3-Methylenecyclobutyl, Cyclopent-3-enyl, and 3-Methylenecyclobutylmethyl Radicals; Absence of Homoallylic Conjugation

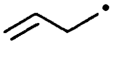
John C. Walton
Department of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST

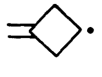
The 3-methylenecyclobutyl radical and the cyclopent-3-enyl radicals show such small e.s.r. hyperfine splittings from the δ- and γ-hydrogens respectively that homoallylic conjugation can be ruled out. Semi-empirical SCF-MO calculations indicated that the through-space interaction of the *p*-orbital at $\dot{C}_\alpha$ with the π-orbitals is negligible because they are >2 Å apart. The 3-methylenecyclobutylmethyl radical rearranges by β-scission to give the 2-allylallyl radicals. The Arrhenius parameters of the rearrangement were determined by kinetic e.s.r. spectroscopy and by study of the reduction of 3-methylenecyclobutylmethyl bromide with tri-n-butyltin hydride. The resonance stabilisation of the rearranged radical causes no significant lowering of the activation energy for β-scission.

Non-classical structures for free radicals have generally been ruled out because product studies do not demand them [1–5] and because of the limited scrambling in deuterium- [6] and carbon-13-labelled species.[7,8] The most decisive evidence came from e.s.r. spectra which showed, for example, that norborn-2-en-5-yl and nortricyclyl radicals are discrete species [9,10] and that but-3-enyl (homoallyl) and cyclopropylmethyl radicals are discrete intermediates.[11] In the latter radical the three methylene groups are not equivalent and if there is a process which interchanges them it is slow on the e.s.r. timescale, *i.e.* the lifetime of individual species must be greater than *ca.* 10^{-7} s.

Although strongly delocalised non-classical structures can be discounted it seemed possible that there might be a small stabilisation in but-3-enyl or related radicals due to weak 'interaction' of the *p*-orbital containing the unpaired election with the π-orbitals of the double bond. It is well known that three *p*-orbitals each containing one electron give a completely delocalised, symmetric structure in the allyl radical which is strongly stabilised.[12] This, together with the known ability of but-3-enyl [13] and related radicals to cyclise [1,10] has given rise to speculation about the possibility of homoallylic conjugation.[14] The e.s.r. spectrum of but-3-enyl radicals (**1**) [$a(2H_\alpha)$ 22.2, $a(2H_\beta)$ 28.8, $a(H_\gamma)$ 0.6, $a(H_\delta)$ 0.4 G*][11,15] shows that very little unpaired spin reaches the double bond, the spin distribution being rather similar to that in a saturated primary alkyl radical. However, in (**1**) internal rotation can occur about both the $\dot{C}_\alpha$–C_β and C_β–C_γ bonds thus removing the *p*-orbital containing the unpaired electron from the most favourable orientation for overlap with the π-bond. The barrier to rotation about $\dot{C}_\alpha$–C_γ in (**1**) is *ca.*0.2 kcal mol^{-1}; [16]† the barrier about the C_β–C_γ bond has not been determined, but in the analogous 1,1,3-trimethylbut-3-enyl radical a value of 3.5 kcal mol^{-1} was obtained.[16] The latter barrier sets an upper limit for any homoallylic stabilisation in (**1**). That homoallylic stabilisation in (**1**) is small was also indicated by the fact that decomposition of peroxides such as $(CH_2{=}CHCH_2CH_2CO_2)_2$ and $(PhCH{=}CHCH_2CH_2CO_2)_2$ showed little enhancement in rate compared with model compounds,[17–19] Similarly, decomposition of peroxides and peresters derived from norbornene showed insignificant rate increases in comparison with model compounds.[20,21]

The best chance of observing homoallylic conjugation will be in radicals where the structure constrains favourable orientation of the *p*- and π-orbitals and where their separation is minimised.


