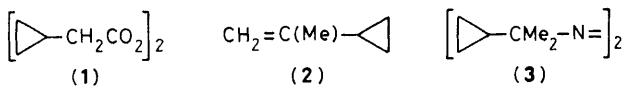
Cyclopropyl Activation of Adjacent Methylene Groups in Spiro[2.*n*]alkanes and Bicyclo[*n*.1.0]alkanes

Charles Roberts and John C. Walton*

Department of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, U.K.

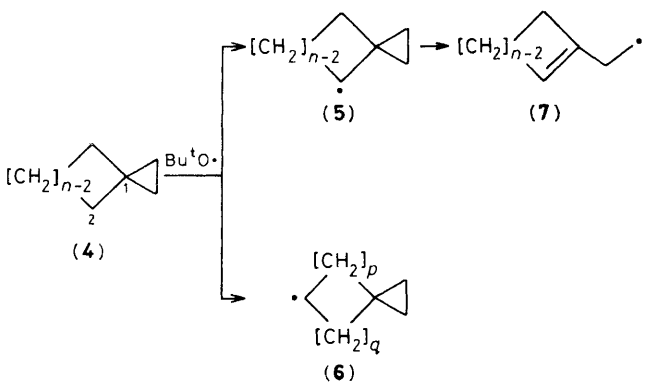
The hydrogens at C(2) in spiro[2.*n*]alkanes are abstracted about five times more rapidly than 'normal' secondary hydrogens by t-butoxyl radicals, because of favourable overlap of the p-orbital at C(2) with the HOMO of the adjacent cyclopropyl ring; the hydrogens at C(2) in bicyclo[*n*.1.0]alkanes are less activated because the cyclopropyl ring orientation is less favourable for overlap.

The cyclopropyl group is known to interact with an adjacent p-(or π-) orbital, leading to thermodynamic stabilisation in the resulting species. The stabilisation of cyclopropylmethyl cations is well known, and is usually attributed to charge delocalisation *via* non-classical structures.[1,2] Cyclopropylmethyl type radicals show a similar though much smaller stabilisation. For example, in the photochlorination of methylcyclopropane with t-butyl hypochlorite hydrogen is abstracted from the methyl group at an enhanced rate.[3] Cyclopropylacetyl peroxide (**1**) decomposes 55 times faster than cyclohexylacetyl peroxide.[4] Free radical addition to 2-cyclopropylpropene (**2**) proceeds more rapidly than addition to 2,3-dimethylbut-1-ene.[5] Cyclopropyl-substituted azo-compounds such as (**3**) decompose considerably more rapidly than 2,2′-azoisobutane.[6] Non-classical structures for cyclopropylmethyl radicals can be ruled out because of the lack of scrambling in ^{13}C-labelled species[1,7] and because the e.s.r. evidence is strongly against this.[8] The enhanced rates of formation of cyclopropylmethyl type radicals have been variously attributed to homoallylic conjugation,[3] development of cationic character in the transition state,[5,9] and ring strain effects.[10]



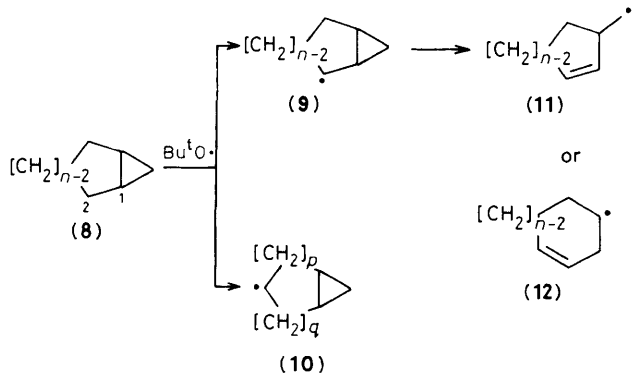
(**1**) (**2**) (**3**)

Hydrogen abstraction from spiro[2.*n*]alkanes (**4**) and *cis*-bicyclo[*n*.1.0]alkanes (**8**) by free radicals occurs virtually exclusively in the larger ring because of the much higher C–H bond strengths in the cyclopropyl rings. Hydrogen abstraction from C(2) leads to the formation of cyclopropylmethyl (cpm) type radicals (**5**) and (**9**) whereas abstraction from other methylene groups gives secondary alkyl radicals (**6**) and (**10**) respectively; see Schemes 1 and 2. In (**5**) the axis of the p-orbital containing the unpaired electron is parallel to



(**5**) (**7**) (**4**) (**6**)

