E.S.R. Study of the Homolytic Ring Fission of Cyclobutenylmethyl Radicals

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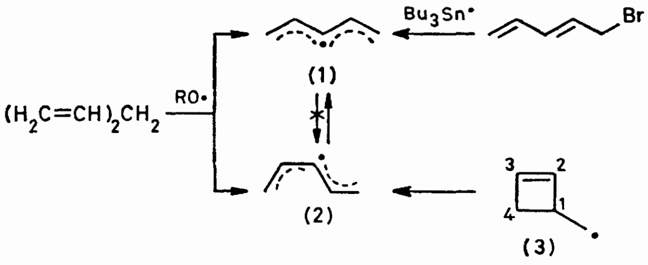
Summary Cyclobutenylmethyl radicals undergo homolytic ring fission at temperatures above 230 K to give *EE* pentadienyl radicals; the unrearranged and rearranged radicals have been observed by e.s.r. spectroscopy.

We showed recently that hydrogen abstraction from penta-1,4-diene gives rise to pentadienyl radicals.[1] At temperatures below about 210 K these radicals can be observed by e.s.r. spectroscopy in both the *EE* (**1**) and the *EZ* conformation (**2**). Similar observations were made by Sustmann and Schmidt who interpreted them in essentially the same way.[2] The *EE* pentadienyl radicals (**1**), when generated directly by bromine abstraction from *trans*-1-bromopenta-2,4-diene, are not converted into (**2**) in the temperature range 143—453 K.



In an attempt to generate the *EZ* radicals (**2**) directly, we have investigated the homolytic ring fission of cyclobutenylmethyl radicals (**3**) which might be expected to yield (**2**).

Cyclobutenylmethyl bromide was synthesised from cyclobutenylmethanol[3] both by treatment with PBr$_3$, and by refluxing the methanesulphonate with LiBr. When a solution of this bromide, triethylsilane, and di-t-butyl

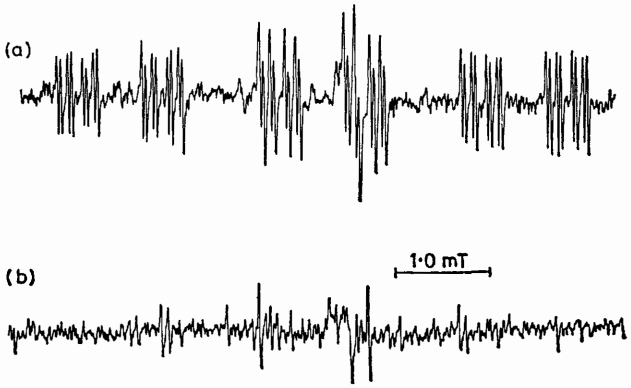
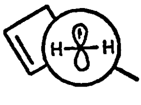


Figure. E.s.r. spectra during photolysis of Bu^{t}OOBu^t with Et$_3$SiH and cyclobutenylmethyl bromide in cyclopropane (a) at 160 K, (b) at 250 K.

peroxide in cyclopropane was photolysed in the cavity of an e.s.r. spectrometer the spectrum shown in the upper trace of the Figure, *i.e.* (a), was obtained, and remained visible, though weakening in intensity, up to temperatures around 230 K. We assign this spectrum to the cyclobutenylmethyl radical (**3**) and the e.s.r. parameters are recorded in the Table. The 2·10 mT coupling constant is normal for α-hydrogens at a planar radical centre. The 0·99 mT coupling constant increased with increasing temperature ($\delta a/\delta T$ = 3·6 μT/K from 140 to 205 K). This must be due to the β-hydrogen. The value of $a(\beta H)$ and its temperature dependence suggest that the radical adopts the staggered form (**4**) as its preferred conformation. In this conformation the orbital containing the unpaired electron and the C(1)–C(4) bond of the cyclobutene ring are nearly eclipsed. Such a conformation should favour scission of the C(1)–C(4) bond[4,5] and at temperatures above 230 K the spectrum shown in the lower half of the Figure, *i.e.* (b), appears which is due to the *EE* pentadienyl radical. (The e.s.r. parameters are identical to those previously reported.[1,2])

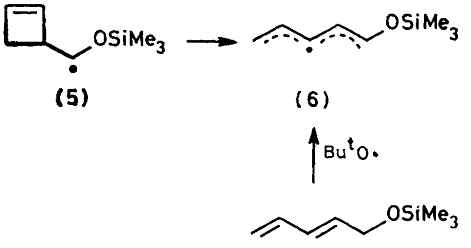
TABLE. E.s.r. parameters of cyclobutenylmethyl radicals.