(**1**)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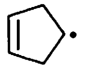
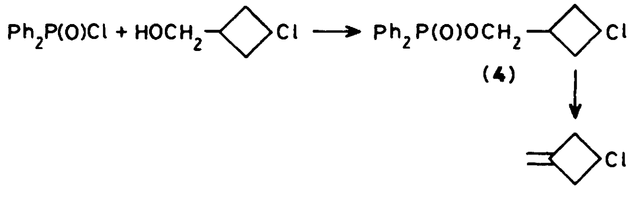

(**3**)

In the 3-methylenecyclobutyl radical (**2**) the *p*-orbital containing the unpaired electron is fixed in an orientation favourable for end-on overlap with the π-bond. In the cyclopent-3-enyl radical (**3**) the *p*-orbital is favourably orientated for side-on overlap with the π-bond. In this paper an examination of these two radicals by e.s.r. spectroscopy and by semi-empirical MO theory is reported. In addition, the 3-methylenecyclobutylmethyl radical has been examined. Ring opening of this radical gives the resonance-stabilised 2-allylallyl radical and therefore a comparatively high rate of rearrangement was anticipated. The kinetics of this process have been examined by e.s.r. spectroscopy and by tri-n-butyltin hydride reduction of the bromide precursor.

Results and Discussion

E.s.r. Study of 3-*Methylenecyclobutyl and Cyclopent*-3-*enyl Radicals.*—Considerable difficulty was experienced in synthesising a suitable precursor for the 3-methylenecyclobutyl radical. It has been postulated as the primary product of the rearrangement of bicyclo[1.1.1]pentan-1-yl radical [22,23] but rearrangement is negligible at 300 K. Attempts to dehydrobrominate 3-bromocyclobutylmethyl bromide so as to obtain 3-bromomethylenecyclobutane were unsuccessful with a variety of reagents. 3-Chloromethylenecyclobutane (**5**) was obtained by flash vacuum pyrolysis of the phosphinate ester (**4**). A mixture of (**5**), triethylsilane, and di-t-butyl peroxide in cyclopropane solvent was photolysed at 160 K in the cavity of the e.s.r. spectrometer. Analysis of the resulting spectrum gave the following hyperfine splittings (h.f.s.) which were confirmed by simulation: $a(2H)$ 43.2, $a(2H)$ 28.2, $a(2H)$ 17.0, $a(1H)$ 1.5 G. This spectrum can be assigned with reasonable certainty to the



(**5**)

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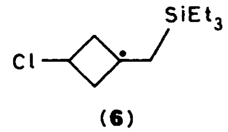
[*] 1 G = 0.1 mT.

[†] 1 cal = 4.18 J.

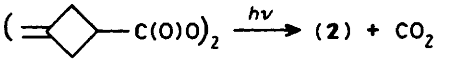
adduct radical (**6**) because the h.f.s. are close to those of the analogous adduct from methylenecyclobutane.[24] Thus, this is



(6)

an unusual case, in that addition of the Et$_3$Si$^\cdot$ radicals to the exocyclic double bond is faster than their abstraction of chlorine from (**5**). Experiments were also carried out with trimethyltin radicals, but no interpretable spectra were obtained in the accessible temperature range.

Finally, the diacyl peroxide (**7**) was made from 3-methylenecyclobutanecarboxylic acid.[25] Photolysis of (**7**) in t-butylbenzene gave a spectrum consisting of a pentet of



(7)

doublets, each component of which showed further fine structure. Two of the low-field lines ($M_\alpha = -\frac{1}{2}$, $M_\beta = -2$ and $M_\alpha = -\frac{1}{2}$, $M_\beta = -1$) are shown in Figure 1 and the h.f.s. are in Table 1. Comparison of the e.s.r. parameters with those of cyclobutyl radicals[26] (Table 1) shows that the h.f.s. of the α- and β-hydrogens are very similar for the two radicals and the spectrum can definitely be assigned to radicals (**2**). The outer low-field line (Figure 1) showed an additional small triplet splitting from the two δ-hydrogens of the double bond. The inner lines also showed this triplet splitting superimposed onto second-order structure. The measured second-order splitting from the multiplet shown in Figure 1 was 0.82 G, which is very close to the value of 0.84 G calculated from the β-h.f.s. using the method of Fessenden.[27]

