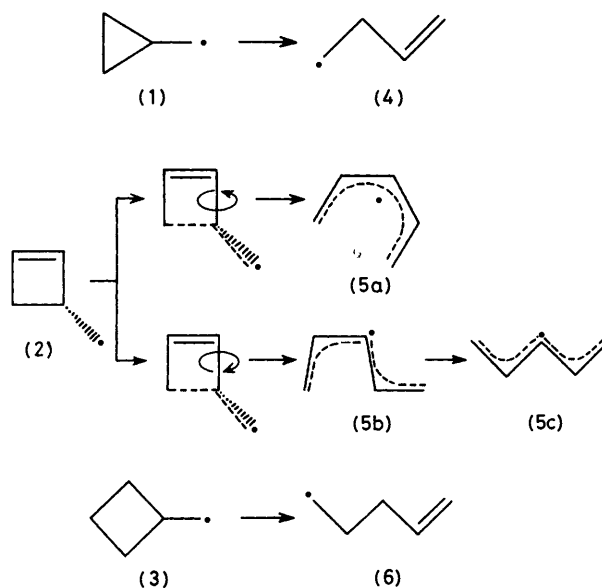


Figure 1. MINDO/3 calculated structures for methylcycloalkanes and cycloalkylmethyl radicals. Bond lengths in Å and angles in °

C_α - C_β bond but are reported for conformers (1a). For each radical the calculated C_α - C_β bonds are exceptionally short and the C_β - C_γ bonds are longer than in the corresponding methylcycloalkanes. Contraction of the C_α - C_β bond and extension of the C_β - C_γ bond has also been observed in *ab initio* calculations on the isobutyl radical, the simplest acyclic analogue of the cycloalkylmethyl radicals, and in other alkyl radicals.^{28,29} On ring fission the C_α - C_β bonds, which are already intermediate in length between single and double bonds, are converted into double bonds and the C_β - C_γ bonds, which are long, break. According to the MINDO/3 predictions therefore, these cycloalkylmethyl radicals are structurally very well adapted for homolytic ring fission.

For each of the cycloalkylmethyl radicals (1)–(3) the appropriate C_β - C_γ bond was chosen as the reaction coordinate and the enthalpy of formation was computed for successive increments thereof until ring fission was complete and the geometry of the ring-opened radicals was obtained (see Scheme 1). The calculated reaction enthalpies (ΔH°) are recorded in the Table. For the cycloalkylmethyl radicals ΔH° can be estimated by the group contributions (GC) method of Benson,³⁰ since all the group equivalents and ring strain contributions are known (see Table). The Table shows that MINDO/3 predicts the ring fission to be less exothermic in each case than does the GC method. The MINDO/3 and GC enthalpies of formation of the ring-opened radicals (4)–(6) are in good agreement but the MINDO/3 ΔH°_f values for the cycloalkylmethyl radicals are all low in comparison with the GC values and this leads to the generally greater values of the MINDO/3 calculated ΔH° values. Dewar and his co-workers have shown that MINDO/3 underestimates the strain energies of small rings¹⁸ and our results are consistent with this trend.



Scheme 1

and MINDO/3 successfully predicts this (Table). In spite of this high exothermicity the experimental activation energy for ring fission of (2) is higher than that of (1) and not much less than that of (3). The MINDO/3 ΔH^\ddagger are all higher than the experimental activation energies by slightly more than a factor of two, but MINDO/3 is successful at reproducing the experimental trend, with (2) intermediate in reactivity.

