An Electron Spin Resonance Study of Pentadienyl and Related Radicals: Homolytic Fission of Cyclobut-2-enylmethyl Radicals

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Pentadienyl radicals were generated from penta-1,4-diene and *cis* and *trans*-1-bromopenta-2,4-diene, and were observed in the *E,E* (1) and *E,Z* (2) conformations in hydrocarbon solution by e.s.r. spectroscopy. The *E,Z*-radicals are converted into the *E,E*-radicals at $T > ca.$ 170 K, but the *E,E*-radicals are not converted into the *E,Z*-radicals in the accessible temperature range. From the estimated barrier to rotation in *E,Z*-pentadienyl radicals the methane based stabilization energy ($E_s^{\text{Me-H}}$) was estimated to be 104 kJ mol^{-1}. Pentadienyl radicals can also be obtained from ring-opening of cyclobut-2-enylmethyl radicals (3). Bromine abstraction from cyclobut-2-enyl methyl bromide by triethylsilyl radicals gave cyclobut-2-enylmethyl radicals at temperatures below *ca.* 230 K. Above this temperature homolytic fission of the cyclobutene ring occurred and pentadienyl radicals in the *E,E*-conformation were detected by e.s.r. Initially, *E,Z*-pentadienyl radicals must be formed, but at the temperature of ring fission these are converted into the *E,E*-radicals and so are not observed. Hydrogen abstraction from neither 3-methylcyclobutene nor from bicyclo[2.1.0]pentane yields (3): instead 3-methylcyclobutenyl radicals and cyclopent-3-enyl radicals are formed, respectively. E.s.r. parameters are also reported for a range of substituted pentadienyl radicals generated from the corresponding 1,4-dienes. Of these radicals only 3-trimethylsiloxypentadienyl was observed in two conformations.

PENTADIENYL is one of the simplest conjugated, acyclic π-radicals and has been the subject of numerous theoretical studies.[1] Despite this intense theoretical interest, the chemical and spectroscopic properties of pentadienyl have, until recently, remained largely unexplored.

In a preliminary communication,[2] we reported the e.s.r. spectra of two conformers of pentadienyl, the *E,E* and the *E,Z* [structures (1) and (2)]. Independently, Sustmann and Schmidt [3] also published an e.s.r. report on pentadienyl; their conclusions were substantially the same as our own. We have now explored the thermodynamic relationship between (1) and (2) in more detail and have obtained an estimate of the resonance energy of pentadienyl. In addition, we amplify a preliminary report [4] on the e.s.r. detection of cyclobut-2-enylmethyl and its ring-opening to pentadienyl. The e.s.r. parameters for a number of substituted pentadienyls are also included.

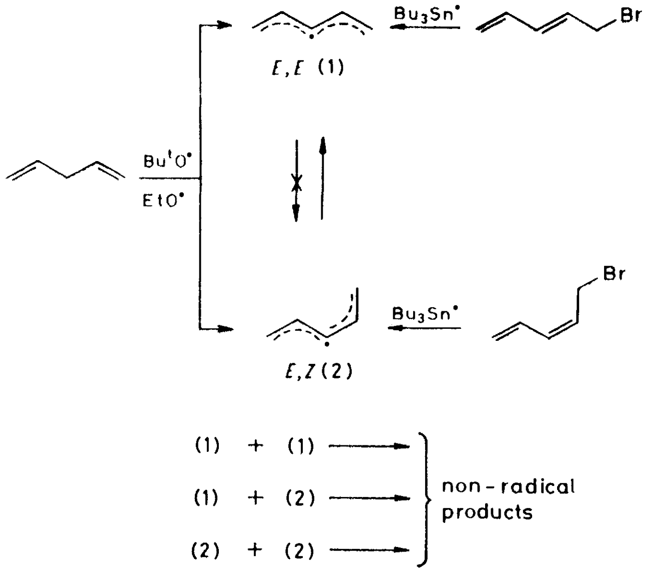

(1)


(2)

RESULTS AND DISCUSSION

Generation of E,E-*Pentadienyl* (1).—An e.s.r. spectrum of pentadienyl in its *E,E*-conformation (1) was obtained by photolysis of a mixture of *trans*-1-bromopenta-2,4-diene and hexa-n-butylditin [5] in the cavity of an e.s.r. spectrometer using propane, cyclopropane, or n-hexadecane as solvent (see Scheme 1). The *E,E*-pentadienyl was the only radical observed in the temperature range 143—453 K. This implies that (1) is not in equilibrium with (2) nor is (1) converted into (2) in this temperature range.

The e.s.r. spectral parameters for (1) are given in Table 1. The spectrum saturated easily and could best be observed at microwave power levels below 1 mW. Comparison of the hyperfine splittings with those of allyl [6a] and cyclohexadienyl [6b] (see Table 1) show a spin distribution in accord with expectation. The smallest hyperfine splitting, $a^{\text{H}(2)}$ ($= a^{\text{H}(4)}$), shows a temperature coefficient of $+0.13$ μT/K, the sign and magnitude of which are similar to those of $a^{\text{H}(2)}$ in allyl.[6a] This temperature coefficient indicates that there is appreciable torsional motion about the C(2)–C(3), and C(3)–C(4), bonds. It arises because additional positive spin reaches H(2) and H(4) by hyperconjugation when the vinyl group to which these hydrogens are attached is twisted out of the radical plane.

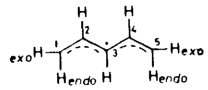
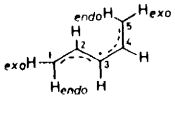
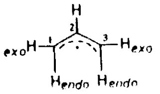
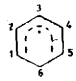


SCHEME 1

An attempt to generate (1) by hydrogen abstraction

Table 1

E.s.r. parameters of pentadienyl and some related radicals

Radical	T/K	g Factor	Expt. h.f.s. (mT)		INDO calc. h.f.s. (mT)
(1) 	233	2.002 64	H(1,5 *exo*) H(1,5 *endo*) H(2,4) H(3)	1.04 0.96 0.33 [b] 1.16	−1.20 (−1.33) [a] −1.23 (−1.31) [a] 0.69 (1.03) [a] −1.26 (−1.26) [a]
(2) 	113	2.002 64	H(4) H(2) H(5 *endo*) H(5 *exo*) H(1 *endo*) H(1 *exo*) H(3)	0.31 [c] 0.36 [d] 0.85 0.92 0.97 1.01 1.44	0.67 0.69 −1.21 −1.27 −1.19 −1.16 −1.26
 [e]	143	2.002 54	H(1,3 *exo*) H(1,3 *endo*) H(2)	1.481 1.390 0.406	−1.46 [f] −1.49 [f] 0.69 [f]
 [g]	—	2.0025	CH_2 H(1,5) H(2,4) H(3)	4.771 0.899 0.265 1.304	9.76 [f] −1.11 [f] 0.51 [f] −0.98 [f]