Radical	*T*/K	*g*-Factor	Hyperfine splitting/mT
(**3**)	190	2·0028	2·10 (2 Hα), 0·99 (1 Hβ) 0·26 (1 H), 0·11 (1 H), 0·05 (1 H)
(**5**)	190	2·0034	1·67 (1 Hα), 1·00 (1 Hβ) 0·141 (1 H), 0·100 (1 H), 0·051 (1 H)



(4)

Homolytic fission of the C(1)–C(4) bond should lead directly to the *EZ* (**2**) or the *ZZ* pentadienyl radicals, depending on the direction of rotation of the C(5) methylene group about the C(1)–C(2) bond. However, the only pentadienyl radical observed is the *EE* conformer (**1**). Although this could in principle be formed directly from (**3**) by rotation about the C(2)–C(3) double bond with concomitant fission of the C(1)–C(4) bond, such a process would seem very unlikely. Semi-empirical SCF MO calculations[6] using the MINDO/3 programme[7] predict that (**3**) will ring-open to give *EZ* pentadienyl radicals (**2**). The calculations show a very much higher activation energy for the process leading directly to (**1**). The most plausible explanation of the experimental observations is that (**3**) ring-opens to give *EZ* pentadienyl radicals (**2**) but that at the temperature when this occurs (**2**) converts immediately into *EE* pentadienyl radicals (**1**). Since the ring fission of (**3**) is exothermic (by *ca.* 95 kJ mol^{-1}) the *EZ* pentadienyls formed will initially possess an excess of energy, which ***might*** accelerate their isomerization to the *EE* form. However such 'hot' radical reactions are very uncommon in solution, and need not be invoked in the present system since the temperature of ring fission (*ca.* 230 K) is *above* the temperature (210 K, see above) at which radicals (**2**) can be observed when thermalized pentadienyls are generated by H-atom abstraction from penta-1,4-diene.



(5) **(6)**

Photolysis of the trimethylsilyl derivative of cyclobutenylmethanol in neat di-t-butyl peroxide leads to the formation of the corresponding cyclobutenylmethyl radical (**5**). The e.s.r. parameters (see the Table) are similar to those of (**3**) except that the $a(\alpha H)$ is smaller owing to the adjacent oxygen; the $a(\beta H)$ shows a strong increase with increasing temperature ($\delta a/\delta T$ = 2·0 μT/K from 150 to 260 K). At temperatures above 280 K a weak spectrum of a new radical appeared which showed coupling to 6 non-equivalent hydrogens. The same spectrum was obtained on photolysis of a solution of *trans*-1-(trimethylsiloxy)penta-2,4-diene and di-t-butyl peroxide in cyclopropane. This indicates that homolytic fission again gives the trimethylsiloxy-substituted pentadienyl radical in the *EE* conformation (**6**). Presumably (**6**) is also formed *via* the corresponding *EZ* pentadienyl radical.

Cyclopropylmethyl radicals[8] and cyclobutylmethyl radicals[9] also show small $a(\beta H)$ hyperfine coupling constants and therefore prefer staggered conformations.

Under e.s.r. conditions cyclopropylmethyl radicals undergo ring fission at *ca.* 150 K with an activation energy of 25 kJ mol^{-1}.[10] Homolytic fission of cyclobutylmethyl radicals has not been observed by e.s.r. spectroscopy. However, the activation energy for this process has been estimated to be *ca.* 55 kJ mol^{-1} from a study of the reaction of cyclobutylmethyl halide with tri-n-butyltin hydride.[11] The activation energy for ring fission of cyclobutenylmethyl radicals lies between these two values.

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