Reaction enthalpies and enthalpies of activation for homolytic ring fissions

	ΔH° / kJ mol ⁻¹ MINDO/3	ΔH° a/ kJ mol ⁻¹ GC	ΔH^\ddagger / kJ mol ⁻¹ MINDO/3	E / kJ mol ⁻¹ Expt.
(1) \rightarrow (4)	-9	-25	59	24.7 ^b
(2) \rightarrow (5b)	-76	-98	93	42.2 ^c
(3) \rightarrow (6)	+30	-19	113	49.7 ^c
(7) \rightarrow (8)	+8		n.s.	
(7) \rightarrow (9)	-123		21	≤ 24 ^d
(7) \rightarrow (2)	+2		84	
(10) \rightarrow (12)	-11		167	
(10) \rightarrow (13)	+18		260	
(10) \rightarrow (14)	-39		211	
(11) \rightarrow (15)	+71		178	
(11) \rightarrow (16)	-142		26	
(17) \rightarrow (19)	-175		107	
(18) \rightarrow (2)	-116		103	
(20) \rightarrow (21)	-71		105	
(20) \rightarrow (13)	+19		84	> 52 ^e

^a Calculated by the group contributions method;³⁰ group equivalents are not available for most of the radicals. ^b Ref. 2. ^c Ref. 5. ^d Ref. 7. ^e Ref. 31 (see text).

In the MINDO/3 transition states the C _{β} -C _{γ} bond lengths are 190, 197, and 205 pm for (1)–(3), respectively, *i.e.* they are in the same order as the activation energies for ring fission. The C _{β} -C _{γ} bonds are longer in the ground state radicals (1)–(3) by 3.2, 1.7, and 1.3 pm respectively than in the corresponding methylcycloalkanes. These bond extensions on radical formation also reflect the order of the activation energies for ring fission. This indicates that the strengths of the bonds undergoing fission are important in controlling the rate of ring fission; a similar conclusion was drawn from the experimental work.⁵ In the cycloalkylmethyl radicals there is already strong π interaction between the orbitals on C _{α} and C _{β} (note the bond lengths in Figure 1) and this increases rapidly so that in the transition states the C _{α} -C _{β} bond lengths are 136, 137, and 136 pm for (1)–(3). Thus the double bonds are essentially fully formed by the time the transition state is reached. The MINDO/3 calculations therefore support the contention that β -scission is favoured in cycloalkylmethyl radicals because of strong interaction between the SOMO and the orbitals of the β,γ bond.

MINDO calculations were carried out for ring fission of (1); the calculated ΔH° value was -24 kJ mol⁻¹ in better agreement with the GC value, but the calculated ΔH^\ddagger (83 kJ mol⁻¹) was in poorer agreement with the experimental value. The calculated geometries for (1) in the ground state and in the transition state were almost identical to those obtained in the MINDO/3 calculations.

There are three conformations of the pentadienyl radical (5a–c) (see Scheme 1) and either (5a or b) could result from ring fission of cyclobut-2-enylmethyl radicals (2) depending on the direction of rotation of the -CH₂ group with respect to the C _{β} -C _{γ} bond. MINDO/3 predicts unambiguously that the *E,Z*-pentadienyl radical (5b) should be formed; the activation enthalpy being lowest for this process. Experimentally it is found that only *E,E*-pentadienyl radicals (5c) can be detected on β -scission of (2).⁶ The direct formation of (5c) would involve rotation about the ring double bond with concomitant fission of the C _{β} -C _{γ} bond, which seems very unlikely. It was investigated by taking the dihedral angle about the ring double bond as the reaction co-ordinate and computing the energy profile. The computed enthalpy of activation for this route was 219 kJ mol⁻¹, *i.e.* much greater than for the