[a] *Ab initio* calculations from references 1*h* and *i*. [b] $\partial a^{H(2,4)}/\partial T = 0.13$ μT/K from 103 to 306 K. [c] $\partial a^{H(4)}/\partial T = 0.15$ μT/K from 103 to 182 K. [d] $\partial a^{H(2)}/\partial T = 0.27$ μT/K from 103 to 182 K. [e] Data from ref. 6*a*. [f] INDO calculations from ref. 28. [g] Data from ref. 6*b*.

from *trans*-penta-1,3-diene using t-butoxyl radical resulted, as with other conjugated dienes,[7] in an addition of the alkoxyl to the diene.

Generation of E,E- *and* E,Z-*Pentadienyl Mixtures* (1) *and* (2).—The most attractive way to explore the thermodynamic and kinetic relationship between (1) and (2) would be to generate each radical separately. We were unable to achieve this for (2) because of difficulties associated with the synthesis of a suitable precursor (see Experimental section). The most satisfactory starting material obtained was a mixture of *trans*- and *cis*-1-bromopenta-2,4-diene. This was prepared by reaction of t-butyl hypobromite with penta-1,4-diene at *ca.* 123 K in CF_2Cl_2 solvent using photochemical initiation. The mixture of bromides was isolated by preparative g.l.c. and although the isomers could not be separated the *trans*-bromide : *cis*-bromide ratio could be estimated to be *ca.* 1.4 : 1.0 by n.m.r. integration.

A mixture of (1) and (2) was generated in cyclopropane solvent in the e.s.r. cavity using the ditin route (see Scheme 1). The spectral parameters for (2) are reported in Table 1 and the approximate (1) : (2) ratios at various temperatures are given in Table 2. At temperatures below *ca.* 160 K the (1) : (2) ratio is approximately the same as the ratio of the concentrations of the starting bromides. Since (1) and (2) have identical molecular weights and are sterically unhindered the rate constants for their bimolecular self (and cross) reactions will be identical (diffusion-controlled).[8] The approximate equivalence of the (1) : (2) and *trans*-bromide : *cis*-bromide ratios at low temperatures therefore implies that tri-n-butylstannyl radicals do not appreciably discriminate between the two bromides (which is not surprising for bromine atom abstraction from species yielding resonance-stabilized radicals since these reactions must be very fast).[9,10] At temperatures above *ca.* 160 K the (1) : (2) ratio increases until at *ca.* 210 K and above only (1) could be detected.

Table 2

Relative concentrations of (1) and (2) formed by bromine abstraction from the *trans,cis*-1-bromopenta-2,4-diene mixture

T/K	[(1)] : [(2)]
133	1.1
153	1.3 [a]
173	1.5
183	2.3
193	2.4 [b]
213	Only (1) remaining

[a] Average of two results. [b] Average of four results.

The simple interpretation of these results is that at temperatures above *ca.* 210 K (2) isomerizes to (1) at rates which compete successfully with the diffusion-controlled radical–radical reactions which destroy (1) and (2). An intrinsically less probable interpretation would be that tri-n-butylstannyl becomes *more* selective in its reactions with the two bromides as the temperature is *raised*. This possibility can be ruled out by results obtained by hydrogen atom abstraction from penta-1,4-diene using t-butoxyl and ethoxyl (see below).

Photolysis of a mixture of di-t-butyl peroxide or diethyl peroxide with penta-1,4-diene in hexadecane, isopentane, cyclopropane, n-propane, or the neat peroxide gave (1) at temperatures from 373 to *ca.* 210 K. At 210 K and below the spectrum of (2) can be seen and this radical becomes predominant at temperatures below *ca.* 180 K for t-butoxyl and *ca.* 150 K for ethoxyl (see Table 3). The similarity of the temperature (210 K) above which (2) cannot be detected in the hydrogen-abstraction and bromine-abstraction reactions provides the necessary proof that (2) isomerizes to (1) at such temperatures.

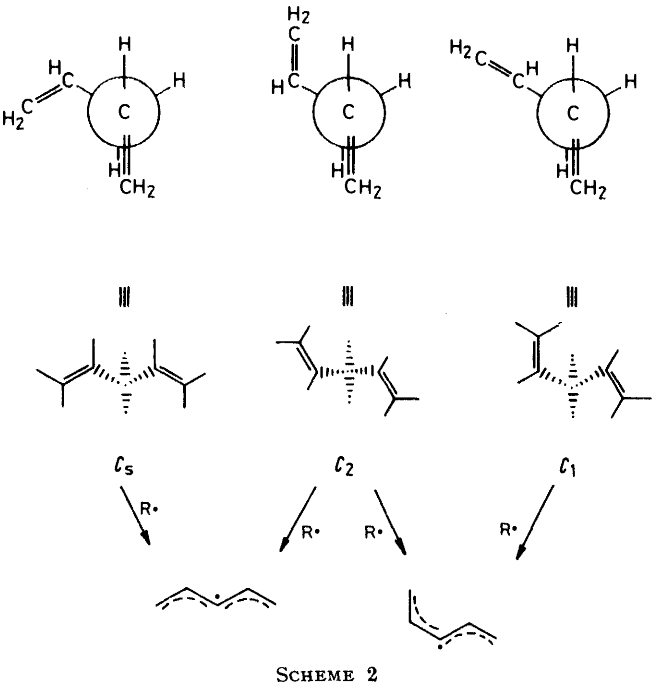
A Raman spectroscopic study of penta-1,4-diene by Gallinella and Cadioli[11] showed that there are three stable conformations having C_s, C_2, and C_1 symmetry (see Scheme 2). From the temperature dependence of the appropriate band intensities the enthalpy difference between the conformers was shown to be very small (0.37 kJ mol^{-1} between one pair and less between the other pair). Similar conclusions were reached in another Raman study[12] and *ab initio* MO calculations provided supporting evidence.[11,13] The relative concentrations of (1) and (2) cannot be controlled by the changing populations of C_s, C_2, and C_1, as the temperature changes, because the energy difference between the conformers is small and therefore this type of control would contravene the Curtin–Hammett principle. If the radical conformers could interconvert then [(1)] : [(2)] should reach a limiting value at higher temperature. In fact, this ratio increases with temperature and only (1) can be seen above *ca.* 210 K (see Table 3).