Scheme 1



Scheme 2

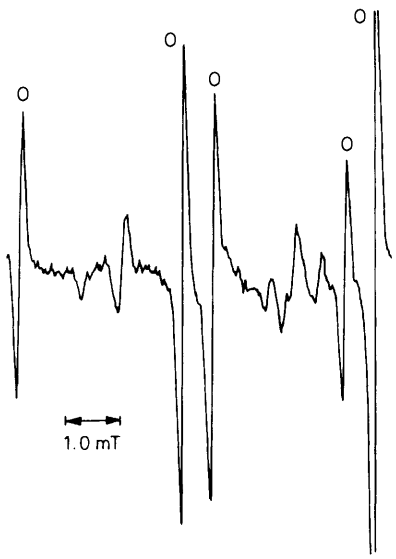


Figure 1. Low field part of the 9.4 GHz e.s.r. spectrum of the radicals obtained on hydrogen abstraction from spiro[2.6]nonane (**4**, $n = 6$) by t-butoxyl radicals in neat di-t-butyl peroxide at 240 K. Circles indicate the resonance lines from cycloheptenylethyl radicals (**7**, $n = 6$); other lines are from secondary radicals (**6**).

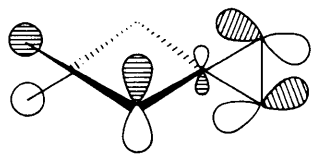
the plane of the cyclopropyl ring, whereas in (**9**) it is tilted out of the parallel orientation by an angle that depends upon the size of the ring. The rates of hydrogen abstraction from C(2) in (**4**) and (**8**) will, therefore, reflect the consequent differing activation at C(2).

We have examined the rates of hydrogen abstraction by t-butoxyl radicals from a series of compounds (**4**) and (**8**) using e.s.r. spectroscopy. The spiro[2.*n*]alkan-2-yl radicals (**5**) rearrange rapidly and completely under e.s.r. conditions to give cycloalkenylethyl radicals (**7**) so that the rate of hydrogen abstraction at the cpm site, C(2), relative to the rate of abstraction at the remaining methylenes, k(cpm)/k(sec), can be estimated from the concentrations of radicals (**7**) and (**6**) respectively, determined by double integration of suitable peaks from the spectra of each radical. Figure 1 shows the e.s.r. spectrum obtained on hydrogen abstraction from spiro[2.6]nonane (**4**, $n = 6$) with the cycloheptenylethyl and secondary radicals well resolved. The bicyclo[*n*.1.0]alkan-2-yl radicals (**9**) also rapidly rearrange to give cycloalkenylmethyl radicals (**11**) [or cycloalkenyl radicals (**12**) for $n \leq 4$].[11,12] In this series the concentrations of the two radicals formed could only be determined for (**8**, $n = 6$); for the lower members of the series signals from radicals (**11**) overlapped with signals from the secondary radicals (**10**) and for the higher members (**8**, $n \geq 7$) the e.s.r. spectra were too weak and poorly resolved.[12]

Table 1. Relative rates of hydrogen abstraction by Bu^{t}O· radicals from spiro[2.*n*]alkanes and bicyclo[*n*.1.0]alkanes.

Compound	Temp./K	[cpm]/[sec]	k(cpm)/k(sec)[a]
(**4**, $n = 5$)	240	5.8 ± 0.5	8.6 ± 0.8
(**4**, $n = 6$)	240	2.3 ± 0.2	4.6 ± 0.4
(**4**, $n = 11$)	240	1.2 ± 0.1	5.2 ± 0.5
(**8**, $n = 6$)	240	0.75 ± 0.25	1.5 ± 0.5

[a] Statistically corrected for the numbers of hydrogens in each environment.



(**13**)

Table 1 shows that the spiroalkanes are attacked at C(2) significantly more readily than at the other methylenes by t-butoxyl radicals. The relative rate [k(cpm)/k(sec)] depends to some extent on ring size, which is not surprising because the rate of hydrogen abstraction from cycloalkanes varies with ring size.[13] Spiro[2.11]tetradecane (**4**, $n = 11$) probably gives the nearest approximation to 'normal' secondary hydrogens, and the result here indicates that hydrogen is abstracted from the cpm site about five times more rapidly than from the 'normal' secondary alkyl site. As expected, the cpm site is less activated towards Bu^{t}O· radicals than the allyl site, for which k(allyl)/k(sec) = 36, or the propynyl (propargyl) site, for which k(propynyl)/k(sec) = 18 at 293 K.[14]