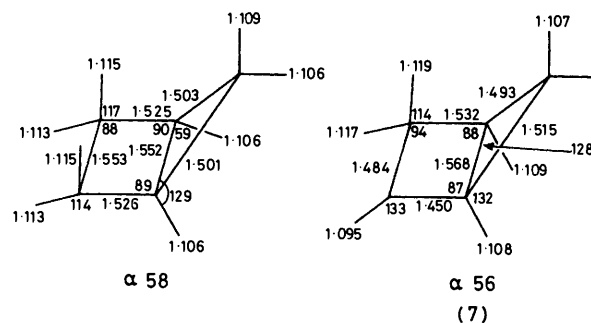
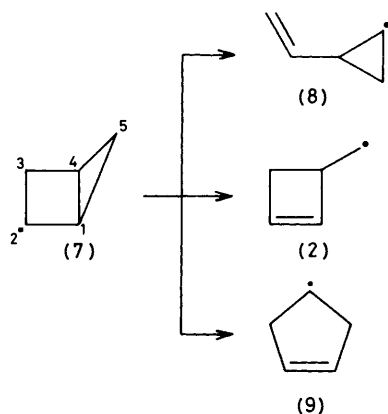


Figure 2. MINDO/3 calculated structures for bicyclo[2.1.0]pentane and the bicyclo[2.1.0]pent-2-yl radical. The acute angle between the planes of the two adjacent rings is α

conversion to (5b) (*cf.* Table). The interconversion of the three conformers of pentadienyl was therefore also investigated by MINDO/3. The computed enthalpies of formation were 232, 228, and 224 kJ mol⁻¹ for (5a–c), respectively, in agreement with the expected stabilities. The enthalpies of activation for the (5a) \rightarrow (5b) conversion, *i.e.* 7 kJ mol⁻¹ and the (5b) \rightarrow (5c) conversion, *i.e.* 9 kJ mol⁻¹ were very low [*cf.* the experimental value of *ca.* 37 kJ mol⁻¹ for (5b) \rightarrow (5c)]. However it is clear that the MINDO/3 calculations support the idea⁶ that radical (2) ring opens to give (5b) initially but that this converts rapidly to (5c) at the temperature of the reaction and hence the latter is the only observable radical.

The Bicyclo[2.1.0]pent-2-yl Radical.—In the bicyclo[2.1.0]pent-2-yl radical (7) the overlap of the SOMO with the orbitals of the β,γ bonds is fixed by the rigid framework of the molecule. It is of particular interest therefore to examine the extent of the overlap with each β,γ bond and to see which should break according to SCF calculations. The MINDO/3 calculated geometry for bicyclo[2.1.0]pentane (Figure 2) is in agreement with the partial structure published by Dewar *et al.*¹⁸ and with the structure established by microwave spectroscopy³¹ except that the calculated C–H bonds are longer by *ca.* 2 pm. The MINDO/3 structure for (7) (Figure 2) with free optimisation of all geometrical variables suggests a non-planar radical centre (ΔH° , 297.5 kJ mol⁻¹). However, the energy is insensitive to the degree of bending and ΔH° rises to only 297.7 kJ mol⁻¹ when planarity is enforced. The geometrical changes on going to the radical (7) are similar to those observed in the non-rigid cycloalkylmethyl radicals. Thus the C(1)–C(2) bond in (7) at 145 pm is clearly well adapted to become a double bond on ring fission. The C(1)–C(5) and C(1)–C(4) bonds are longer than in the parent hydrocarbon by 1.4 and 1.6 pm respectively but these bond extensions are too similar to give an unambiguous prediction of whether fission would occur preferentially in the C(1)–C(5) or the C(1)–C(4) bonds.

The three different β -scission routes open to radicals (7) are shown in Scheme 2 and the MINDO/3 calculated ΔH° and ΔH^\ddagger values are in the Table. The fission of C(3)–C(4) bond to give 2-vinylcyclopropyl radicals (8) is endothermic according to MINDO/3, fission of the C(1)–C(5) bond to give cyclobutenylmethyl radicals (2) is practically thermoneutral and fission of the C(1)–C(4) bond to give cyclopent-3-enyl radicals (9) is predicted to be strongly exothermic. MINDO/3 calculations taking bonds C(1)–C(5) and C(1)–C(4) as reaction co-ordinates indicated fission of the latter to have a much lower enthalpy of activation. Thus on both thermodynamic and kinetic grounds MINDO/3 predicts that β -scission of (7)