TABLE 3

Relative concentrations of (1) and (2) formed by hydrogen abstraction from penta-1,4-diene with t-butoxyl and ethoxyl

$Me_3CO^•$		$EtO^•$	
T/K	[(1)] : [(2)]	*T*/K	[(1)] : [(2)]
100 [a]	0.26	153	1.1
104 [a]	0.28	173	1.9
108 [a]	0.33	193	2.4
113	0.38	213	Only (1) remaining
118 [a]	0.60		
123 [a]	0.54		
133	0.53		
143 [a]	0.91		
153	0.75		
173	0.87		
183	0.95		
193	1.81		
203	2.26		
213	3.00		
223	Only (1) remaining		

[a] n-Propane as solvent; cyclopropane for all others.



SCHEME 2

Models of the three conformers of penta-1,4-diene show that hydrogen abstraction from C_s yields (1) with least readjustment of the molecule, C_2 yields (1) or (2) with equal facility, whereas abstraction from C_1 yields (2) most readily (see Scheme 2). Furthermore, the models suggest that hydrogen abstraction should, for steric reasons, occur slightly more readily from C_1 than from C_s. This conclusion seems to be supported by the fact that abstraction by the less bulky ethoxyl gave relatively more (1) than did t-butoxyl. In the temperature range studied (153—193 K) the data can be represented by equation (1).

$$\{[(1)] : [(2)]\}_{EtO^•} = 1.6\{[(1)] : [(2)]\}_{ButO^•} \qquad (1)$$

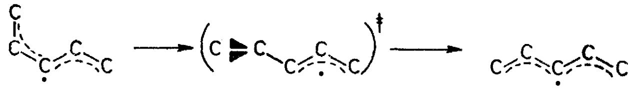
The Stabilization (*Resonance*) *Energy of Pentadienyl*.—From the e.s.r. results obtained when (1) and (2) were generated from their respective bromides, we estimate that at 193 K *ca.* 50% of (2) is converted into (1) despite competition from radical–radical reactions. Under typical e.s.r. conditions, this means that the rate constant for isomerization is *ca.* 10^3 s^{-1}.[14] Taking a 'normal' pre-exponential factor of 10^{13} s^{-1},[15] the activation energy for bond rotation is estimated to be *ca.* 37 kJ mol^{-1}.

In the transition state for the (2) $\xrightarrow{\Omega}$ (1) isomerization, which is illustrated in Scheme 3, the unpaired electron is confined to an allyl moiety of the pentadienyl system. The stabilization energy (E_s) for pentadienyl can therefore be considered to equal the sum of the energy associated with the barrier to rotation which converts (2) into (1), plus the allyl stabilization energy. Unfortunately, it is not easy to define the latter quantity. Benson and his co-workers[16] defined E_s (allyl) as being equal to the difference in the primary C–H bond strengths in ethane and propylene, *D*[Et–H] − *D*[Allyl–H], which leads to a value of *ca.* 42 kJ mol^{-1}. However, Krusic *et al.*[17] showed by e.s.r. spectroscopy that the barrier to rotation in allyl must be $\geqslant$70 kJ mol^{-1}, *i.e.*, nearly 30 kJ mol^{-1} greater than the accepted stabilization energy. Part, at least, of this anomaly can be attributed to the fact that Benson used ethane as the reference compound. Ethyl can, itself, be considered to be stabilized, presumably by hyperconjugation, by *ca.* 25 kJ mol^{-1} since *D*[Me–H] − *D*[Et–H] = 25 kJ mol^{-1}. The discrepancy between the rotation barrier for allyl[17] and Benson's E_s (allyl) can be largely removed by redefining the stabilization energy of allyl as *D*[Me–H] − *D*[Allyl–H], which gives *ca.* 67 kJ mol^{-1}. For clarity, we will call a stabilization energy, defined in this way, a methane based stabilization energy and give it the symbol $E_s^{\text{Me-H}}$. For a radical R$^•$ the value of $E_s^{\text{Me-H}}$ (R$^•$) is given by equation (2).

$$E_s^{\text{Me-H}}(\mathrm{R}^•) = \Delta H_f(\mathrm{CH_3}^•) - \Delta H_f(\mathrm{CH_4}) - [\Delta H_f(\mathrm{R}^•) - \Delta H_f(\mathrm{RH})] \qquad (2a)$$

$$i.e.\ E_s^{\text{Me-H}}(\mathrm{R}^•) = D[\text{Me–H}] - D[\text{R–H}] \qquad (2b)$$

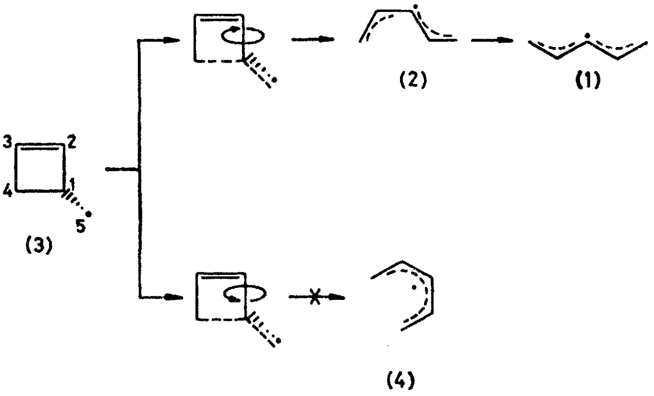
In this connection we note that Dewar *et al.*[18] have also recently drawn attention to the difficulty of defining stabilization energies for odd conjugated systems. They too, have suggested using methyl as the reference species. They suggest that the energy difference be called the resonance energy but since the stabilization can arise from factors other than electron delocalization (*e.g.*, relief of steric strain in RH) we believe that the term 'methane based stabilization energy' will be less confusing.



