An E.S.R. Study of Bicyclo[1.1.1]pent-1-yl Radicals

Bernard Maillard[a] **and John C. Walton**[b]

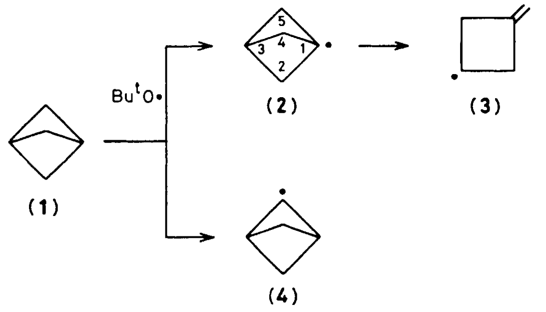
[a] *Laboratoire de Chimie Appliquée, Université de Bordeaux I, 33405 Talence-Cedex, France*
[b] *Department of Chemistry, The University, St. Andrews, Fife KY16 9ST, Scotland*

The e.s.r. spectrum of bicyclo[1.1.1]pent-1-yl radicals shows a very large hyperfine splitting from the bridgehead γ-hydrogen; this is probably due to the through space and through bond orbital interactions reinforcing one another.

Very few strained bicycloalkyl radicals have been observed by e.s.r. spectroscopy,[1–3] and even fewer with bridgehead radical sites. The bicyclo[1.1.1]pent-1-yl radical (2) has been the subject of several theoretical studies[4,5] and is of unique importance for the assessment of through bond (TB) and through space (TS) orbital interactions. Although the rearrangement of this radical to yield 3-methylene cyclobutyl radicals (3) is strongly exothermic (ΔH° *ca.* -175 kJ mol^{-1}) it is predicted to be kinetically disfavoured,[5] and unrearranged products have been observed;[6] thus, this radical appeared to be a good candidate for direct e.s.r. detection.

Bicyclo[1.1.1]pentane (1) was prepared by the method of Wiberg and co-workers[6,7] and purified by preparative g.l.c. When cyclopropane was used as a solvent the main species observed was the cyclopropyl radical, *i.e.* hydrogen abstraction from (1) by t-butoxy radicals is much slower than from ordinary alkanes. The spectrum shown in Figure 1 was obtained on photolysis of a mixture of (1) and di-t-butyl peroxide. The radical observed had the following e.s.r. parameters, which were essentially independent of temperature: $g = 2.0028$; $a(1\text{H}) = 6.96$, $a(6\text{H}) = 0.12$, and $\Delta H_{\text{pp}} = 0.015$ mT, and it can be identified as (2). Traces of other radicals could be observed (see Figure 1), but the intensities were too low for identification, and the alternative bicyclo[1.1.1]pent-2-yl radical (4) could not be detected. Thus, unexpectedly, Bu^{t}O$\cdot$ radicals preferentially abstract hydrogen from the bridgehead sites in (1). Wiberg and Williams also found preferential attack at the bridgehead sites in (1) by chlorine atoms.[6]

The radical (2) could be observed up to temperatures of *ca.*



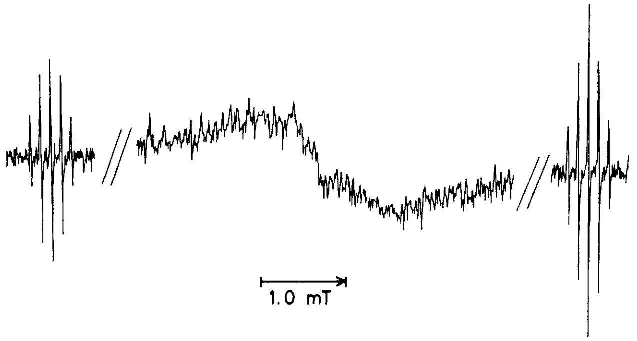
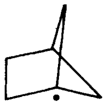


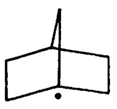
Figure 1. 9.4 GHz E.s.r. spectrum of bicyclo[1.1.1]pent-1-yl radicals (**2**) in neat di-t-butyl peroxide at 240 K.

310 K, and none of the rearranged radical (**3**) was detectable. Above 320 K the signal intensities were too poor to distinguish individual species. Under the usual e.s.r. conditions this means that the rate constant for rearrangement must be[8] $< 10^3$ s^{-1} at 310 K. Taking a normal pre-exponential factor of 10^{13} s^{-1},[9] the activation energy for rearrangement is estimated to be >60 kJ mol^{-1}, which may be compared with the theoretically derived value[5] of 107 kJ mol^{-1}. The experimental observations clearly support the prediction that the rearrangement is kinetically disfavoured.

The 6.96 mT hydrogen hyperfine splitting (h.f.s.) is one of the largest known for carbon centred radicals. It can be attributed to the single bridgehead γ-hydrogen H(3) in (**2**). A very large long range H–H coupling (18 Hz) between H(1) and H(3) in (**1**) was also observed in the ^{1}H n.m.r. spectrum.[7] The distance between C(1) and C(3) in (**2**) is about 1.75 Å[4,5] so that direct TS interaction of the orbitals will be significant.[10]



(**5**)



(**6**)

In addition, spin density can reach H(3) *via* three identical TB routes each involving two C–C bonds. For each of these routes the SOMO and the C–H bond orbitals are virtually in the ideal *trans*-arrangement (W plan). Theory[10,11] predicts that the TS and TB interactions should reinforce one another when the TB interaction occurs through two bonds, as here. The large h.f.s. for H(3) in (**2**) is consistent with this analysis. The h.f.s. of the analogous bridgehead hydrogens in bicyclo[2.1.1]hex-1-yl (**5**)[2] and bicyclo[2.2.1]hept-1-yl radicals (**6**)[12] are 2.25 and 0.25 mT respectively. Thus the h.f.s. increases very steeply with the number of short (two C–C bond) TB interaction routes which are available. INDO calculations for (**2**)[4] suggest that the TB interaction is the most important and predict a[H(3)] = 8.39 mT, in reasonable agreement with the experiment.

We thank N.A.T.O. for a Research Grant without which the present work could not have been undertaken.

Received, 1st June 1983; Com. 702

References

1 P. J. Krusic, J. P. Jesson, and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 4566.
2 T. Kawamura and T. Yonezawa, *J. Chem. Soc., Chem. Commun.*, 1976, 948.
3 A. J. Kennedy, J. C. Walton, and K. U. Ingold, *J. Chem. Soc., Perkin Trans.* 2, 1982, 751.
4 M. Ohsaku, A. Imamura, K. Hirao, and T. Kawamura, *Tetrahedron*, 1979, **35**, 701.
5 J. R. Bews, C. Glidewell, and J. C. Walton, *J. Chem. Soc., Perkin Trans.* 2, 1982, 1447.
6 K. B. Wiberg and V. Z. Williams, *J. Org. Chem.*, 1970, **35**, 369.
7 K. B. Wiberg and D. S. Connor, *J. Am. Chem. Soc.*, 1966, **88**, 4437.
8 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317.
9 A. L. J. Beckwith and K. U. Ingold in 'Rearrangements in Ground and Excited States,' ed. P. de Mayo, Academic Press, New York, 1980, p. 161.
10 M. N. Paddon-Row, *Acc. Chem. Res.*, 1982, **15**, 245.
11 J. W. Verhoeven, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 369.
12 T. Kawamura, M. Matsunaga, and T. Yonezawa, *J. Am. Chem. Soc.*, 1975, **97**, 3234.