Scheme 2

should occur in the C(1)-C(4) bond to give radicals (9); basically because this relieves all the ring strain in a single bond fission. A simple drawing of (7) suggests that the SOMO overlaps most effectively with the orbitals forming the C(1)-C(5) bonds; although it has been suggested⁷ that the C(1)-C(4) bond is bent and actually overlaps the SOMO quite well. Examination of the bond order matrix from the MINDO/3 treatment of (7) indicated that in fact the SOMO overlaps most strongly with the orbitals on C(1) which are bonding to C(5) although there is significant overlap with the orbitals bonding to C(4). INDO calculations were carried out for (7) using the optimum geometry of Figure 2 and here again the density matrices confirmed that the SOMO interacts most strongly with the orbitals forming the C(1)-C(5) bond. Thus the stereoelectronic effect favours fission of C(1)-C(5) to give (2) and is in opposition to the ring strain effect which favours fission of the C(1)-C(4) bond; the MINDO/3 calculations predict that the latter effect should prevail.

Experimentally both product studies and e.s.r. evidence agree that (7) ring opens exclusively by fission of the C(1)-C(4) bond to give (9)^{7,8} in agreement with the MINDO/3 predictions. Ring fission occurred too rapidly for the kinetics of the process to be studied but an upper limit for the activation energy of ring fission was estimated to be 24 kJ mol⁻¹ which is very close to the computed enthalpy of activation (21 kJ mol⁻¹). This ring fission is one of the very few which occurs rapidly but in the direction contrary to that expected on stereoelectronic grounds and MINDO/3 successfully predicts the outcome of this test case.

The Bicyclo[2.1.0]pent-1-yl and Bicyclo[2.1.0]pent-5-yl Radicals.—In addition to the bicyclic radical (7) there are two isomeric radicals (10) and (11) based on the same carbon framework, and in each of these, as in (7), the overlap of the SOMO with the β, γ bonds is dictated by the rigidity of the C₅ skeleton. The MINDO/3 optimised structures of these two radicals are summarised in Figure 3. In the bicyclo[2.1.0]pent-1-yl radical (ΔH_f° , 311.7 kJ mol⁻¹) there are three C-C bonds which are β, γ to the radical centre [C(2)-C(3), C(3)-C(4), and C(4)-C(5)], while the three remaining C-C bonds are all α, β to the radical centre: of these β, γ bonds C(2)-C(3) is shorter than in the parent bicyclo[2.1.0]pentane by 2.6 pm, C(3)-C(4) is essentially unchanged, and C(4)-C(5) is longer by 2.7 pm, while of the α, β bonds, C(1)-C(2) is shorter than in the parent by 3.1 pm, C(1)-C(4) is shorter by 1.5 pm, and C(1)-C(5) is shorter by 4.3 pm. These variations indicate that C(4)-C(5) should cleave, with double bond formation at C(1)-C(5), as the most favoured ring-opening process for this radical.

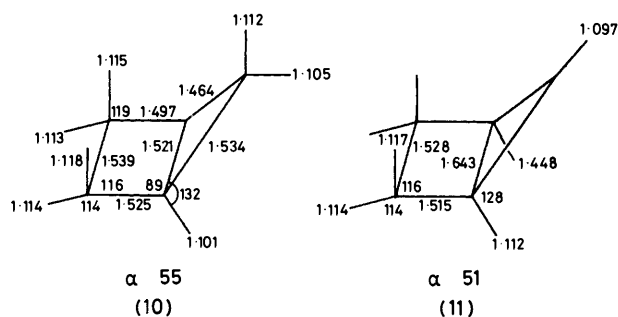
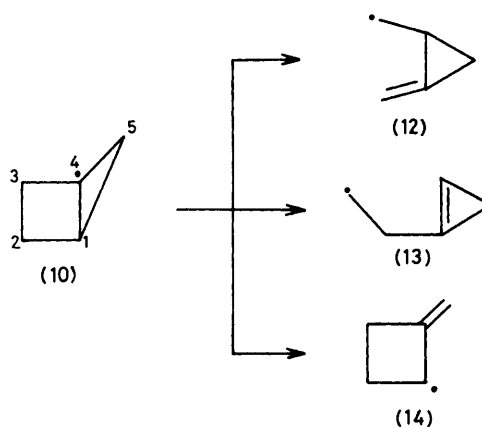