SCHEME 3

The $E_s^{\mathrm{Me-H}}$ value for pentadienyl can be estimated to be *ca.* 101 kJ mol^{-1} *using the above definition* and the appropriate bond dissociation energies.[19,20] This thermodynamically derived value for $E_s^{\mathrm{Me-H}}$(pentadienyl) is in excellent agreement with the value obtained by adding together $E_s^{\mathrm{Me-H}}$(allyl) and the barrier to pentadienyl rotation measured by e.s.r., *viz.*, $67 + 37 = 104$ kJ mol^{-1}. Because *E,Z*-pentadienyl isomerizes to *E,E*-pentadienyl the latter radical must have a somewhat larger $E_s^{\mathrm{Me-H}}$ than the former. The difference, RE(1)–RE(2), can be estimated by Benson's group contribution method[21] to be *ca.* 4 kJ mol^{-1}.

Generation of Pentadienyls by Ring-opening Reactions.—The ring opening of cyclobut-2-enylmethyl (3) should, in principle, yield *E,Z*-pentadienyl (2) and, possibly, the *Z,Z*-isomer (4) (see Scheme 4).

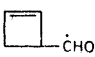


SCHEME 4

Photolysis of a solution of cyclobut-2-enylmethyl bromide, triethylsilane, and di-t-butyl peroxide[5] in cyclopropane at 190 K gave a spectrum that can be assigned to the cyclobut-2-enylmethyl radical (3).[4] The e.s.r. spectral parameters are given in Table 4. The hyperfine splitting of 2.10 mT is typical for α-hydrogens at a planar radical centre. The hyperfine splitting of 0.99 mT, wihch increases with increasing temperature ($\partial a^{\mathrm{H}}/\partial T = +3.6$ μT/K from 140 to 205 K), is assigned to the β-hydrogen. Its magnitude and temperature dependence imply that this radical, like cyclopropylmethyl[22] and cyclobutylmethyl,[23] adopts either (5a or b) as its preferred conformation. The dihedral angle, θ, will be *ca.* 65° provided the unusual hybridization at the β-carbon does not invalidate the normal relationship between $a^{\mathrm{H}\beta}$ and θ.

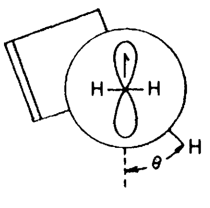
TABLE 4

E.s.r. parameters at 190 K for two cyclobut-2-enylmethyl radicals, for 3-methylcyclobutenyl, and for cyclopent-3-enyl

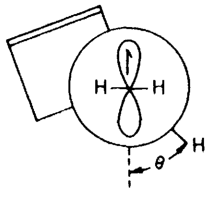
Radical	*g* Factor	H.f.s. (mT)
(3) 	2.0028	2.10 (2 H_α), 0.99^a (1 H_β) 0.26 (1 H), 0.11 (1 H), 0.05 (1 H)
(6) 	2.0034	1.67 (1 H_α), 1.00^b (1 H_β) 0.141 (1 H), 0.100 (1 H), 0.051 (1 H)
(9) 	2.0028	1.50 (1 H_1), 0.24 (1 H_2) 0.42 (2 H_4) 1.61 (3 $H_{\mathrm{CH_3}}$)
(12) 	2.0030	2.12 (1 H_α), 3.69 (4 H_β) 0.046 (2 H_γ)

^{a} $\partial a^{\mathrm{H}\beta}/\partial T = 3.6$ μT/K from 140 to 205 K. ^{b} $\partial a^{\mathrm{H}\beta}/\partial T = 2.0$ μT/K from 150 to 260 K.

At temperatures above *ca.* 230 K the spectrum due to (3) disappears and is replaced by that due to *E,E*-pentadienyl (1). Homolytic fission of the C(1)–C(4) bond should be favoured over fission of the C(1)–C(2) bond for thermodynamic reasons. For stereoelectronic reasons fission of the C(1)–C(4) bond will occur most readily from conformation (5a) in which this bond and the semi-occupied C_α $2p_z$ orbital are nearly eclipsed.[15,24] Such ring-opening would lead directly to the *E,Z* (2) *or* to the *Z,Z*-pentadienyl (4) radical, depending upon the direction of rotation of the C(5) methylene group about the C(1)–C(2) bond (see Scheme 4). However, the temperature at which cyclobut-2-enylmethyl undergoes ring-opening (230 K) is *above* the temperature where (2) is converted rapidly into (1). For this reason, (3) appears to ring-open directly to (1).

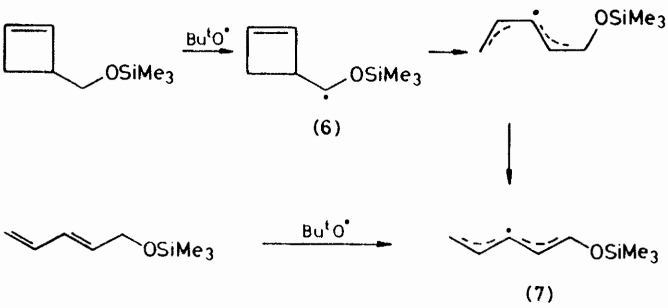


(5a)



(5b)

An attempt to measure the rate constants for the ring-opening of cyclobut-2-enylmethyl by the standard kinetic e.s.r. procedure[14] was frustrated by overlapping spectral lines which made it impossible to determine the absolute concentration of (1) in the presence of (3). However, in e.s.r. experiments of this kind it is generally found[25] that the rate constant for the rearrangement is *ca.* 10^3 s^{-1} at the temperature of rearrangement. We presume, therefore, that this reaction has a rate constant of 10^3 s^{-1} at some temperature in the range 210—230 K.