The cyclopent-3-enyl radical was generated previously by rearrangement of bicyclo[2.1.0]pentan-2-yl radicals and the e.s.r. parameters briefly noted[28] (Table 1). The spectrum showed a small triplet splitting from the two γ-hydrogens and second-order splittings of 0.82 and 0.41 G. These latter compare very well with the values of 0.84 and 0.42 G calculated from the β-h.f.s.

Although both radicals (**2**) and (**3**) show h.f.s. from the hydrogens attached to the double bonds the striking feature of the e.s.r. results is the small magnitude of these splittings. In both (**2**) and (**3**) the spin density at the carbon atoms of the double bonds is comparable in magnitude to that of but-3-enyl radicals. It follows that even in rigid structures like (**2**) and (**3**) very little unpaired spin reaches the double bond and consequently homoallylic conjugation (and stabilisation) is negligible.

Semi-empirical SCF-MO Calculations.—The optimum geometries and corresponding enthalpies of formation, ΔH_f, were calculated for radicals (**2**) and (**3**) using the MINDO/3[29] and MNDO[30] methods. The spin density distribution was computed using the INDO[31] and ZINDO[32] methods; the latter technique also gave the optimum geometry. Some of the main geometrical parameters are listed in Table 2. For radicals (**2**) and (**3**) all three methods gave planar symmetrical structures with reasonable consistency in the calculated geometries. The MINDO/3 ΔH_f values were 57 and 37 kcal mol^{-1} for (**2**) and (**3**) respectively and the MNDO values were 46 and 29 kcal mol^{-1}. As has usually been found for alkyl radicals[33,34] the $\dot{C}_\alpha$–C_β bonds are slightly shortened and the C_β–C_γ bonds slightly lengthened in comparison with the parent hydrocarbons. In

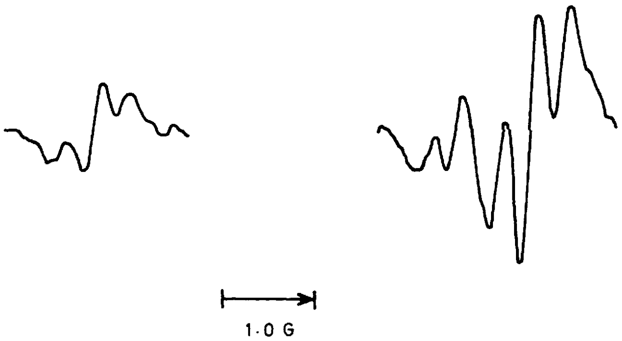
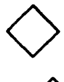
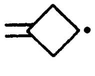
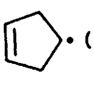
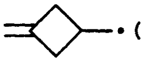


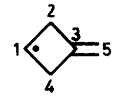
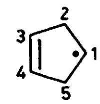
Figure 1. Lowfield resonance lines ($M_\alpha = -\frac{1}{2}$, $M_\beta = -2$ and $M_\alpha = -\frac{1}{2}$, $M_\beta = -1$) from the 9.4 GHz e.s.r. spectrum of 3-methylenecyclobutyl radicals (**2**) at 210 K in t-butylbenzene solvent

Table 1. E.s.r. parameters of 3-methylenecyclobutyl, cyclopent-3-enyl, and related radicals

Radical	T/K	g Factor	Expt.	h.f.s.	INDO[c]	ZINDO[d]
 [a]	193		H_α	H_α	21.2	
				$4H_\beta$	36.7	
				$2H_\gamma$	1.1	
 (**2**)	206	2.003	H_α	22.0	−18.4	−15.0
			$4H_\beta$	37.6	46.8	40.9
			$2H_\delta$	0.35	−0.81	−0.71
 [b] (**3**)	200	2.003	H_α	21.2	−18.6	−15.1
			$4H_\beta$	36.9	47.7	41.9
			$2H_\gamma$	0.46	−0.87	−0.79
 (**9**)	217		$2H_\alpha$	22.0		
			H_β	14.2		
			$4H_\gamma$	0.73		
			$2H_\varepsilon$	0.73		