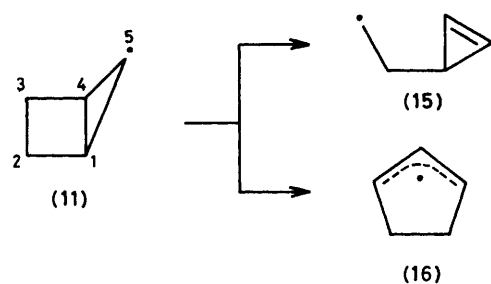
Figure 3. MINDO/3 calculated structures for the bicyclo[2.1.0]pent-1-yl (10) and bicyclo[2.1.0]pent-5-yl radicals (11)



Scheme 3

Three radicals can be formed from bicyclo[2.1.0]pent-1-yl (Scheme 3): cleavage of C(2)-C(3) yields the 2-methylenecyclopropylmethyl radical (12) whose ΔH_f° is calculated as 300.3 kJ mol⁻¹, cleavage of C(3)-C(4) yields the 2-(cyclopropenyl)ethyl radical (13) (ΔH_f° , 329.7 kJ mol⁻¹), and cleavage of C(4)-C(5) yields 2-methylenecyclobutyl (14), whose ΔH_f° is 272.6 kJ mol⁻¹. The favoured cleavage as judged from the structure changes upon radical formation is that to yield (14), which is also the most exothermic process: however the calculated activation barriers for the formation of (12), (13), and (14) from (11) are 166.5, 259.8, and 211.3 kJ mol⁻¹, so that none of these processes is expected to occur rapidly.

In the isomeric bicyclo[2.1.0]pent-5-yl radical, which has C₂ symmetry, there are two bonds β, γ to the radical centre, C(1)-C(2) and C(1)-C(4), but only one, C(1)-C(5) equivalent to C(4)-C(5), α, β to it. Comparison of the structure of this radical with that of the parent C₅H₈ molecule (Figure 3) indicates that radical formation causes a slight shortening of C(1)-C(2), by 1.3 pm, a marked lengthening of C(1)-C(4), by 11.5 pm, and a shortening of C(1)-C(5) by 5.9 pm. Two radicals can be formed by β -cleavage in bicyclo[2.1.0]pent-5-yl (Scheme 4): cleavage of C(1)-C(2) yields the radical (15) (ΔH_f° , 372.4 kJ mol⁻¹) while cleavage of C(1)-C(4), which is the process suggested as most favoured by the structure of the radical, yields the cyclopropenyl radical (16), whose calculated ΔH_f° is 155.6 kJ mol⁻¹. Here again, as with the isomeric bicyclo[2.1.0]pent-1-yl radical, the cleavage indicated by stereoelectronic considerations is the more exothermic process. For formation of (15), which is endothermic by 74.4 kJ mol⁻¹ the activation energy is calculated to be 177.8 kJ mol⁻¹, but formation of (16), which is strongly exothermic, has a calculated activation energy of only 26.4 kJ mol⁻¹.