The highest occupied of the Walsh orbitals of cyclopropane consist of a degenerate pair constructed from p-orbitals in the plane of the cyclopropyl ring.[15] In spiro[2.*n*]alkan-2-yl radicals (**5**) the p-orbital at C(2) is held in the ideal orientation for interaction with either member of this cyclopropyl HOMO. The main contributions to the SOMO of radicals (**5**) are illustrated in (**13**); semi-empirical calculations (INDO,[16] MINDO/3,[17] and MNDO-UHF[18]) on the spiro[2.3]hexan-2-yl radical support this representation. The analogy between (**13**) and the SOMO of the allyl radical is striking, but the less favourable overlap accounts for the smaller activation at cpm sites compared to allyl sites.

In bicyclo[6.1.0]nonane (**8**, $n = 6$) there is little, if any, activation at C(2) (Table 1); however, the e.s.r. spectra for the lower members of this series (**8**, $n \leq 5$) indicated that C(2) is the major site of attack, although the effect could not be quantified. In the most stable conformation of (**8**, $n = 6$)[19] the axis of the p-orbital at C(2) is approaching the perpendicular orientation with respect to the plane of the cyclopropyl ring and interaction of the type shown in (**13**) is not possible. The lack of activation at C(2) is therefore easily understood. For the smaller members of this series models suggest that the axis of the p-orbital at C(2) will be between the parallel [as in (**13**)] and perpendicular orientations. Some overlap, and hence some activation, can be expected and this accounts for the preferential attack observed at C(2) in the bicyclo[*n*.1.0]al-

kanes (**8**, $n \leq 5$) for both t-butoxyl radicals[12] and chlorine atoms.[20]

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References

1 J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, 1951, **73**, 2509; *ibid.*, 1959, **81**, 4390.
2 C. U. Pittman and G. A. Olah, *J. Am. Chem. Soc.*, 1965, **87**, 2998, 5123; G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *ibid.*, 1970, **92**, 2544; J. S. Staral, I. Yavari, J. D. Roberts, G. K. S. Prakash, D. J. Donovan, and G. A. Olah, *ibid.*, 1978, **100**, 8016.
3 C. Walling and P. S. Fredricks, *J. Am. Chem. Soc.*, 1962, **84**, 3326.
4 H. Hart and D. P. Wyman, *J. Am. Chem. Soc.*, 1959, **81**, 4891; H. Hart and R. A. Cipriani, *ibid.*, 1962, **84**, 3697.
5 F. S. Huyser and D. T. Wang, *J. Org. Chem.*, 1963, **28**, 3442.
6 J. C. Martin and J. W. Timberlake, *J. Am. Chem. Soc.*, 1970, **92**, 978; C. G. Overberger and M. B. Berenbaum, *J. Am. Chem. Soc.*, 1951, **73**, 2618.
7 E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *J. Am. Chem. Soc.*, 1961, **83**, 1987.
8 J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Am. Chem. Soc.*, 1969, **91**, 1877, 1879.
9 See reference 6 for a discussion of this possibility.
10 D. C. Neckers and A. P. Schaap, *J. Org. Chem.*, 1967, **32**, 22.
11 C. Jamieson, J. C. Walton, and K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1366.
12 C. Roberts and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1983, 879.
13 J. M. Tedder and J. C. Walton, *Adv. Free-Radical Chem.*, 1980, **6**, 155.
14 E. Bascetta, F. D. Gunstone, and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1983, 603.
15 A. D. Walsh, *Trans. Faraday Soc.*, 1949, **45**, 179; R. Hoffman, *J. Am. Chem. Soc.*, 1968, **90**, 1475; P. Hemmersbach and M. Klessinger, *Tetrahedron*, 1980, **36**, 1337.
16 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.
17 M. J. S. Dewar, Quantum Chemistry Program Exchange, No. 309, University of Indiana, Indiana, 1976.
18 W. Thiel, P. Weiner, J. Stewart, and M. J. S. Dewar, Quantum Chemistry Program Exchange, No. 428, University of Indiana, Indiana, 1981.
19 R. P. Corbally, M. J. Perkins, A. S. Carson, P. G. Laye, and W. V. Steele, *J. Chem. Soc., Chem. Commun.*, 1978, 778; W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, 1967, **32**, 2976.
20 P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *J. Org. Chem.*, 1968, **33**, 1448; R. S. Boikess, M. MacKay, and D. Blithe, *Tetrahedron Lett.*, 1971, 401.