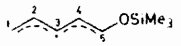
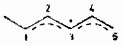
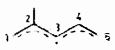
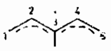
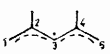
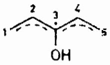
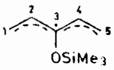
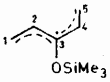
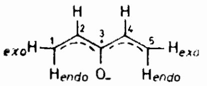
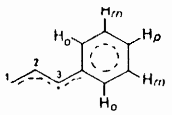
SCHEME 5

Results rather similar to those described above were obtained by hydrogen abstraction with t-butoxyl from the trimethylsilyl derivative of cyclobut-2-enylmethanol (see Scheme 5). At temperatures below 280 K the ring-unopened secondary alkyl (6) was observed (e.s.r. parameters given in Table 4). At temperatures above 280 K the spectrum due to (6) was replaced by one assigned to 1-trimethylsiloxypentadienyl in the *E,E*-conformation (7). This assignment rests on the fact that the e.s.r. parameters (see Table 5) were identical to those of the radical obtained by photolysis of *trans*-1-(trimethylsiloxy)penta-2,4-diene and di-t-butyl peroxide in cyclopropane at temperatures above 190 K (Scheme 5). Again, ring-opening probably yields the *E,Z*-conformer but this must isomerize rapidly to the *E,E*-form.

Attempted Formation of Cyclobut-2-enylmethyl (3) *by*

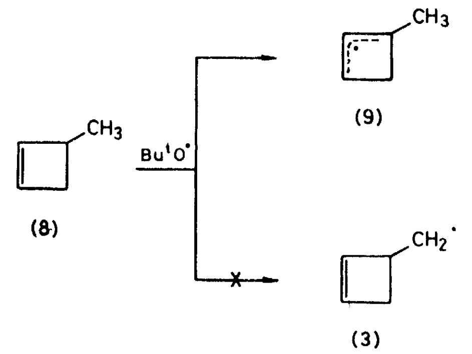
TABLE 5

E.s.r. parameters for substituted pentadienyl radicals

	Radical	T/K	g Factor	Expt. h.f.s. (mT)	INDO calc. h.f.s. (mT)
(7)		210		H (3) 1.11 H (1 *exo*) 1.02 H (1 *endo*) 0.95 H (5 *endo*) 0.88 H (2) 0.30 H (4) 0.27	
		233	2.002 80	CH_3 1.12 H (1,5 *endo*) 0.95 H (2,4) 0.32 H (5 *exo*) 1.02 H (3) 1.19	
		233	2.002 83	CH_3 0.26 H (4) 0.35 H (1 *exo*) 1.02 H (1 *endo*) [a] 0.90 H (5 *exo*) 1.08 H (5 *endo*) 0.97 H (3) 1.17	−1.13 0.68 −1.22 −1.19 −1.18 −1.21 −1.22
		208	2.002 60	CH_3 0.99 H (2,4) 0.31 H (1,5 *exo*) 0.99 H (1,5 *endo*) 0.92	2.13 0.62 −1.11 −1.16
		248	2.002 81	CH_3 (2,4) 0.26 H (1,5 *exo*) 0.98 H (1,5 *endo*) 0.92 H (3) 1.23	
		233	2.003 21	OH 0.07 H (1,5 *exo*) 0.97 H (1,5 *endo*) 0.92 H (2,4) 0.27	
(13)		117	2.002 76	H (1,5 *exo*) 0.98 H (1,5 *endo*) 0.92 H (2,4) 0.27	
(14)		117	2.002 79	0.25 0.33 0.83 0.87 0.95 1.02	
	 [b]			H (1,5 *exo*) 0.876 H (1,5 *endo*) 0.840 H (2,4) 0.199	
		238	2.002 81	2H (*meta*) 0.13 2H (*ortho*) 0.35 H (*para*) 0.40 H (2) 0.35 H (1 *exo*) 1.11 H (1 *endo*) 1.03 H (3) 1.27	

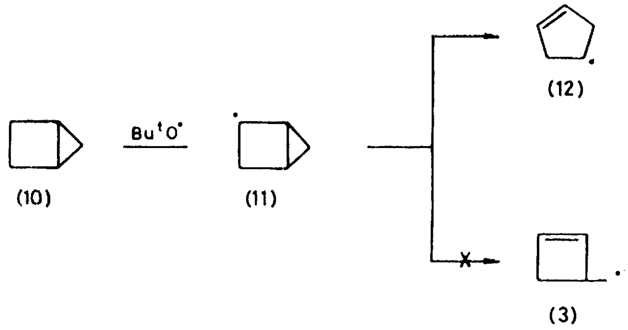
[a] Assignment to particular hydrogens is uncertain. [b] Data from F. Gerson, R. Gleiter, G. Moshuk, and A. S. Dreiding, *J. Am. Chem. Soc.*, 1972, **94**, 2919; M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 1973, **77**, 2662.

Hydrogen Abstraction.—Photolysis of 3-methylcyclobutene (8) and di-t-butyl peroxide in cyclopropane at temperatures from 140 to 200 K gave a mixture of two radicals. One of the radicals was identified as 3-methylcyclobutenyl (9) since its e.s.r. spectral parameters (see Table 4) are similar to those reported for cyclobutenyl (*viz.*[26] $a^{H(1,3)}$ 1.520, $a^{H(2)}$ 0.241, and $a^{H(4,CH_2)} = 0.445$ mT). The identity of the second radical [a^{H}(6H) 0.33, a^{H}(1H) 3.84 mT] is currently under investigation.



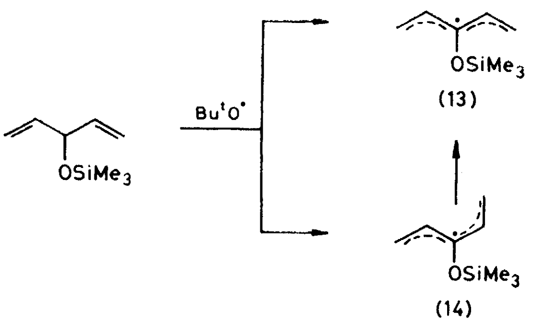
Photolysis of bicyclo[2.1.0]pentane (10) in neat di-t-butyl peroxide or with cyclopropane or ethylene solvent gave, as we have previously reported,[27] only the cyclopent-3-enyl radical (12) (see Table 4) at temperatures from 113 to 373 K. This product radical was somewhat unexpected [27] since the usual stereoelectronic arguments [15,24] would suggest that the initial bicyclo[2.1.0]pentan-2-yl radical (11) would undergo cleavage of the C(1)–C(5) bond to form cyclobut-2-enylmethyl (3). The observed cleavage of the C(1)–C(4) bond, which has been further confirmed by product studies,[27] must be attributed to the immediate relief of virtually all the ring strain in (11).