[a] From ref. 26. [b] From ref. 28. [c] INDO Calculations with MINDO/3 geometry, $\langle S^2 \rangle = 0.7636$ and 0.7629 for (**2**) and (**3**) respectively. [d] INDO Calculations with INDO-optimised geometry and quartet annihilation, $\langle S^2 \rangle = 0.7501$ [both (**2**) and (**3**)].

Table 2. Semi-empirical calculated geometries for 3-methylenecyclobutyl and cyclopent-3-enyl radicals[a]

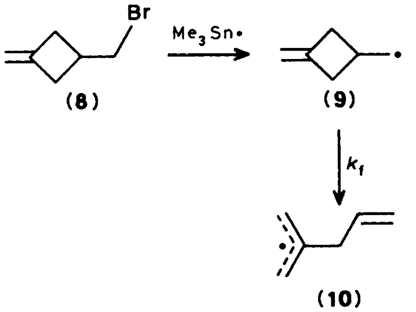
	MNDO	MINDO/3	ZINDO
C(1)–C(2)	1.50	1.48	1.46
C(2)–C(3)	1.53	1.53	1.49
C(3)–C(5)	1.33	1.33	1.33
C(1)–C(3)	1.95	2.10	2.05
C(1)–C(2)–C(3)	88	88	88
C(2)–C(3)–C(4)	134	135	135
			
C(1)–C(2)	1.50	1.49	1.46
C(2)–C(3)	1.52	1.51	1.48
C(3)–C(4)	1.35	1.35	1.34
C(1)–C(3)	2.36	2.35	2.28
C(1)–C(2)–C(3)	103	103	102
C(2)–C(3)–C(4)	111	111	112

[a] Bond lengths in Å; angles in degrees.

both (**2**) and (**3**), however, the double bond shows no significant lengthening, as would be expected if homoallylic conjugation were important and, particularly in (**2**), the bond angles deviate only marginally from 90°, *i.e.* the ring is only very slightly 'squashed'. The geometries suggest that the *p*-orbital on C(1) does not interact significantly with the π-orbitals of the double bonds. The calculated distances between the *p*-orbital on C(1) and the orbitals on C(3) are *ca.* 2.1 and 2.3 Å for (**2**) and (**3**), respectively. At these distances direct through-space overlap of the orbitals is almost negligible. The calculated coefficients of the SOMOs confirmed this picture in that they indicated very small contributions from the p_z orbitals on C(3). The h.f.s. calculated from the spin densities (Table 1) are in fair agreement with experiment and confirm that the unpaired spin associated with the hydrogens attached to the doubly bonded carbon atoms are very small.

The semi-empirical calculations show that the absence of homoallylic conjugation in (**2**) and (**3**) is due to the >2.0 Å distance between the *p*-orbital on C(1) and the π-orbitals of the double bond. At this distance direct overlap is too small to produce chemically significant effects. Instead, the *p*-orbital has its main overlap with the hydrogen 1*s* and the $2p_z$ orbitals on the β-carbon atoms, leading to high $a(H_\beta)$ values. It follows that homoallylic conjugation can only be expected in radicals whose geometry constrains the *p*-orbital containing the unpaired electron to approach the π-bond at a distance <2 Å. It is clear that no simple radical can fulfil this criterion but obviously such a structure could be realized in a complex polycyclic radical.