Scheme 4

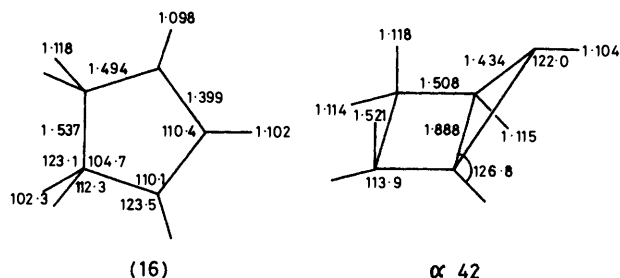


Figure 4. MINDO/3 structures for the cyclopentenyl radical (16) and the transition state in the C(1)–C(4) bond fission of radical (11)

We conclude that no cleavage is expected in the case of the radical (10), but that radical (11) will rearrange to the monocyclic radical (16): in this respect bicyclo[2.1.0]pent-5-yl is similar to bicyclo[2.1.0]pent-2-yl in that the favoured product is that which relieves as much as possible of the ring strain with formation of a single C_5 ring.

The structures of radical (16) and of the transition state for its formation from (11) are shown in Figure 4. Radical (16) has exact C_{2v} symmetry so that both the C_5 ring and the radical centre are exactly planar. The geometry and the eigenvectors for (16) indicate that this radical is simply a disubstituted allyl radical in which the two substituents form part of a ring. The transition state on the other hand is still markedly non-planar, with an inter-ring angle α of 42° , compared with 51° in the parent radical (11). Detailed comparison of the geometry of this transition state with that of the product (16) (Figure 4) indicates that rather little change in the geometrical parameters occurs on going to the transition state, apart from the decrease in α and an increase in the cross ring CC distance from 1.643 to 1.888 Å, although this distance is still well short of the 2.296 Å calculated for the product radical (16). The sum of the bond angles at the radical centre is 326.4° in the transition state, compared with 319.0° in (11) and 360.0° in (16).

Bicyclo[1.1.1]pentyl Radicals.—Bicyclo[1.1.1]pentane is calculated by MINDO/3 to have a structure of exact D_{3h} symmetry, whose principal features are shown in Figure 5, and to have ΔH_f° of $245.9 \text{ kJ mol}^{-1}$. Two experimental studies have been made of this compound, one of which reports³² a D_3 structure having the CH_2 twisted out of the equatorial plane, while the other reports³³ a D_{3h} structure, as calculated here. The experimental CC distances, 1.558(2) Å (D_3) and 1.547(6) Å (D_{3h}) and the equatorial CCC angles, $74.2(2)^\circ$ (D_3) and $73.3(10)^\circ$ (D_{3h}) are not significantly different in the two determinations, and are in excellent agreement with the values calculated by MINDO/3, 1.549 Å and 73.9° .

Two radicals may be formed from bicyclo[1.1.1]pentane (Scheme 5) by loss of either an axial hydrogen to yield the

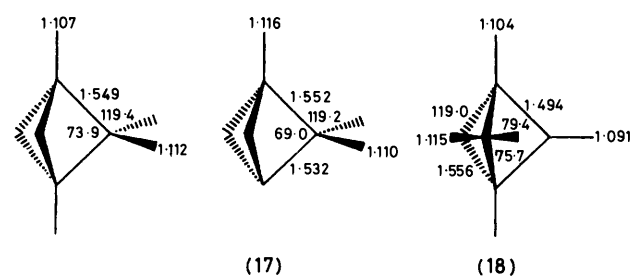
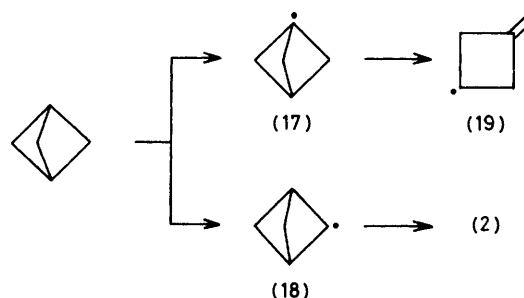


Figure 5. MINDO/3 structures for bicyclo[2.1.1]pentane and the axial (17) and equatorial (18) bicyclo[1.1.1]pentyl radicals. For clarity some of the equatorial hydrogens have been omitted



Scheme 5

radical (17) or an equatorial hydrogen to yield (18). The axial radical (17) (ΔH_f° , $414.0 \text{ kJ mol}^{-1}$) has C_{3v} symmetry in which the equatorial hydrogen atoms are still coplanar with the equatorial carbon atoms, as in the parent bicyclo[1.1.1]pentane: the equatorial radical (18) (ΔH_f° , $415.2 \text{ kJ mol}^{-1}$) has only C_{2v} symmetry, with again the equatorial hydrogens coplanar with the equatorial carbons: in (17) the radical centre is necessarily non-planar (sum of angles 271.0°), but in (18) the radical centre is planar.