Formation and E.s.r. Spectra of Substituted Pentadienyls.—E.s.r. spectra were obtained for 1-methyl-, 2-methyl-, 3-methyl-, 2,4-dimethyl-, and 3-hydroxy-pentadienyl radicals by photolysis of di-t-butyl peroxide solutions of the corresponding 1,4-dienes. The e.s.r. signals were fairly weak and decreased rapidly with time concurrently with the accumulation of polymeric material in the sample tubes. The spectra were, however, too weak to analyse when hydrocarbon solvents were added and therefore the lowest temperature that could be reached was *ca.* 233 K, the freezing point of di-t-butyl peroxide.



It is probably for this reason that each of the above mentioned pentadienyls was obtained in only one conformation, which we presume to be the *E,E*-form in all cases. The e.s.r. parameters for these radicals are reported in Table 5. The assignments of hyperfine splittings were made by comparison with pentadienyl and on the basis of internal consistency [6a] within this set of radicals. The only ambiguity comes with the hyperfine splittings on C(1) and C(5) of 2-methylpentadienyl which cannot be assigned with certainty.

The 3-trimethylsiloxypentadienyl radical could, in contrast to the above mentioned substituted pentadienyls, be readily observed when generated by hydrogen abstraction from the parent 1,4-diene in cyclopropane or propane at low temperatures. At temperatures above *ca.* 190 K only the *E,E*-conformer (13) could be detected. At lower temperatures the *E,Z*-conformer (14) could also be observed and it became increasingly important as the temperature decreased, the *E,E* : *E,Z* ratio reaching 1.2 at 117 K. It seems reasonable to conclude that the *E,E* : *E,Z* ratio at low temperatures is controlled by hydrogen abstraction from different conformers of the parent pentadiene and that the *E,Z* conformer isomerizes to *E,E* at temperatures above *ca.* 160 K.



The e.s.r. parameters for 3-phenylallyl, which was generated by hydrogen abstraction from allylbenzene, are included in Table 5. The hyperfine splittings, where comparable, are rather similar to those of pentadienyl which implies that the spin distribution over the allyl units is similar for the two radicals.

SCF MO Calculations on Pentadienyl Radicals.—Semi-empirical and other SCF MO calculations have been reported for pentadienyl radicals in both the *E,E* (1) and *Z,Z* (4) conformations.[1] Hinchliffe [1h,i] has also carried out *ab initio* calculations on (1) using high quality Gaussian basis sets. Sustmann and Schmidt [3] made INDO [28] level calculations on both radicals (1) and (2). We carried out INDO calculations using 'standard' bond lengths and angles (r_{CC} 140, r_{CH} 108 pm, $\widehat{CCC} = \widehat{CCH} = 120°$)[28] without energy minimization for radicals (1), (2), 2-methylpentadienyl, and 3-methylpentadienyl. The spin unrestricted wavefunctions used in the INDO method are not eigenfunctions of S^2 so that the final calculated ground state wavefunctions of open-shell systems contain contaminating contributions from components of higher multiplicity spin states. For the pentadienyl radicals calculated $\langle S^2 \rangle$ values were *ca.* 0.9, indicating that contamination is particularly serious [*cf.* $S(S+1) = 0.75$ for the pure doublet state]; the INDO wavefunctions are poor, and no great confidence can be placed in the calculated energies and other properties. This problem was examined by Beveridge and Dobosh[29] who calculated spin densities for a large number of radicals, including some with $\langle S^2 \rangle$ values as great as those found for pentadienyl. From the good correlation of the calculated spin densities with experimental e.s.r. coupling constants they concluded that the presence of contaminating spin components does not introduce serious errors. Their correlation, which introduces some empirical compensation for the contamination, is used in the INDO program[30] for converting spin densities into hyperfine coupling constants.

Our INDO calculations gave conformer (1) 9 kJ mol^{-1} lower in energy than conformer (2) (Sustmann and Schmidt[3] found an 8 kJ mol^{-1} difference). The INDO calculations predict that the introduction of a methyl group at C(2) or C(3) will bring the radical conformers closer in energy (ΔE 2.9 and 3.9 kJ mol^{-1}, respectively). The calculated hyperfine splittings are given in Tables 1 and 5. Hinchliffe's[1h,i] *ab initio* results for (1) are also included in Table 1. The calculated hyperfine splittings are in reasonable agreement (*ca.* ±0.3 mT) with the experimental results and suggest positive signs for the hydrogen hyperfine splittings at C(2) and C(4), which agrees with the deduction made from their experimental temperature dependencies. However, neither INDO nor *ab initio* calculations (which also gave large $\langle S^2 \rangle$ values) agree with the assignment of the higher hyperfine splittings to the *exo*-hydrogens of C(1) and C(5). A similar disagreement has been observed for the case of the allyl radical.[6a] Thus, calculations are not sufficiently precise to provide much aid in the assignment of the experimental hyperfine splittings.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on Varian EM 360 and/or HA 100 instruments on CCl_4 solutions at room temperature with Me_4Si as internal standard. Mass spectra were obtained with an A.E.I. MS 902 spectrometer. G.l.c. analyses were carried out on a Pye 105 instrument with columns packed with Embaphase silicone oil, tritolyl phosphate, or β,β′-oxydipropiononitrile as stationary phases except where otherwise indicated. E.s.r. spectra were recorded on Varian E-104 and/or Bruker ER 200D spectrometers.

Commercial di-t-butyl peroxide was passed through a column of alumina and distilled *in vacuo*. Hexa-n-butylditin was obtained commercially, distilled *in vacuo*, and stored under nitrogen. The 1,4- and 1,3-dienes were commercial products whose purity was checked by g.l.c. and/or n.m.r. spectroscopy.

trans-1-*Bromopenta*-2,4-*diene*.—This compound was prepared from 3-hydroxypenta-1,4-diene by the method of Prévost *et al.*[31] Data on the ^{1}H n.m.r. are given below.

cis-1-*Bromopenta*-2,4-*diene*.—Initial attempts to prepare this compound were planned to follow the sequence 1-hydroxypent-2-yn-4-ene ⟶ *cis*-1-hydroxypenta-2,4-diene ⟶ *cis*-1-bromopenta-2,4-diene. The 1-hydroxypent-2-yn-4-ene was prepared *via* the Grignard reagent from vinylacetylene and formaldehyde by the method of Crombie *et al.*[32], b.p. 341—343 K at 20 Torr; ν_{OH} 3320 cm^{-1}; δ 3.6 (1 H, s), 4.3 (2 H, s), and 5.6 (3 H, m). Freshly distilled substrate was stirred with redistilled quinoline, purified ethyl acetate, and Lindlar's catalyst under an atmosphere of hydrogen according to the method of Boehm and Whiting.[33] However, contrary to their report, we found that 2 mol equiv. of hydrogen were rapidly taken up without any pause in the rate of uptake. The substrate was purified by chromatography on silica gel but gave the same result. Commercial Lindlar's catalyst (Roche) and material freshly prepared according to the method of Lindlar and Dubois[34] also gave similar results. G.l.c. analysis of the product showed a complex mixture of components. Some *cis*-hydroxypenta-2,4-diene could perhaps have been separated by treatment with urea, but it was obvious that not enough could be obtained to make its conversion into *cis*-1-bromopenta-2,4-diene a practicable proposition.