3-*Methylenecyclobutylmethyl Radical*.—Radical (**9**) was generated from the parent bromide (**8**) in t-butylbenzene by bromine abstraction with photochemically generated trimethyltin radicals. The e.s.r. spectrum at 217 K consisted of a triplet of doublets, each component of which was further split into a septet (Table 1). The e.s.r. parameters show a basic similarity to those of cyclobutylmethyl radicals.[35] The small magnitude of $a(H_\beta)$ and the fact that this h.f.s. increased with increasing temperature indicates that (**9**) adopts the staggered conformation in which H_β approaches the nodal plane of the *p*-orbital on C_α, as do other cyclobutylmethyl radicals.[35] The radical shows a sizeable h.f.s. from the two ε-hydrogens (equal to that from the γ-hydrogens). Resolvable ε-h.f.s. are rare in alkyl radicals but this splitting cannot be taken as evidence of any special effect because other cyclobutylmethyl radicals show unusually well resolved long-range h.f.s.[35]



At temperatures above *ca.* 210 K the spectrum of (**9**) weakened and that of a new radical appeared; by *ca.* 250 K the new radical with *a*(2H) 14.8, *a*(2H) 14.0, *a*(2H) 2.7, and *a*(1H) 0.35 G was the only observable species. These h.f.s. correspond well with those expected for the 2-allylallyl radical (**10**) which could be formed by ring scission of (**9**). The measured concentrations of (**9**) and (**10**) in the temperature range 211—245 K are given in Table 3, together with the values of $k_f/2k_t$ derived by the usual kinetic treatment,[13,36] $2k_t$ being the rate constant for bimolecular self-reaction of (**9**). The termination rates of small to moderately sized transient radicals are diffusion controlled in solution and do not depend on the structure at the radical centre but rather on the solution viscosity.[36,37] We have used Fischer's accurate data for the self-termination of t-butyl radicals in heptane[36] corrected for the difference in viscosity between n-heptane and t-butylbenzene at each temperature to give equation (1). The rate constants for ring scission (k_f)

$$\log[2k_t(\mathrm{Bu^t})/\mathrm{dm^3\ mol^{-1}\ s^{-1}}] = 12.17 - (3.5\ \mathrm{kcal\ mol^{-1}})/2.3\,RT \quad (1)$$

derived in this way are shown in Figure 2.

Table 3. Kinetic e.s.r. study of ring opening in 3-methylenecyclobutylmethyl radical (**9**)[a]

T/K	10^7[(**9**)]/M	10^7[(**10**)]/M	$10^7k_f/2k_t$ (mol dm^{-3})
211	3.85	0.34	0.37
215	2.97	0.57	0.67
217	3.88	0.57	0.65
223	3.97	0.78	0.94
228	3.44	0.84	1.05
230	1.73	0.82	1.20
240	1.51	0.66	0.94
236	1.83	1.07	1.69
239	1.82	1.31	2.25
245	1.07	1.41	3.27

[a] In t-butylbenzene.

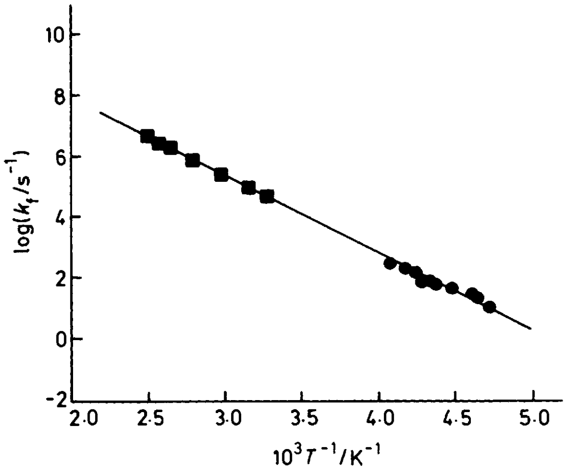


Figure 2. Arrhenius plot of rate constants for ring scission in 3-methylenecyclobutylmethyl radicals (**9**). Squares, tin hydride results; circles, kinetic e.s.r. results