In (17) there are three equivalent C–C bonds α, β to the radical centre and three equivalent β, γ bonds: in comparison with the parent bicyclo[1.1.1]pentane molecule the C–C distances are very little altered in this radical: the α, β bond is shortened by 1.7 pm and the β, γ bond is lengthened by only 0.3 pm. Although the cleavage of this radical to yield (19) (ΔH_f° , $239.0 \text{ kJ mol}^{-1}$) is strongly exothermic, it requires an activation energy of $107.0 \text{ kJ mol}^{-1}$. In the equatorial radical (18) there are two equivalent α, β bonds, shortened by 5.5 pm in comparison with the parent molecule, and four equivalent β, γ bonds, very slightly longer than those in the parent molecule: again cleavage to radical (2) is exothermic, but the activation energy is $103.1 \text{ kJ mol}^{-1}$. In neither of the radicals (17) and (18) are the C–C distances markedly altered from those in the parent molecule, and accordingly the activation energies for rearrangement are both high.

Homolytic ring fission in (17) and (18) has not specifically been studied experimentally, but chlorination of bicyclo[1.1.1]pentane was examined.¹¹ When *t*-butyl hypochlorite was used as the halogenating agent, the axial and equatorial chlorides derived from (17) and (18) were the only monochlorides observed, *i.e.* no ring fission was detected. Photochlorination with molecular chlorine at *ca.* 275 K gave the same two monochlorides as the main products along with the monochloride derived from (19) and some polychlorides. It is evident that while some rearrangement of (17) takes place the activation energies for ring fission in both (17) and (18) are high in comparison with those in (1) and (7).

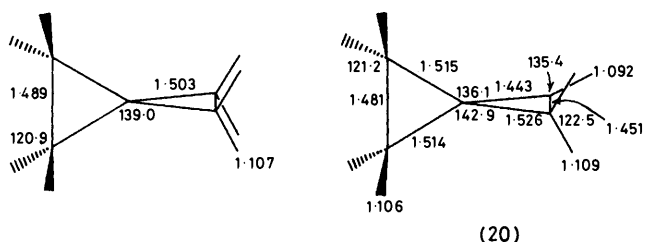
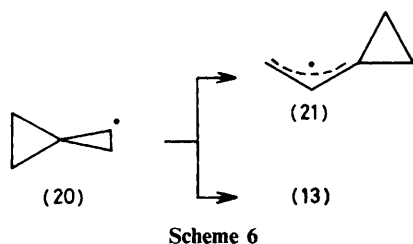


Figure 6. MINDO/3 structures for spiropentane and the spiro-pentyl radical



The Spiropentyl Radical.—Spiropentane optimises to a structure of D_{2d} symmetry in which there are four C—C distances of 1.503 Å and two of 1.489 Å: the major structural features as calculated are shown in Figure 6. The principal difference between the calculated structure and that found experimentally³⁴ lies in the magnitudes of the inner and outer CC distances: the calculated values are 1.503 and 1.489 Å, respectively, while the experimental values are 1.469(1) and 1.519(3) Å, so that the relative magnitudes have been reversed in the calculation compared with experiment.