Next, attempts were made to brominate *cis*-penta-1,3-diene. This compound (5 g), *N*-bromosuccinimide (NBS) (13.5 g), benzoyl peroxide (0.3 g), and CCl_3F (75 ml) were heated in a rocking bomb at *ca.* 350 K for 14 h. The liquid product was filtered and the solvent removed by distillation. G.l.c. analysis of the residue showed mainly dibromide but there were also two trace components with retention times in the expected range for monobromides. One of these compounds was shown to be *trans*-1-bromopenta-2,4-diene. Reactions at several different temperatures and lasting different times gave essentially the same results. The *cis*-diene (1 g) was then photolysed with CCl_3Br (4 g) at room temperature in a thin-wall Pyrex tube with light from a Hanovia UVS 220 medium pressure mercury arc for 6 h. G.l.c. analysis of the products on a variety of columns showed a trace of chloroform, but no monobromides. The main products were two long retention time peaks which were isolated by preparative g.l.c. The first of these had M^+ 264 ($^{12}C_6H_8{}^{35}Cl_3{}^{79}Br$ requires M, 264) and the ^{1}H n.m.r. spectrum was consistent with the 1,4-adduct structure $CCl_3CH_2CH{=}CHCHBrCH_3$, δ 1.8 (3 H, d), 3.4 (2 H, d), 4.6 (1 H, quintet), and 5.8 (2 H, m). The second (and minor) component was the 1,2 adduct $CCl_3CH_2CHBrCH{=}CHCH_3$, δ 1.4 (3 H, d), 3.2 (1 H, m), 3.9 (2 H, d), and 5.8 (2 H, m).

Next, penta-1,4-diene (2.9 g), NBS (7.9 g), benzoyl peroxide (0.4 g), and CCl_3F (75 ml) were heated at *ca.* 360 K in a rocking bomb for 5 h. The liquid was filtered and solvent removed by distillation. G.l.c. analysis of the residue showed one component with a retention time identical with that of *trans*-1-bromopenta-2,4-diene, but the main product was a long retention time peak. The residue was distilled through a Vigreux column giving oil (0.4 g), b.p. 338—342 K at 15 Torr. The mass spectrum suggested this compound was a dibromide and the ^{1}H n.m.r. is consistent with the structure $CH_2BrCHBrCH_2CH{=}CH_2$, δ 2.6—2.9 (2 H, m), 3.4—4.4 (3 H, m), and 5.0—6.3 (3 H, m).

Finally, when the significance of our e.s.r. results on the radicals produced by hydrogen abstraction with t-butoxyl from penta-1,4-diene was realized, it was immediately obvious that the desired *cis*-1-bromopenta-2,4-diene could be obtained by a free-radical reaction of penta-1,4-diene and t-butyl hypobromite at very low temperatures. The hypobromite[35] (1.5 g) was placed in a Pyrex bomb and degassed on a vacuum line; CF_2Cl_2 (*ca.* 3 ml), penta-1,4-diene (2.5 g), and further CF_2Cl_2 (10 ml) were distilled into the bomb, which was sealed under vacuum and warmed to 195 K in a dry-ice chest in the dark and shaken to dissolve the hypobromite. The bomb was then transferred to an unsilvered Dewar flask containing isopentane at 123 K and was irradiated at this temperature with the light from a tungsten filament lamp. The brownish colour of the hypobromite faded almost entirely after 3 h. The bomb was opened and the CF_2Cl_2 blown off in a stream of N_2 as the Dewar warmed to *ca.* 250 K. The products were examined by g.l.c. on a Varian 3700 gas chromatograph using a 12 ft column packed with 12% OV-101 on Chromosorb W. The chromatogram showed t-butyl alcohol and a peak whose retention time was identical to that of *trans*-1-bromopenta-2,4-diene, together with many minor high-boiling materials. There was no readily identifiable peak which might be attributed to the *cis*-isomer. The peak attributed to the *trans*-bromide was isolated by preparative g.l.c. using a Varian 920 gas chromatograph fitted with a 5 ft column packed with 5% OV-101 on Chromosorb A. The material collected in this way (*ca.* 100 μl) was shown by ^1H n.m.r. to be a mixture of *trans*- and *cis*-1-bromopenta-2,4-dienes in a ratio (obtained by integration of peaks due to CH_2Br protons) of *ca.* 1.4 : 1.0, δ (pure *trans*-bromide) 4.01 (2 H, d, *J* 7.0 Hz) and 5.1—6.5 (5 H, m); δ (*cis*-bromide from mixture) δ 4.09 (2 H, d), *J* 7.8 Hz) and 5.1—6.5 (5 H, m).

Cyclobut-2-*enylmethyl Bromide*.—A sample of 3-chlorocyclobutanecarboxylic acid [36] was converted into its methyl ester with thionyl chloride and methanol. The ester (20.4 g) in dry ether (100 ml) was added drop by drop to an ice-cold suspension of $LiAlH_4$ (6.0 g) in ether (200 ml). After 2 h of further stirring water was added slowly, the ether layer separated and dried (Na_2SO_4), and the ether evaporated. The remaining liquid was distilled through a Vigreux column to give 3-chlorocyclobutylmethanol (12.7 g), b.p. 375 K at 20 Torr (lit.,[37] 365—366 K at 10 Torr); δ 2.4 (5 H, m), 3.4 (1 H, s), 3.6 (2 H, m), and 4.4 (1 H, m).