The ring-scission of radicals (**9**) was also studied by using the reduction of the bromide (**8**) with tri-n-butyltin hydride. Only two products, 3-methylmethylenecyclobutane (**11**) and 2-methylpenta-1,4-diene (**12**), were detectable. Reactions were carried out in t-butylbenzene solvent over the temperature range 304—400 K, the products being quantitatively analysed by g.l.c. (Table 4). The kinetics of other rearrangements have been studied previously by this method[38,39] and the rate

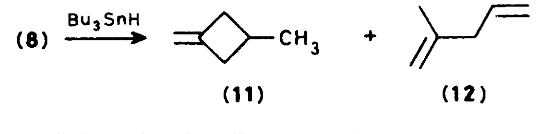


Table 4. Kinetic study of ring opening in 3-methylenecyclobutylmethyl radical by the tin hydride method[a]

T/K	$10^3[(\mathbf{11})]_f{}^b$/M	$10^3[(\mathbf{12})]_f{}^b$/M	k_f/k_H
304	3.70	5.80	0.0186
316	6.72	6.78	0.0282
334	16.7	7.86	0.0580
357	36.9	8.50	0.112
377	78.6	8.67	0.213
388	97.0	7.85	0.285
400	120.0	7.70	0.341

[a] Initial bromide (**8**) and Bu_3SnH concentrations 0.323 mol dm^{-3} in PhBu^t. [b] Final concentrations after 30 min photolysis.

constant ratio k_f/k_H, where k_H is the rate constant for hydrogen-abstraction by the radicals (**9**) and (**10**) from Bu^n_3SnH, was evaluated using a similar procedure. Beckwith's integrated rate expression[38] was used, the best values of k_f/k_H at each temperature being found by use of an iterative computer program.

The k_f values were obtained by use of the k_H value determined by Ingold and co-workers from laser flash photolysis experiments [equation (2)].[40] The excellent agreement between

$$\log(k_H/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = 9.07 - (3.69\ \mathrm{kcal\ mol^{-1}})/2.3\ RT \quad (2)$$

the two sets of k_f values (Figure 2) derived from independent techniques is evidence for the reliability of both methods and the trustworthiness of the reference rate constants $2k_t$ and k_H. The Arrhenius parameters derived from the data in Figure 2 are given by equation (3). The experimental pre-exponential factor

$$\log(k_f/\mathrm{s^{-1}}) = 12.9 \pm 0.3 - (11.5 \pm 0.3\ \mathrm{kcal\ mol^{-1}})/2.3\ RT \quad (3)$$

is close to the 'normal' value of $\log(A/\mathrm{s^{-1}}) = 13$ which is further evidence of the reliability of the results.

The interesting aspect of this reaction is that the activation energy for ring scission, E_f, in (**9**) is only 0.2—1.3 kcal mol^{-1} lower than that of cyclobutylmethyl radicals for which E_f values of 11.7[35] and 12.8[38] kcal mol^{-1} have been determined. The methylenecyclobutyl radical contains 2.6 kcal mol^{-1} more strain than the cyclobutyl ring and, in addition, the rearranged 2-allylallyl radical is stabilized by resonance and other effects to an extent variously estimated in the range 11.5—14.5 kcal mol^{-1}.[12,41—44] The absence of a corresponding decrease in the E_f value for (**9**) indicates that the resonance stabilization of the rearranged radical does not develop early enough on the reaction co-ordinate to cause significant lowering of the activation barrier. The standard enthalpies of formation of radicals (**9**) and (**10**), calculated by the group contributions method[45] and incorporating the methylenecyclobutane ring strain[41] of 28.8 kcal mol^{-1}, are 69.8 and 49.9 kcal mol^{-1}, respectively, which leads to a $\Delta H°$ value of -19.9 kcal mol^{-1} for the rearrangement. It was shown previously[35] that the $\Delta H°$ values of alkyl-substituted cyclobutylmethyl radicals are given by the Evans–Polanyi-type relationship $E_f = 0.94\,\Delta H° + 16.2$. The experimental E_f of 11.5 kcal mol^{-1} for (**9**) thus leads to a calculated $\Delta H°$ of -5.0 kcal mol^{-1}. The difference between this figure and the group contributions $\Delta H°$ value, *i.e.* 14.9 kcal mol^{-1}, is very close to the allyl stabilization energy and this also shows that the allyl resonance is not 'felt' by the transition state. That the stabilization due to resonance does not contribute to a lowering in the activation energy for rearrangement of (**9**) is not surprising because scission of the C_β–C_γ bond must be followed by a 90° rotation of the $C_\gamma H_2$ group with flattening of the same centre before resonance delocalization can develop. Evidently this reorganization takes place too slowly and too late on the reaction co-ordinate.