The spiro-pentyl radical (20) has no symmetry: the radical centre is non-planar with a sum of angles about carbon of 331.7°. There are two C—C bonds, α, β to the radical centre, one inner, which is reduced in length by 6.0 pm in comparison with the parent molecule, and one outer which is reduced by 3.8 pm: there are in addition three C—C bonds β, γ to the radical centre (there would be just two if the symmetry were C_s , which the C_5 skeleton approaches); that in the same ring as the radical centre is 2.3 pm longer than in the parent molecule, while those in the other ring are longer by 1.1 and 1.2 pm, respectively. These data suggest that cleavage (Scheme 6) should occur preferentially in the same ring as contains the radical centre to yield the radical (21) (ΔH^\ddagger , 239.1), a strongly exothermic process, rather than in the second ring, which would yield radical (13) in a slightly endothermic process. Each of these processes has a large calculated activation energy 105.1 kJ mol⁻¹ for formation of (21) and 84.1 kJ mol⁻¹ for formation of (13).

The spiro-pentyl radical has been observed by e.s.r. spectroscopy⁹ which agrees with the non-planar structure at the radical centre. No rearrangement of (20) was observed in the e.s.r. experiments up to temperatures of 270 K and studies of the halogenation of (20)^{9,10} indicated that the radicals do not undergo ring fission even at 380 K. It was estimated that the rate constant for rearrangement of (20) is $<10^3$ s⁻¹ at 270 K,⁹ which is equivalent to an activation energy of >52 kJ mol⁻¹. These observations provide general support for the MINDO/3 predictions.

The Interconversion of Cyclopropyl and Allyl Radicals.—The prototype of radical ring opening reactions is the conversion of cyclopropyl to allyl: although this is apparently a very simple process, the potential surface over which it occurs is

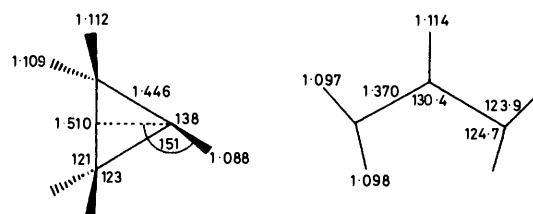


Figure 7. MINDO/3 structures for cyclopropyl and allyl radicals

very complex, but the importance of the reaction has nevertheless given rise to a number of studies,³⁵ most of which have made at least some geometrical assumptions, in particular¹⁶ concerning both the structures of the two equilibrium radicals, and the symmetry (C_2 or C_s) of the transition state.

The structures calculated here for cyclopropyl (calculated ΔH^\ddagger , 225.7 kJ mol⁻¹: cf. experimental ΔH^\ddagger , 278 \pm 12 kJ mol⁻¹,³⁶ and 279.9 \pm 1.0 kJ mol⁻¹³⁷), and allyl (calculated ΔH^\ddagger , 183.7 kJ mol⁻¹) are shown in Figure 7. In cyclopropyl, the radical centre is non-planar and the C_β — C_β bond is longer than the C_α — C_β bond by 6.4 pm.

Dewar has found³⁸ that catastrophic descents are likely to be encountered on reaction surfaces which incorporate imposed symmetry, and that¹⁷ the minimum energy pathways in a wide variety of electrocyclic processes do not involve concerted rotations of terminal groups, so that studies such as that of Peyerimhoff,¹⁶ which involved *ab initio* calculations (double zeta + CI) with assumed C_2 or C_s symmetry may be exploring chemically insignificant parts of the potential energy surface.

We have calculated a conformational energy map for CH_2CHCH_2 in terms of the two variables, taken as the rotation angles of the two CH_2 groups from the CCC plane: at each point on the map, all remaining geometrical variables were optimised. The map shows (a) that concerted rotations require higher activation energies than non-concerted rotations, (b) that one CH_2 rotation is almost completed before the other commences, whichever mode, conrotatory, or disrotatory, is considered, (c) the values of ΔH^\ddagger for the minimum energy pathways are ca. 127 (disrotatory) and ca. 77 kJ mol⁻¹ (conrotatory), so that both modes are effectively forbidden.

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