3-Chlorocyclobutylmethanol (15.6 g) in dry DMSO (40 ml) was added dropwise to $KOBu^t$ (32 g; dried by pumping at 0.002 mmHg for 8 h at 343 K) suspended under nitrogen in DMSO (200 ml). The mixture was slowly heated during 24 h up to 323 K and then poured into ice–water and neutralized with 2N-H_2SO_4. The solution was saturated with salt and extracted with ether (5 × 200 ml). The ether was dried (anhydrous Na_2SO_4) and removed by distillation. The residual liquid was distilled through a Vigreux column to give cyclobut-2-enylmethanol (2.8 g), b.p. 309—311 K at 3.5 Torr (lit.,[37] 317—320 K at 10 Torr), ν_{OH} 3 350 and 1 020 cm^{-1}; $\nu_{C=C}$ 685 and 3 050 cm^{-1}; δ 2.6 (2 H, m), 3.0 (1 H, m), 3.57 (2 H, d), 3.9 (1 H, s), and 6.1 (2 H, s). Attempts to dehydrohalogenate 3-chlorocyclobutylmethanol were made with other reagents in an effort to improve the yield. However, 1,5-diazabicyclo[4.3.0]non-5-ene, sodium in liquid ammonia, and $NaNH_2$–Bu^tONa in THF all gave no reaction and the starting material was recovered unchanged. Attempts at halogen exchange with KF in acetone and KBr in acetone were also unsuccessful.

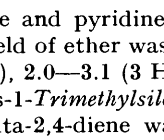
A mixture of cyclobut-2-enylmethanol (2.0 g), dry pyridine (0.5 g), and light petroleum (3 ml) was cooled to 263 K and PBr_3 (2.5 g) added to the stirred solution. After stirring for a further 2 h, water was added and the organic layer separated, washed with water, sodium carbonate solution, then water again, and dried (Na_2SO_4). The solvent was removed and the oil examined by g.l.c. which showed two components that were separated by preparative g.l.c. on silicone oil at 323 K (distillation resulted in decomposition). The mass spectrum showed the first component to be C_5H_7Br, *m/e* 146 and 148 (M^+), and the i.r. and ^1H n.m.r. spectra confirmed the structure as cyclobut-2-enylmethyl bromide, $\nu_{C=C}$ 3 050 and 685 cm^{-1}; δ 6.15 (2 H, AB), 3.4—3.1 (3 H, m), 2.75 (1 H dd), and 2.2 (1 H, d). The mass spectrum showed the second component also to be C_5H_7Br, *m/e* 146 and 148(M^+); and the ^1H n.m.r. spectrum suggested it was 4-bromocyclopentene, δ 2.8 (4 H, m), 4.45 (1 H, dt), and 5.65 (2 H, s).

Cyclobut-2-enylmethanol was also converted into the bromide *via* its mesylate. The alcohol (1.1 g) and triethylamine (3.0 g) in dry CH_2Cl_2 (100 ml) were cooled to 263 K and methanesulphonyl chloride (2.1 g) was added dropwise under an atmosphere of nitrogen. The mixture was stirred for 20 min, then washed with chilled solutions of 2N HCl, 5% brine, saturated $NaHCO_3$, and water, and then dried (Na_2SO_4). The CH_2Cl_2 was removed on a rotary evaporator to give the mesylate (3.1 g). I.r. spectroscopy showed the presence of the characteristic bands at 1350 (O=S=O) and 1170 cm^{-1} (CH_3–S). The mesylate and anhydrous LiBr (3.5 g) were refluxed in dry acetone for 20 h. The precipitate of lithium mesylate was separated and the acetone removed by distillation. The residue was taken up in ether, washed with water, dried (Na_2SO_4), and the ether removed at atmospheric pressure. This gave cyclobut-2-enylmethyl bromide (0.9 g) after distillation which was shown by i.r. and g.l.c. retention time comparisons to be identical to the first component of the mixture from the PBr_3 reaction.

Trimethylsilylation of Cyclobut-2-*enylmethanol*.—The alcohol was treated with equimolar amounts of trimethylsilyl chloride and pyridine in n-pentane at room temperature. The yield of ether was 64%, b.p. 322 K at 27 Torr; δ 0.09 (9 H, s), 2.0—3.1 (3 H, m), 3.8 (2 H, d), and 6.00 (2 H, s).

trans-1-*Trimethylsiloxypenta*-2,4-*diene*.— *trans*-1-Hydroxypenta-2,4-diene was prepared by $LiAlH_4$ reduction of vinylacrylic acid according to the method of Crombie *et al.*[38] The alcohol was trimethylsilylated as described above to give the ether (74%), b.p. 325 K at 18 Torr; δ 0.2 (9 H, s), 4.25 (2 H, d), and 4.9—6.5 (5 H, m).

3-*Methylcyclobutene*.—*trans*-Penta-1,3-diene (2 g) and n-hexane (250 ml) were degassed and sealed in a quartz tube which was photolysed with light from a 150 W Hanovia medium pressure mercury lamp at room temperature for 1 month.[39] The resulting solution was distilled through a 25 cm packed column, material boiling below 308 K being collected. 3-Methylcyclobutene was then separated by preparative g.l.c., samples being obtained from both silicone oil and β,β-oxydipropiononitrile columns. The mass spectrum showed the correct molecular ion and the ^1H n.m.r. spectrum confirmed the structure. Chemical shifts and coupling constants were obtained by computer simulation of the spectrum.



δ 1.14 (CH_3^a, J_{cb} 7Hz),
2.90 (H^b, J_{bc} 1, J_{bd} 4Hz),
1.95 (H^c, J_{cd} 12Hz),
2.66 (H^d),
5.90 (H^e, J_{ef} 3Hz),
5.98 (H^f)

Bicyclo[2.1.0]pentane was prepared from cyclopentadiene and diethyl azodicarboxylate, *via* diethyl 2,3-diazabicyclo-

[2.2.1]heptane-2,3-dicarboxylate and 2,3-diazabicyclo[2.2.1]-hept-2-ene by the method of Gassman and Mansfield.[40] The spectral and other characteristics of the product agreed with the literature and g.l.c. showed no impurities.

3-(Trimethylsilyloxy)penta-1,4-diene was prepared from the corresponding hydroxydiene in the usual way.

[0/1138 *Received*, 18*th July*, 1980]

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