Experimental

E.s.r. spectra were recorded with a Bruker ER200D spectrometer on degassed samples sealed in Spectrosil tubes, irradiated with light from a 500 W high-pressure Hg arc. ^{1}H N.m.r. spectra were recorded with a Bruker WP 80 instrument on $CDCl_3$ solutions at ambient temperature with Me_4Si as internal standard. Mass spectra were obtained with an A.E.I. MS 902 spectrometer.

3-*Chlorocyclobutylmethyl Diphenylphosphinate* (**4**).—This was prepared from 3-chlorocyclobutylmethanol[46] by the method of Berlin *et al.*[47] To the alcohol (5.8 g) and triethylamine (13 ml) in dry ether (30 ml) under N_2 was added diphenylphosphinic chloride (16.5 g) in dry ether (100 ml) over 15 min. The solution was refluxed for 30 min, water (100 ml) was added, the ether layer was separated, washed with 10% sodium hydrogencarbonate, 2M-HCl, and water. The pink solution was dried ($MgSO_4$), the ether removed on a rotary evaporator, and the solid residue recrystallized, m.p. 65 °C, yield 80%, δ_H 2.0—3.0 (6 H, m), 4.10 (2 H, t, $J_P = J_H = 7$ Hz), and 7.4—8.2 (10 H, m), δ_P 31.4 p.p.m. (relative to D_3PO_4).

3-*Chloromethylenecyclobutane* (**5**).—Conventional pyrolysis of the phosphinate ester gave no useful product, but flash vacuum pyrolysis at 800 °C under a pressure of 10^{-2} Torr gave a pyrolysate which contained benzene, phosphinic acid, and *ca.* 50% (**5**). The combined pyrolysates from several runs on a 1.0 g scale were distilled and the 3-chloromethylenecyclobutane was finally purified by preparative g.l.c. using a 15 ft column packed with 10% Carbowax 20 M operated at 90 °C, δ_H 2.8—3.6 (4 H, m), 4.50 (1 H, pentet, J 7 Hz), and 4.96 (2 H, pentet, J 2 Hz), δ_C 45.0 (2C), 48.4, 107.5, and 141.5 p.p.m., m/z 102 and 104 (M^+) 67, and 40.

Bis-3-*methylenecyclobutyl Peroxide* (**7**).—3-Methylenecyclobutanecarboxylic acid was prepared by hydrolysis of the nitrile obtained from allene and acrylonitrile.[25] The acid (1.3 g) was refluxed with thionyl chloride (5.0 g) for 30 min and then distilled. The acid chloride, b.p. 36—40 °C at 20 Torr, was obtained in 91% yield, δ_H 1.8 (1 H, br s), 3.1 (4 H, m), and 4.9 (2 H, pentet, J 2 Hz). The acid chloride (0.34 g) in ether (1 ml) was cooled to -10 °C and 9M-H_2O_2 (0.3 ml) was added dropwise followed by pyridine (0.21 ml). The mixture was stirred for 2 h at 0 °C, neutralized with cold 2M-sulphuric acid, and extracted with ether. The ether solution was washed with cold 2M-H_2SO_4, sodium hydrogencarbonate solution, and water and then dried (Na_2SO_4). The ether was removed on a rotary evaporator at 0 °C. The partly crystalline peroxide was used without further purification, δ_H 1.9 (2 H, m), 3.2 (8 H, m), and 4.9 (4 H, m), δ_C 29.4, 35.6, 107.6, 142.8, and 170.7 p.p.m.

3-*Methylenecyclobutylmethanol*.—3-Methylenecyclobutanecarboxylic acid was reduced under normal conditions with lithium aluminium hydride to give the methanol (74%), b.p. 130 °C at 15 Torr, δ_H 1.77 (1 H, s), 2.2—3.1 (4 H, m), 3.65 (2 H, d, J 7 Hz), and 4.77 (2 H, pentet, J 2 Hz).

3-*Methylenecyclobutylmethyl Bromide* (**8**).—3-Methylenecyclobutylmethanol (2.6 g) and Et_3N (2.8 g) in dry CH_2Cl_2 (120 ml) were stirred at ice temperature and CH_3SO_2Cl (3.5 g) was added slowly. The mixture was stirred at room temperature for 30 min, then water was added; the CH_2Cl_2 layer was washed with 2M-HCl, brine, and saturated $NaHCO_3$, dried (Na_2SO_4), and the solvent evaporated at room temperature. The mesylate was added to LiBr (7.0 g) in dry acetone (85 ml) and the solution refluxed for 9 h. The solution was filtered, acetone distilled off, and water added. The mixture was extracted with light petroleum which was then dried (Na_2SO_4) and chromatographed on silica gel. The bromide which was eluted in the first 100 ml of light petroleum, was distilled (48%), b.p. 75 °C at 20 Torr, δ_H 2.2—3.1 (5 H, m), 3.48 (2 H, d, *J* 7 Hz), and 5.83 (2 H, pentet, *J* 2 Hz) (Found: M^+, 159.9879. $C_6H_9{}^{79}Br$ requires *m/z*, 159.9888).

Reaction of (**8**) *with Tri-n-butyltin Hydride*.—The bromide (100 μl, 0.93mM) and Bu_3SnH (267 μl, 0.93mM) were placed in a Pyrex tube, degassed by several freeze–pump–thaw cycles and then irradiated at 20 °C with light from a 250 W medium-pressure Hg arc for 60 min. The volatile products were distilled out on a vacuum line (0.08 g) and examined by g.l.c. on a 10 ft column packed with 10% MS 200/50 at 70 °C. This showed two products in addition to *ca.* 20% unchanged bromide. G.c.–m.s. examination showed both products to be hydrocarbons with molecular ions at *m/z* 82. The second eluted component was present in great excess and the ^1H n.m.r. spectrum, δ_H 1.16 (3 H, d, *J* 7 Hz), 2.0—3.0 (5 H, m), and 4.73 (2 H, m), showed this to be 3-methylmethylenecyclobutane (**11**). A second photolysis, carried out at 155 °C, gave the same two products in roughly equal proportions. The ^1H n.m.r. spectrum showed the first eluted product to be 2-methylpenta-1,4-diene (**12**), δ_H 1.72 (3 H, s), 2.5—3.0 (2 H, m), 4.7—5.2 (4 H, m), and 5.6—6.1 (1 H, m).

Kinetics of Reduction with Tri-n-butyltin Hydride.—t-Butylbenzene (0.50 ml) was placed in a Pyrex tube, heated to the desired temperature, and degassed by bubbling nitrogen for *ca.* 15 min. To this was added the bromide (20 μl), Bu_3SnH (45 μl), and cyclohexane (10 μl) as internal standard. The solution was photolysed for 30min with light from a 250 W medium-pressure Hg arc and then analysed by g.l.c. using a 10 ft column packed with 10% MS 200/50 at 70 °C. The values of k_f/k_H were obtained at each temperature from the initial Bu_3SnH concentration (0.323 mol dm^{-3}) and the final concentrations of (**11**) and (**12**) using the integrated rate equation of Beckwith and Moad.[39] The best values of the rate constant ratio were located with an iterative computer program.

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